



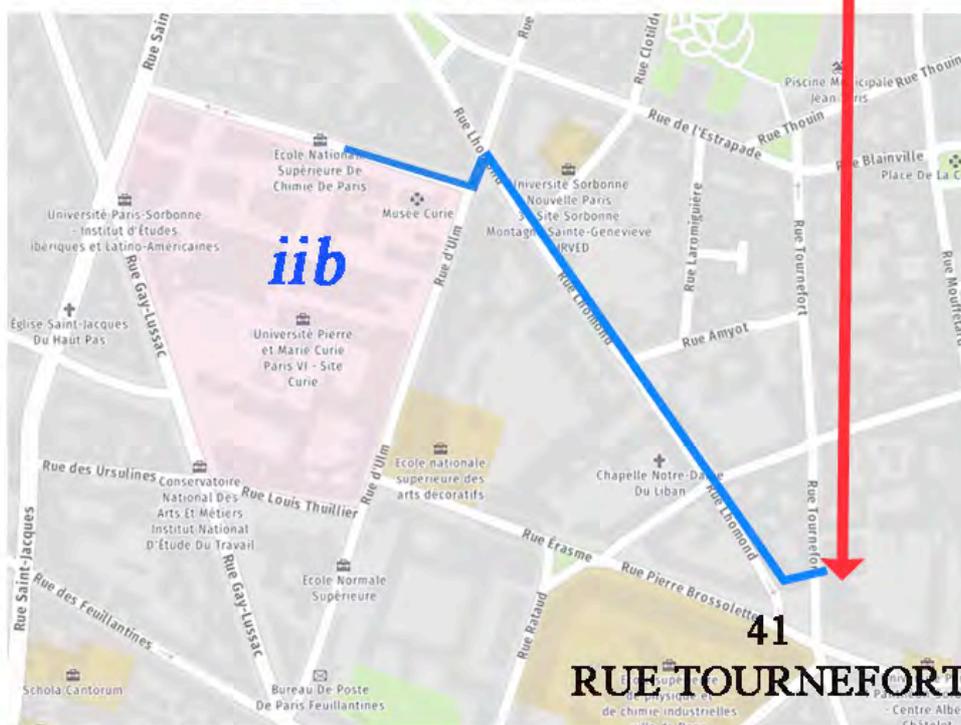
XVI International Conference on Intergranular and Interphase Boundaries in Materials Paris July 1-5

Program Abstracts



Lunches

CONCORDIA



Access to the GALA DINNER:
see inside back cover

PREFACE

IIB2019 (iib-2019) can be considered as the XVIth triennial international conference on « Intergranular and Interphase Boundaries in Materials », even if other important conferences in the field occurred, since a conference dedicated to Properties of Grain Boundaries in 1960 in Gif-sur-Yvette (CEA-Saclay)) under the presidency of Professor Georges Chaudron.

The current name, IIB (*iib*), was established thirty years ago, in Paris. IIB is taking place again in Paris at the École de Chimie ParisTech, a School created by Charles Friedel, a chemist and mineralogist who studied the relations between physical properties and twins from the point of view of symmetry.

The *iib*-conferences represent a unique international forum bringing together the specialists working in different areas of Interface Science and strongly promote an interdisciplinary approach in the field of grain boundaries and interphase boundaries structure and properties in a wide range of materials.

About 180 researchers from twenty countries contributed to this Edition and their contributions are gathered in this book which also contains the schedule program and practical informations. Oral contributions are given according to the program order and poster contributions are given afterwards, in the alphabetical order of the presenting authors.

As for the previous *iib*-conferences, participants are invited to submit their contributions as regular manuscripts (review papers being encouraged) to Journal of Materials Science under the category ‘Special IIB2019 Issue.’

We thank all the participants and we also specially thank

- The École de Chimie, Chimie ParisTech-PSL, for welcoming us and the gracious lend of the Charles Friedel and the Georges Chaudron Lecture rooms
- The Société Française de Métallurgie et de Matériaux which supported the event
- All the Sponsors, the list and logos of which are provided onto the back cover page
- Philippe Vermaut and Frédéric Prima, from Chimie ParisTech, for their help
- Claude Foubert, our PCO, for his kindness and enthusiasm for the organization.

The website is iib2019.org.

*This iib is dedicated to Donald McLean (1915-2017)
and Lasar Shvindlerman (1935-2018)*

Sylvie Lartigue-Korinek and Olivier Hardouin Duparc
Conference Chairs

The *iib*2019 logo has been designed by Sylvie Lartigue-Korinek and Lætitia-Lan Hardouin Duparc.

Chairpersons

Sylvie Lartigue-Korinek, ICMPE-CNRS
Olivier Hardouin Duparc, École Polytechnique, LSI-CNRS-CEA

International scientific committee (alphabetically)

Paul Bristowe, Univ. of Cambridge, UK
Barry C. Carter, Univ. of Connecticut, USA
Sergiy Divinski, WW Univ. of Münster, Germany
Olivier Hardouin Duparc, École Polytechnique, France
James M. Howe, Univ. of Virginia, USA
Yuichi Ikuhara, Univ. of Tokyo, Japan
Suk-Joong L. Kang, AIST, Korea
Wayne D. Kaplan, Technion, Israel
Alexander H. King, Purdue University, USA
Masanori Kohyama, AIST, Japan
Philomela Komninou, AUTH, Greece
Sylvie Lartigue-Korinek, CNRS-ICMPE, France
Douglas L. Medlin, Sandia Nat. Lab., USA
Dmitri A. Molodov, Aachen Univ., Germany
Stephen J. Pennycook, NUS, Singapore
Eugen Rabkin, Technion, Israel
Gregory Rohrer, CMU, USA
Manfred Rühle, MPI, Germany
David Seidman, Northwestern Univ., USA
Anna Serra, UPC, Spain
David J. Srolovitz, Pennsylvania Univ., USA
Boris B. Straumal, ISSP, Russia
Antoni Tomsia, Lawrence Berkeley Nat. Lab., USA
Thomas Walther, Univ. of Sheffield, UK
Wenzheng Zhang, Tsinghua Univ., China

Additional local scientific committee (alphabetically)

Alain Jacques, IJL, Nancy
Jean-Luc Maurice, PIMC-ÉP, Palaiseau
Philippe Vermaut, CPT-PSL, Paris

Organising committee (alphabetically)

Claude Foubert, Agence Vert-Com
Olivier Hardouin Duparc
Sylvie Lartigue-Korinek
Frédéric Prima, CPT-PSL, Paris
Philippe Vermaut, CPT-PSL, Paris

List of previous international conferences on Grain Boundaries and Interfaces in Materials

<i>Saclay</i>	<i>France</i>	<i>1960</i>	<i>Properties of Grain Boundaries</i>
<i>Yorktown Heights</i>	<i>USA</i>	<i>1971</i>	<i>Grain Boundaries and Interfaces</i>
<i>Saint-Étienne</i>	<i>France</i>	<i>1975</i>	<i>Int^{al} Colloquium on Grain Boundaries in Metals</i>
<i>Chernogolovka</i>	<i>Russia</i>	<i>1979</i>	<i>Structure and Properties of Grain Boundaries</i>
<i>Milwaukee</i>	<i>USA</i>	<i>1979</i>	<i>Grain Boundary Structure and Kinetics</i>
<i>Chernogolovka</i>	<i>Russia</i>	<i>1982</i>	<i>Structure and Properties of Grain Boundaries</i>
<i>Caen</i>	<i>France</i>	<i>1982</i>	<i>Structure and properties of Intergranular Boundaries</i>
<i>Cincinnati</i>	<i>USA</i>	<i>1982</i>	<i>Character of Grain Boundaries (in Ceramics)</i>
<i>Ufa</i>	<i>Russia</i>	<i>1983</i>	<i>Structure and Properties of Grain Boundaries</i>
<i>Philadelphia</i>	<i>USA</i>	<i>1983</i>	<i>Computer Simulation in the Study of Solid-Solid Interfaces</i>
<i>Irsee</i>	<i>Germany</i>	<i>1984</i>	<i>Int^{al} Conf. on the Structure and Properties of Internal Interfaces</i>
<i>Minakami</i>	<i>Japan</i>	<i>1985</i>	<i>Grain Boundary Structure and Related Phenomena</i>
<i>Lake Placid</i>	<i>USA</i>	<i>1987</i>	<i>Interface Science and Engineering</i>
<i>Paris</i>	<i>France</i>	<i>1989</i>	<i>Intergranular and Interphase Boundaries (IIB) in Materials</i>
<i>Thessaloniki</i>	<i>Greece</i>	<i>1992</i>	<i>IIB</i>
<i>Lisboa</i>	<i>Portugal</i>	<i>1995</i>	<i>IIB</i>
<i>Prague</i>	<i>Czech Rep.</i>	<i>1998</i>	<i>IIB</i>
<i>Haifa</i>	<i>Israel</i>	<i>2001</i>	<i>IIB</i>
<i>Belfast</i>	<i>UK</i>	<i>2004</i>	<i>IIB</i>
<i>Barcelona</i>	<i>Spain</i>	<i>2007</i>	<i>IIB</i>
<i>Mie</i>	<i>Japan</i>	<i>2010</i>	<i>IIB</i>
<i>Chalkidiki</i>	<i>Greece</i>	<i>2013</i>	<i>IIB</i>
<i>Moscow</i>	<i>Russia</i>	<i>2016</i>	<i>IIB</i>
<i>Paris</i>	<i>France</i>	<i>2019</i>	<i>IIB</i>

In roman (non italic) type: the conferences which gathered the community with a persisting international scientific committee such that an acronym, IIB, was coined in 1989. IIB2019 (iib2019) can thus be considered as the XVIth triennial IIB conference.

Conference Program

Monday, July 1st

8:00 am Registration

9:00 am Opening Ceremony

Chair Persons: **Diana Farkas & Frédéric Lançon**

Grain Boundary Thermodynamics: Atomic and Electronic Structure 1

9:20 am **Denis Gratias** - Beyond bicrystallography: polycrystallography 2

9:40 am **Gregory Rohrer** - Grain boundary energy and curvatures measurements from the three dimensional structure of polycrystalline materials 3

10:00 am **Yuichi Ikuhara** (*Invited*) - Grain boundary atomic structure and their dynamic behavior in oxides 4

10:30 am Coffee break

11:00 am **Mitsuhiro Saito** - 1D ordered atomic structure in grain boundary 5

11:20 am **Rong Yu** - Twinning in NiO and CuO 6

11:40 am **Pierre Hirel** - Numerical simulation of grain boundaries in oxides 7

12:00 pm **James Quirk** - Electronic structure and charge trapping at {112} and {110} twin boundaries in anatase 8

12:20 pm **Renaud Belin** - Determination of grain boundaries energy in uranium dioxide bicrystal 9

LUNCH

Chair Person: **Paul Bristowe**

2:00 pm **Frédéric Lançon** - Get 3D coordinates from electron microscopy images, built approximants, solve the structure: incommensurate interface in silicon and silver-ratio 10

2:20 pm **Diana Farkas** - Grain boundary structure in high entropy alloys 11

2:40 pm **Lorenz Romaner** - On the temperature dependence of grain boundary and surface energies in tungsten 12

3:00 pm **Eric Hoglund** - Nano-scale mapping of the electron density at Al grain boundaries and correlation with grain-boundary energy 13

Grain Boundary Thermodynamics: Segregation 14

3:20 pm	Yuri Mishin (<i>Invited</i>) - Interaction of moving grain boundaries with solutes	15
3:50 pm	Thomas Schuler - A generalization of McLean's segregation formula using a low temperature expansion	16

4:10 pm **Coffee break**

Chair Persons: **Yuichi Ikuhara & David Seidman**

4:40 pm	Masanori Kohyama - Mechanism of grain-boundary segregation of 3d transition-metal solutes in bcc Fe: ab initio local-energy analysis	17
5:00 pm	Anastasia Kholtobina - Solutes segregation at the CSL $\Sigma 3\{111\}$ Fe GB	18
5:20 pm	Christophe Domain - Solute segregation at $\{100\}$ and $\{110\}$ tilt grain boundaries in bcc Fe at the atomic scale	19
5:40 pm	Martina Mazalová - A combined effect of vacancies and segregated impurities at grain boundaries in nickel	20
6:00 pm	Lola Lilenstein - Compositional analyses at interfaces using atom probe tomography	21

6:30 pm Welcome reception

Tuesday, July 2

Chair Persons: **Masanori Kohyama & Gregory Rohrer**

Grain Boundary Thermodynamics: Segregation

8:00 am	Thomas Walther - Comparison of different ways to evaluate interfacial excess atomic areal density from atom probe data of grain boundaries	22
8:20 am	Bin Feng - Investigation of grain boundary solute segregation behavior using atomic-resolution STEM-EDS	23
8:40 am	Yutaka Ohno - Impact of misorientation at symmetric grain boundaries on segregation ability; for $\Sigma 3\{111\}$ tilt boundaries in Si	24
9:00 am	Camille Perrière - Sintering of yttrium aluminium garnet (YAG) for laser applications: role of additives on the subsequent (micro-) structural evolution	25
9:20 am	Huan Zhao - Segregation assisted grain boundary precipitation in a model Al-Zn-Mg-Cu alloy	26
9:40 am	David Seidman - An atom-probe tomography study of the temporal evolution of concentration retention excesses and depletions at $\alpha(\text{F.C.C.})/\gamma'(\text{L12})$ Interfaces in a Ni-Al-Cr-Re superalloy	27

10:00 am **Coffee break**

Chair Persons: **Andriy Ostapovets & Boris Straumal**

Grain Boundary Dynamics: Diffusion, Corrosion 28

10:30 am	Sergiy Divinski (<i>Invited</i>) - Grain-boundary phase transition probed by tracer diffusion measurements	29
11:00 am	Vladimir Esin - Experimental evidence for anomalous grain boundary diffusion of Fe in Cu and Cu-Fe alloys	30
11:20 am	Mojmir Šob - The effect of grain boundary segregation on embrittlement: current advances, challenges and problems	31
11:40 am	Dirk Ponge - Physical metallurgy of segregation and its impact on embrittlement and austenite reversion in medium Mn steels	32
12:00 pm	Poster presentations (see list and pages below)	

LUNCH

2:00 pm **POSTER SESSION**

Chair Persons: **Pavel Lejček & Sergiy Divinski**

Grain Boundary Dynamics: Corrosion, Wetting 33

5:10 pm	Boris Straumal - Grain boundary wetting by a second solid phase in the iron-based alloys	34
5:30 pm	Kristina Tsoy - Wetting of grain boundaries by intermetallic compounds in an industrial magnesium alloy	35
5:50 pm	Alexander Straumal - Influence of the grain boundary structure on the wetting transition in EZ33A cast alloy	36
6:10 pm	Jun Sun - Grain boundary wetting correlated to the grain boundary properties: a laboratory-based multimodal X-ray tomography investigation	37
6:30 pm	Simone Guiso - Intergranular corrosion modelling: a cellular automata approach	38

Wednesday, July 3

Chair Persons: **Wenzheng Zhang & Ulrich Dahmen**

Grain Boundary Dynamics: Migration, Phase Transformation 39

8:00 am	David Srolovitz (<i>Invited</i>) - The how and why of grain boundary dynamics: a disconnection perspective	40
8:30 am	Ian Chesser - Visualizing grain boundary properties with octonions	41
8:50 am	Jiake Wei - Direct imaging of atomistic grain boundary migration	42
9:10 am	Anna Serra - Dislocation mediated shear coupled migration of (112) tilt grain boundary in α -Fe	43
9:30 am	Sylvain Queyreau - An attempt to connect grain boundary migration to their atomic structure by mean of molecular dynamics	44

9:50 am **Thomas Philippe** - A regularized phase field model for anisotropic motion-by-curvature 45

10:10 am **Coffee break**

Chair Persons: **Anna Serra & David Srolovitz**

10:40 am **Ulrich Dahmen** (*Invited*) - Atomic-scale observations of step structure and migration mechanisms in interfaces 46

11:10 am **Silvère Akamatsu** - Grain boundaries interacting with the diffusion-controlled growth of alloys 47

11:30 am **Reza Darvishi Kamachali** - Grain boundary spinodal and transient spinodal in FeMn system: phase-field and experimental study 48

11:50 am **Francesco Maresca** - Theory and modeling of the austenite-martensite interface structure and glissile transformation in steels 49

12:10 pm **Wenzheng Zhang** - Migration of fcc/bcc interfaces—In situ TEM study and MD simulation 50

LUNCH

Free Afternoon - Visits

Thursday, July 4

Chair Person: **Si-Young Choi**

8:00 am **Chen Li** (*Invited*) - Grain boundaries in solar cells: structure-property correlations 51

Two parallel sessions on Thursday morning:

A: Functional Properties and Low Dimensional Systems 52
(Charles Friedel Lecture room)

Chair Persons: **Si-Young Choi & Thomas Walter**

8:45 am **Alexandra Andreeva** - Universal dynamic response in polycrystals of advanced superionic conductors 53

9:05 am **Shun Sasano** - Atomic structure and Li-ion conductivity at (La,Li)TiO₃ high-angle tilt grain boundaries 54

9:25 am **Jürgen Spitaler** - Ab-initio investigation of structure, chemistry and electronic properties of doped grain boundaries in ZnO 55

9:45 am **Esmail Adabifiroozjaei** - AgNWs heat-treatment at low temperature (60°C): a combined STEM and MD investigation 56

10:05 am **Dor Amram** - Higher temperatures yield smaller grains in a thermally stable phase-transforming nanocrystalline alloy 57

10:25 am **Coffee break**

11:00 am **Douglas Medlin** - Extended crystal defects in layered chalcogenide materials: atomic scale structural investigations 58

11:20 am **Luchan Lin** - Fast mass transportation of metastable AgCu alloys in confined AlN/AgCu/AlN nanolayer sandwiches 59

11:40 am **Yuanshen Qi** - Anisotropic intermixing in Au-Fe bimetallic nanowhiskers 60

12:00 pm **Jean-Luc Maurice** - Generation of 2H polytype at an incoherent second-order twin boundary in a silicon nanowire 61

12:20 pm **Stanislav Krasnitckii** - Axial strain relaxation in core-shell nanowires with a polyhedral core due to the nucleation of misfit prismatic dislocation loops 62

12:40 pm **Dan Mordehai** - The deformation mechanism of bi-crystalline twinned Au nanowires 63

B: Mechanical Properties 64

(Georges Chaudron Lecture Room)

Chair Persons: **Anne-Françoise Gourgues-Lorenzon & Frédéric Momprou**

8:45 am **Aleksandra Vakaeva** - Stress concentration and distribution in ceramic composites with triple junction heterogeneities 65

9:05 am **Alexandre Dimanov** - Crystal slip and Grain Sliding: A two-stroke engine driving ductile localization 66

9:25 am **Gregory Gerstein** - Microstructural investigation of damage evolution at the intersection of shear bands 67

9:45 am **Hiromi Miura** - Strengthening mechanisms in heavily cold-rolled stainless steels by heterogeneous nano-structures 68

10:05 am **Oliver Renk** - Effect of interface character on the deformation behaviour of nanostructured metals – a case study on nickel 69

10:25 am **Coffee break**

11:00 am **Maxime Sauzay** - Homogenization model accounting for the internal stresses induced in slip bands 70

11:20 am **Elena Astafurova** - Experimental study on mechanisms of age-hardening in V-alloyed and V-free high-nitrogen steels 71

11:40 am **Bertrand Sicaud** - Mechanical behaviour of nickel symmetric CSL grain boundaries under triaxial loading: from dislocation nucleation to decohesion 72

12:00 pm **Dôme Tanguy** - Cohesive stress heterogeneities and the transition from intrinsic ductility to brittleness 73

12:20 pm **David Tingaud** - First principles investigation of H interaction with a $\Sigma 5$ [100] twist grain boundary in Al during a uniaxial tensile test 74

LUNCH

Chair Persons: **Hosni Idrissi & Eugen Rabkin**

	Plasticity Mechanisms	75
2:30 pm	Frédéric Mompiau (<i>Invited</i>) - Using in-situ TEM to probe interface related plasticity mechanisms	76
3:00 pm	Cyril Cayron - Unconventional twin interfaces revealed by EBSD in a single crystal of magnesium	77
3:20 pm	Andriy Ostapovets - On the interaction of a stacking fault with the (1 0 -1 2) twin boundary in magnesium	78
3:40 pm	Mayerling Martinez - Deformation mechanisms of polycrystalline cobalt. A quantitative study by electron microscopy	79
4:00 pm	Xaolei Chen - Effect of anisotropic elasticity on dislocation pile-ups and stress-induced slip transmission at grain boundaries	80
4:20 pm	Coffe break	

Chair Person: **Olivier Hardouin Duparc**

4:50 pm	Hosni Idrissi - Dislocation/coherent twin boundary interactions: new insights from quantitative in-situ TEM tensile testing	81
5:10 pm	Ayrat Nazarov - Atomistic simulation on nonequilibrium grain boundaries	82
5:30 pm	Eugen Rabkin - The role of interface diffusion in deformation of metal nanostructures	83
5:50 pm	Boris Straumal - In memoriam Lasar Shvindlerman	
8:00 pm	GALA DINNER	

Friday, July 5

Chair Persons: **Dominique Mangelinck & Rong Yu**

8:30 am	Si-Young Choi (<i>Invited</i>) - Unveiling metal-insulator transition in vanadium oxide	84
	Interphase Boundaries	85
9:00 am	Mathis Plapp - Influence of interphase boundary anisotropy on lamellar eutectic solidification microstructures	86
9:20 am	Arthur Marceaux dit Clément - Atom probe tomography study of austenitic transformation interfaces in high-formability dual-phase steels	87

9:40 am	Anne-Françoise Gourgues-Lorenzon - Effect of austenite stability on the competition between ductile and interfacial fracture in a medium-Mn, ultra-fine-grained steel for automotive applications	88
10:00 am	Romuald Béjaud - Twin-interface interactions in bimetallic systems: molecular dynamics study	89
10:20 am	Julien Guénoilé - Numerical and experimental evidences of matrix slip across complex precipitate interfaces	90

10:40 am	Coffe break
----------	--------------------

Chair Person: **Mathis Plapp**

11:10 am	Joël Ribis - Zr-Cr interface stability of irradiated chromium-coated Zircaloy-4 alloy	91
11:30 am	Aakash Kumar - Metal/ceramic interfaces: a new class of high-diffusivity paths	92
11:50 am	Dominique Mangelinck - Some mechanisms controlled by diffusion at interphases: lateral growth and dewetting of silicides thin films	93
12:10 am	Rong Yu - Coherent topotactic interfaces	94
12:30 am	Zaoli Zhang - Interface effects in the protective hard coatings – insight into the structure-property relationship at the atomic scale	95
12:50 pm	Closing Ceremony	

Poster presentations

Posters	96
Khadidja Abib - On some features of interfacial intermetallics in Al/Mg/Al laminated composite fabricated by accumulative roll bonding	97
Sergey Astafurov - On realization of superplastic flow in V-alloyed high-nitrogen steel	98
Sergey Astafurov - On the anisotropy of the mechanical properties in additively-manufactured stainless steel	99
Elena Astafurova - Microstructure and grain growth inhomogeneity in austenitic steels produced by wire-feed electron beam melting	100
Quentin Barrès - Ion irradiation-induced grain boundary segregation in a Fe ₁₂ Cr model alloy: a coupled TKD/APT study	101
Carolina Baruffi - Atomic structure of (111) twist grain boundaries in diamond	102
Romuald Béjaud - In silico (CD) study of hexagonal diamond (HD) silicon nanowire surfaces	103
Paul Bristowe - Modeling the effect of chemical doping on the strength of a Ag/ZnO interface	104
Océane Buggenhoudt - Properties of interfaces between cementite and a dilute alpha-Fe lattice from electronic structures	105
Nathalie Capron - Electronic transport in cubic-HfO ₂ grain boundaries: a first principles study	106
Reza Darvishi Kamachali - A model for grain boundary thermodynamics based on a relative density parameter	107
Alexander Despotuli - Modeling of ion-transport processes in space charge region on ideally polarized heterojunction	108
Adrien Emery - Intergranular corrosion of austenitic industrial stainless steels in oxidizing nitric media	109
Svetlana Fedotova - Application of the complex of methods to assess the level of grain-boundary segregation in nuclear reactor pressure vessel steels	110
Jérôme Hazan - Prediction of grain boundary micro-crack initiation during cyclic deformation	111
Seiichiro II - Geometrical analysis for misorientation angle dependence of grain boundary - dislocation interaction	112
Kazutoshi Inoue - Mathematical analysis of grain-boundary atomic arrangements and atomic-scale observations	113
Saki Ishihara - Dopant effects on the surface morphology of alpha-alumina	114
Won-Seok Ko - Role of grain boundaries on the martensitic phase transformation in NiTi shape-memory alloys: An atomistic simulation	115
Shigeaki Kobayashi - Control of low-angle boundary network for improving high-cycle fatigue in 430 ferritic stainless steel	116
Sergey Kostyrko - Surface and interface effect on mechanical properties of wrinkled film coating with nanosized thickness	117
Izabella Kwiecien - Interface of Al/Ni connections manufactured by explosive welding	118
Melvyn Larranaga - Elementary mechanisms of shear coupled grain boundary migration	119
Sylvie Lartigue-Korinek - Interfaces structure and defects in directionally solidified oxide-oxide eutectics	120

Sabine Lay - Experimental study of twist grain boundaries in WC-Co alloys	121
Sabine Lay - Study of dislocations in AlN films deposited on sapphire: a geometrical approach	122
Yong Li - Topology evolution during coarsening of nanoporous gold via kinetic Monte Carlo-simulation	123
Yong Liu - Interfacial structure in AZ91 alloy composites reinforced by graphene nanosheets	124
Philippe Maugis - Boron segregation at austenite grain boundaries: an equilibrium phenomenon	125
Ilyès Médouni - Atom probe tomography investigation of solute atom segregation during thermal ageing in the carbon-depleted heat-affected zone of dissimilar metal welds	126
Estelle Meslin - BCC-FCC interface leading to Ni precipitation under irradiation in a FeNi alloy	127
Jean-Baptiste Molin - 3D-Laue micro diffraction to characterize fatigue damage in bi-crystalline micro cantilevers	128
Valentina Moskvina - The effect of VN-based precipitates on tensile properties and fracture micromechanism of high-nitrogen steel	129
Valentina Moskvina - The effect of post-built annealing on mechanical characteristics of additively-manufactured AISI 304 stainless steel	130
Shamil Mukhtarov - Effect of grain size and boundaries on mechanical behaviour and fracture of Re-rich nickel-based superalloy	131
Kamilla Mukhtarova - Effect of severe plastic deformation and annealing on the microstructure and microhardness of Inconel 718 produced by selective Laser melting	132
Alexandre Mussi - Characterization of recovery by boundary migration and dynamic recrystallization in experimentally deformed polycrystalline olivine	133
Atsutomo Nakamura - Structures and electrical conduction properties of boundary dislocations at low-angle grain boundaries in SrTiO ₃	134
Gahee Noh - STEM analysis of interfacial structure in Mn ₃ GaN/Mn ₃ Ga Superlattice film	135
Yutaka Ohno - Impact of polymorphic nanostructures at grain boundaries on segregation ability; for asymmetric $\Sigma 9\{111\}/\{115\}$ tilt boundaries in silicon	136
Nicholas Orr - Grain boundary location and misorientation measurement from particle coordinates	137
Yu Oshima - Slip deformation behavior of zinc sulfide crystals under controlled light conditions	138
Marina Panchenko - The effect of age-hardening on hydrogen embrittlement in high-nitrogen austenitic steel	139
Yuanshen Qi - Pores pinning and Bi diffusion induced grain boundary migration in ultrafine grain Cu processed by high pressure torsion	140
Marianne Quiquandon - Z-module defects in a NiZr alloy	141
Eugen Rabkin - Thermal stability of thin Ni-Fe films on sapphire	142
Alexey Romanov - Mesoscopic modeling and computer simulation of intercrystallite boundaries in graphene	143
Maxime Sauzay - Comparison between cohesion curves of various carbide-metal interfaces predicted by DFT and the universal binding energy relationship (UBER) theory	144

Yoshinori Shiihara - Local stress analyses of grain boundaries in iron based on artificial neural network potential	145
Tomotsugu Shimokawa – Work hardening by grain boundarie transformation in multilayer nanopillars	146
Dmitriy Sineglazov - Modeling of the magnetoplastic effect in polycrystalline Cu-Be alloys	147
Mojmir Šob - Tuning the grain boundary magnetization by ab initio grain boundary segregation engineering	148
Kyung Song - Self-assembled (Ti, V)O ₂ superlattices by spinodal decomposition	149
Leonel Stermann - An experimental set up to study the micro-mechanisms of stress corrosion cracking	150
Alexander Straumal - Comparative analysis of grain boundary spectra in Cu-Ag and Cu-In polycrystalline systems.	151
Alexander Straumal - Distribution of SiC particles in silicide eutectic alloys of the Mo-W-Si-C system	152
Alexander Straumal - Observations of grain boundary phase transformations in copper-based alloys using differential scanning calorimetry	153
Alexander Straumal - Effective activation enthalpy of grain boundary motion	154
Boris Straumal - The effect of individual layer thickness on the Cu/W nano-multilayer to a nanocomposite transformation	155
Boris Straumal - Energetics of intergranular and interphase boundaries in Ti-6Al-4V alloy	156
Shabnam Taheriniya - Dual-phase lamellar high entropy alloys produced via high-pressure torsion	157
Sadahiro Tsurekawa - Critical stress required to propagate yield Past the grain boundary	158
Naoki Uemura - Reaction dynamics of tricresyl phosphate on Fe ₃ O ₄ (111) surface: a hybrid quantum-classical simulation with coarse-grained particles	159
Masayuki Uranagase - Free energy calculation of the interface between liquid and polymer-grafted surface	160
Masayuki Uranagase - Microscopic mechanisms of weakening of adhesion strength at aluminum-epoxy resin interface under moist condition	161
Hao Wang - First-principles computational tensile tests of grain boundaries: effects of a bulk-region size and local-energy and local-stress analysis	162
Chihiro Watanabe - Hardness distribution in a heterogeneous nano-structured austenitic stainless steel	163
Yujeong Yang - Scanning transmission electron microscopy analysis of the modified layered structure by thermal process in lithium batteries	164
Min Zhang - Effect of laser surface remelting on the microstructure and mechanical properties of a Mn-Si series bainite steel	165
Zaoli Zhang - Segregation of Ca dopant at bismuth ferrite – strontium titanate interfaces	166
Hannes Zschiesche - Quantitative measurement methods of atomic excess at triple junction - Ti segregation in CoSi ₂ thin films	167

Conference Photo



(Thursday, 4th July, about 1 pm)

Grain Boundary Thermodynamics: Atomic and Electronic Structure

Beyond bicrystallography: polycrystallography

M. Quiquandon and D. Gratias*

*denis.gratias@chimie-paristech.fr

CNRS IRCP/Chimie-ParisTech, UMR 8247, 11 rue Pierre et Marie Curie, 75005 Paris, France

Abstract

We present here a simple derivation of how to define the space group H of the dichromatic pattern for a homophase boundary using an interface space operation a and the space group G of the structure. This formulation extends easily to polychromatic patterns of any finite order as will be exemplified by a simple 2D example of boundaries generated by a group-subgroup phase transformation.

Polycrystallography

An interface boundary in a homophase crystalline solid of space group G is characterized by a coset aG where a is a space operation that transforms crystal I into crystal II. The symmetry group of the bicrystal (see [1]) is made of two kinds of symmetry elements:

-those that leave both adjacent crystals **simultaneously invariant** and thus belong to the intersection of the two space groups:

$$\mathcal{I} = G \cap \hat{a}G\hat{a}^{-1}$$

-those that **exchange the two crystals** and thus belong to the intersection (if not empty) of the coset aG and its inverse:

$$\mathcal{E} = \hat{a}G \cap G\hat{a}^{-1}$$

The union of these two sets form a group called the space group of the bicrystal. It is homomorphic to the permutation group of two objects (bichromatic pattern):

$$\mathcal{H} = \mathcal{I} \cup \mathcal{E} = \mathcal{I} \cup \epsilon\mathcal{I}, \epsilon \in \mathcal{E}; \quad \mathcal{H}/\mathcal{I} = \mathcal{S}_2$$

The generalization to polychromatic patterns generated by N boundaries follows by considering the permutation group of N objects instead of 2 in the previous quotient relation. Hence, in the example of Fig. 1 of a group-subgroup phase transformation generating three variants where the space group of the trichromatic pattern is isomorphic to the high symmetry group $p3m1$ decomposes according to:

$$\mathcal{H} = \{\hat{1}_z + \hat{3}_{jz}^1 + \hat{3}_{jz}^2 + \hat{m}_z^x + \hat{m}_{jz}^y + \hat{m}_{jz}^{xy}\}p1(a, b)$$

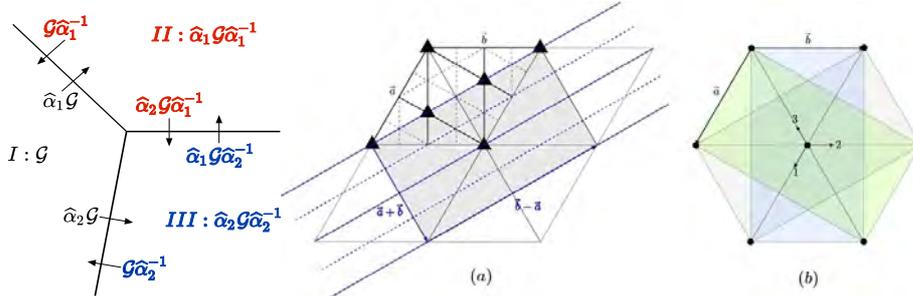


Fig. 1 : Example of three boundaries generating a trichromatic pattern (b) issued from a 2D phase transformation (a) from $p3m1(a,b)$ to $cm(a+b,b-a)$.

[1] R. C. Pond and D. S. Vlachavas, Proc. R. Soc. London **A386**, 95—143 (1983)

Grain boundary energy and curvatures measurements from the three dimensional structure of polycrystalline materials

Gregory S. Rohrer¹

rohrer@cmu.edu

¹ Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, USA

Grain growth occurs to eliminate excess grain boundary energy while also balancing topological requirements for space-filling and local interfacial equilibrium at triple junctions. During this process, grain boundaries are thought to move at a velocity proportional to their energy and curvature. As a result, energy and curvature are two influential factors in microstructure evolution. In this talk, I will describe recent efforts to measure the grain boundary energy and curvature in polycrystalline metals and ceramics as a function grain boundary misorientation and grain boundary plane orientation. The microstructural measurements are carried out by automated serial sectioning in a focused ion beam microscope and the energy [1] and curvature [2] are determined by analyzing local geometries. With these data, it should be possible to predict how a certain grain boundary will move during annealing. The predictions from these measurements will be compared to the actual motion of boundaries in a polycrystal monitored by high-energy diffraction microscopy.

[1] Y.-F. Shen, X. Zhong, H. Liu, R.M. Suter, A. Morawiec, G.S. Rohrer, "Determining Grain Boundary Energies from Triple Junction Geometries without Discretizing the Five-Parameter Space," *Acta Materialia*, **166** (2019) 126-134.

[2] X. Zhong, D.J. Rowenhorst, H. Beladi, and G.S. Rohrer, "The Five-Parameter Grain Boundary Curvature Distribution in an Austenitic and Ferritic Steel," *Acta Materialia*, **123** (2017) 136-145.

Grain boundary atomic structures and their dynamic behavior in oxides

Yuichi Ikuhara^{1,2,3}

ikuhara@sigma.t.u-tokyo.ac.jp

¹ *Institute of Engineering Innovation, The University of Tokyo, 2-11-16, Yayoi, Bunkyo-ku, Tokyo 113-8656, Japan*

² *Nanostructures Research Laboratory, Japan Fine Ceramics Center, 2-4-1,*

Mutsumo, Atsuta, Nagoya 456-8587, Japan

³ *WPI Research Center, Advanced Institute for Materials Research, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai, Miyagi 980-8577, Japan*

Oxides have been widely used for structural applications because of their superior mechanical properties at high temperatures. It has been known that the behavior of GB sliding and migration is strongly dependent on the GB characters such as misorientation angle between two adjacent crystals and GB plane. However, such effect on the properties have not been clarified yet. In addition, this effect is much influenced by the dopant segregation at GBs. In this study, in order to clarify the atomistic mechanisms of GB sliding and migration and its dopant effect in Al₂O₃ ceramics, several types of the bicrystals including GBs with specific geometrical configuration were systematically fabricated, and some of them were doped by rare-earth elements to enhance the GB segregation. Then, the atomic structures and chemistry in thus fabricated GBs were characterized by atom-resolved STEM, and the relationship between GB characters, segregated dopants, GB sliding and migration in Al₂O₃ will be discussed in detail.

It has been reported that several oxides can be plastically deformed even at R.T. by dislocation slip or twin deformation like metals. So far, many experimental investigations have been tried for understanding the dislocation-grain boundary and twinning interaction, but these experiments were mostly carried out statically, and the fundamental atomistic processes are still not well understood yet. In this study, TEM *in situ* nanoindentation experiments were conducted for SrTiO₃ and Al₂O₃ single crystals and their bicrystals. Several kinds of TEM specimens for these experiments were prepared, that are single crystals and bicrystals including various types of GBs. The SrTiO₃ and Al₂O₃ single crystals were indented with the sharp diamond tip, and the dislocation and twinning dynamics were successfully observed for respective specimens.

For GBs in SrTiO₃ bicrystals, the interaction between the introduced lattice dislocations and the GBs were directly observed. It was found that the dislocation-GBs interaction is strongly dependent on the GB characters. For Al₂O₃, the deformation twinning often occurs in the present indentation experiments, and the mechanism can be explained by a shear process for each lattice layer, which is caused by twinning dislocations. It has been suggested that the non-basal twinning systems, such as the rhombohedral twinning in Al₂O₃, can be completed by not only simple shear but also atomic shuffling. But, the dynamic behavior and the atomic structures of the twinning dislocations have not been well understood. In this study, the dynamic behavior and atomic structures of the twinning dislocations were investigated for rhombohedral twinning in Al₂O₃ by TEM *in situ* nanoindentation experiments. Furthermore, the twin-GB interaction and its dependence on the GB characters will be discussed in detail.

[1] S. Kondo, N. Shibata, T. Mitsuma, E. Tochigi, Y. Ikuhara, *Appl. Phys. Lett.*, 100(18), 181906(2012)

[2] S. Kondo, T. Mitsuma, N. Shibata, Y. Ikuhara, *Sci. Adv.*, 2[11], e1501926(2016).

1D ordered atomic structure in grain boundary

Mitsuhiro Saito^{1,2}, Deqiang Yin^{2,3}, Chunlin Chen^{2,4}, Kazutoshi Inoue², and Yuichi Ikuhara^{1,2,5}

msaito@sigma.t.u-tokyo.ac.jp

¹ Institute of Engineering Innovation, University of Tokyo, Tokyo, Japan.

² Advanced Institute for Materials Research, Tohoku University, Sendai, Japan.

³ College of Aerospace Engineering, Chongqing University, Chongqing, China.

⁴ Shenyang National Laboratory for Materials Science, Chinese Academy of Sciences, Shenyang, China.

⁵ Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, Japan.

Abstract

Solid usually can be defined by either one of three types of phases, that is, crystalline, quasi-crystalline, and amorphous phase with degrading the degree of order for crystal structure. In this work, a phase with randomly distributed 1D ordered atomic structure, which does not belong to any type of these solid phases, were found out in confined regions of ceramic grain boundaries (GBs) and GB triple junctions by scanning transmission electron microscopy (STEM).

Results

Real materials including metals and ceramics are, in general, of polycrystalline nature, and the presence of GBs often influences their mechanical, electrical and physical properties significantly. In many cases, GBs show some periodical atomic structures that are well described by the array of structure units (SUs) in coincidence-site lattice (CSL) GBs with low Σ values. Structural characterization of various types of GBs at atomic scale is essential to elucidate the origin of material properties in polycrystalline materials.

In this work, we investigated the microstructures of the textured polycrystalline MgO thin film on the substrate which were fabricated by the sputtering method. Observations along a plan-view direction at atomic scale were conducted by spherical aberration (Cs)-corrected STEM (JEOL JEM-ARM200F (200kV)). A band gap of the obtained structure was measured via low loss spectrum in electron energy loss spectroscopy (EELS) by using Cs-STEM (JEOL JEM-2400FCS (60kV)) with monochromator. To understand the electronic properties, density functional theory (DFT) calculations were performed by using the generalized gradient approximation (GGA) functional method.

The ABF-STEM image showed the amorphous-like structure in MgO GB triple junction (FIG.). Nevertheless, the intensity at each atomic column in the GB junction was the same as that in bulk region. This means that each atomic column has a one-dimensional (1D) long-range order with a crystal translational periodicity. It was also found that these atomic columns form structural units (SUs) which are randomly orientated around the observing direction of [001] axis. Therefore, 1D ordered arrangement and 2D randomness coexist in the GB triple junction. In spite of intrinsic insulating nature in bulk MgO, the low loss measurement and the DFT calculation suggested a semiconductor-like behavior owing to this specific 1D ordered atomic structure [1].

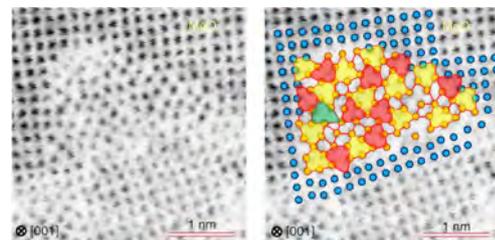


FIG. ABF-STEM images showing the MgO 1D ordered structure composed of many hexagonal units (colored shading) in GB triple junction [1].

[1] Yin, D., Chen, C., Saito, M., Inoue, K. & Ikuhara, Y., *Nature Materials* **18**, 19–23 (2019).

Twinning in NiO and CuO

Y. N. Zhao¹, W. D. Xing², R. Yu², F. Y. Meng^{1,*}

*meng7707@sas.ustb.edu.cn

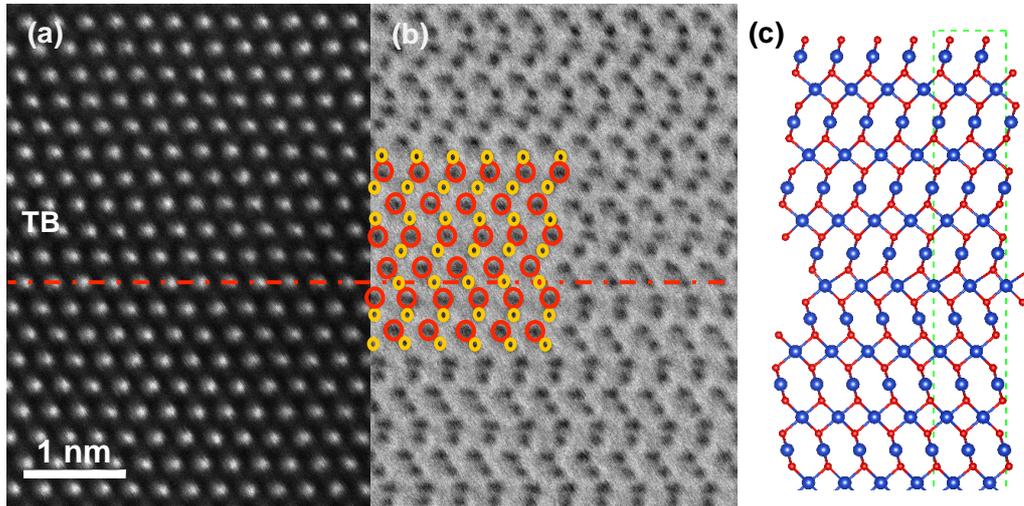
Department of Physics, University of Science and Technology Beijing, Beijing, 100083, China
National Center for Electron Microscopy in Beijing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China.

Abstract

Twinning is a popular phenomenon in crystal growth and deformation and plays a key role in tuning mechanical and transport properties of materials. Although neighboring in the periodic table, the oxides of Ni and Cu have different type of chemical bonding, crystal structure, and twinning behavior. In this work, the atomic configuration and electronic structure of the twin boundaries in rock-salt type NiO and monoclinic CuO are studied combining aberration-corrected TEM and first-principles calculations. For NiO, the twinning occurs at the (111) plane, with oxygen atoms located at the twin boundary and antiferromagnetic coupling between the mirroring Ni atomic planes. The configuration gives much lower twin boundary energy (0.54 J/m^2) than those with different terminating twin plane or different magnetic coupling. For CuO, the twinning occurs in the (001) plane. Different from the case of NiO, it is copper that is located at the twin boundary of CuO, and there is no mirror relationship in twins of CuO. Careful comparison between the experimental TEM measurements and computational relaxation of the atomic twin boundary structure reveals the importance of the van der Waals interaction in CuO.

Atomic configuration of CuO twin boundary

The twin boundary viewed along the [110] zone axis of CuO. The twinning occurs at the (001) plane. (a) STEM-HAADF images of twin boundary; (b) ABF image shows the both Cu and O positions; (c) The corresponding atomic model of the twin boundary.



Numerical simulation of grain boundaries in oxides

Pierre Hirel^{1*}, Philippe Carrez¹, Patrick Cordier¹

*pierre.hirel@univ-lille.fr

¹ Université de Lille, CNRS, INRA, ENSCL, UMR 8207 UMET, 59000 Lille, France

Complex oxides, whether synthesized experimentally or occurring naturally, often grow as polycrystals. As a result, grain boundaries are bound to play a key role in their deformation. Contrary to metals, grain boundaries in ceramics or minerals raise the question of stoichiometry and charge compensation. For instance, grain boundaries in perovskite materials are often found to be oxygen deficient. The chemical composition of a grain boundary is therefore of paramount importance, since it has an influence on its energy, mobility, and on diffusion.

We use systematic atomic-scale simulations to investigate the properties of grain boundaries in complex ionic oxides, such as magnesium oxide (MgO) and strontium titanate (SrTiO₃). The atomic structure and energies of both symmetric and non-symmetric tilt grain boundaries are obtained. We address their interaction with vacancies in order to obtain their optimal stoichiometry, and present first results about the influence of stoichiometry on the mobility of grain boundaries.

Electronic structure and charge trapping at {112} and {110} twin boundaries in anatase

JA Quirk^{1,*}, VK Lazarov¹ and KP McKenna¹

*jaq502@york.ac.uk

¹Department of Physics, University of York, Heslington, York, YO10 5DD, United Kingdom

The behaviour of charge carriers in anatase titanium dioxide (TiO₂) is important to its performance in applications including photocatalysts and solar cells. Grain boundaries impose differing coordination upon the atoms near the boundary, which can provide sites for polaronic trapping. We present first-principles calculations of the electronic structure and charge-trapping behaviour of {112} and {110} twin boundaries in anatase using an accurate hybrid density functional theory approach [1]. The {112} twin has been demonstrated to occur commonly, and has been characterised experimentally using transmission electron microscopy (TEM) [2]. However, simulated images demonstrate that the {110} twin boundary is ‘invisible’ to TEM (Fig. 1), making experimental study difficult. For the {112} twin boundary, it is shown that hole polarons preferentially form at the boundary (with trapping energies 0.16-0.18eV lower than the bulk). Conversely, the {110} twin boundary provides less favourable hole polaron sites than the bulk (with trapping energies 0.22eV higher than the bulk). Neither boundary is found to form electron polarons, implying that both boundaries would be relatively benign to the performance of anatase as an n-type electrode.

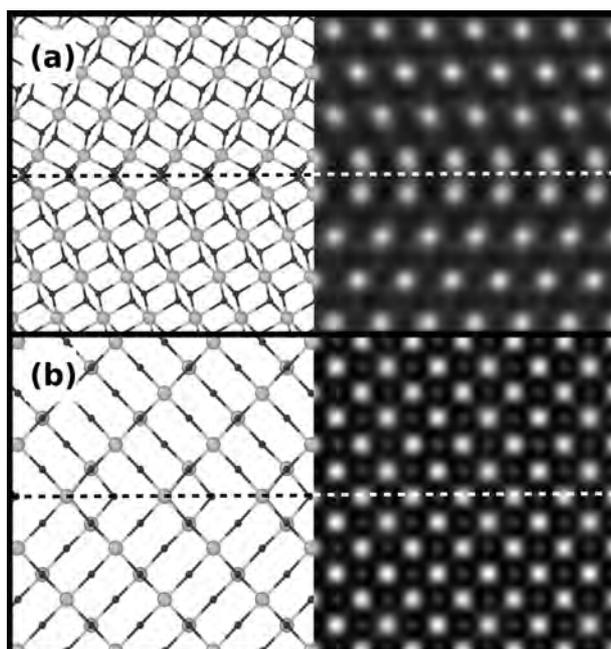


Figure 1. Optimised structures of the (a) {112} twin boundary viewed down [110] and the (b) {110} twin boundary viewed down [001]. For clarity, only two atomic layers have been shown for the {110} boundary. On the right is an inlaid simulated TEM image for each case. Large pale spheres are titanium and small dark spheres are oxygen. Dashed line indicates the location of the boundary.

[1] Elmaslmane, Abdul Razak et al., Journal of chemical theory and computation, 14.7 (2018) 3740-3751.

[2] Penn, R. Lee et al., American Mineralogist, 84.5-6 (1999) 871-876.

Acknowledgments We acknowledge support from the EPSRC. This work made use of Archer, the UK’s national high-performance computing facility, via our membership in the UK HPC Materials Chemistry Consortium.

Determination of grain boundaries energy in uranium dioxide bicrystals

A. Ksibi¹, G. Lapertot², E. Bourasseau¹, X. Iltis¹, A. Pena³, B. Menaert³, D. Drouan¹, A. Miard¹, J.-P. Brison²
and R. C. Belin¹

renaud.belin@cea.fr

¹ CEA, Centre de Cadarache-DENDEC, 13108 St Paul Les Durance, France

² CEA, Centre de Grenoble-DRF/INAC/PHELIQS/IMAPEC, 38054 Grenoble Cedex 9, France

³ Institut Néel CNRS/UJF, 25 rue des Martyrs, BP 166, F38042 Grenoble Cedex 9, France

It is well-known that grain boundaries (GBs) play a major role in the macroscopic properties of polycrystalline materials. That is particularly true for uranium dioxide (UO₂) ceramics intended for use as nuclear fuels, which have to withstand severe conditions. Under irradiation, grain boundaries are strongly affected both by the thermomechanical stress induced by the temperature gradient and by the accumulation of fission gases bubbles. Depending on the operating conditions of the reactor, these two phenomena eventually induce the decohesion of grain boundaries. Consequently, a better knowledge of grain boundaries in UO₂ including formation energies, toughness, or mechanical properties is needed. That requires a multi-scale approach from the atomic scale to that of the polycrystalline sample.

In the present work, our goals were (1) to identify the GBs of interest in the polycrystalline UO₂ by considering the distribution of coincidence site lattice (CSL) GBs using EBSD-SEM and (2) to determine the energies of geometrically defined GBs.

GBs were simulated at the atomic scale and their energy was calculated by molecular dynamics using different empirical potentials. In parallel with these calculations, grain boundaries energies were determined experimentally. Although it can be done on polycrystals, this approach ideally requires the use of synthetic UO₂ bicrystals, materials that are elaborated in such a way as to be closest to the model system simulated with molecular dynamics. Indeed, the bicrystal is the only system allowing a perfect knowledge of all five geometrical degrees of freedom for a given GB. Bicrystals were elaborated by diffusion-bonding at high temperature from two suitably orientated single-crystals. Most of the single-crystals were obtained from slow cooling of melted UO₂ batches. We are also currently working on synthesizing high-quality, chemically pure single-crystals by chemical vapor transport method.

Grain boundaries energies were evaluated using the thermal grooving technique, which consists in performing a thermal etching to reveal the grain boundary grooves and in measuring their dihedral angle with atomic force microscopy. Grain boundaries energies were finally estimated from the Herring equation.

In the presentation, we will focus more thoroughly on the synthesis of single-crystals and on the methodology used to elaborate selected bicrystals. Then, we will present first results obtained on polycrystals and will compare measured and calculated energies for selected CSL grain boundaries. Such a coupled experimental - simulation approach gives confidence in the reliability of the experimental results while strengthening the simulation by allowing the choice of the best-suited potential. This will ultimately allow extending numerical simulations to other properties such as cleavage energies and toughness.

Get 3D coordinates from electron microscopy images, built approximants, solve the structure: Incommensurate interface in silicon and silver-ratio

Frédéric Lançon^{1,*}, Nina Gunkelmann², Damien Caliste¹ and Jean-Luc Rouvière¹

**Frederic.Lancon@cea.fr*

¹Univ. Grenoble Alpes, CEA, Mem, F-38000 Grenoble, France

²Institute of Applied Mechanics, Technische Universität Clausthal, D-38678 Clausthal-Zellerfeld, Germany

Direct Si-wafer bonding can be used to produce artificial interfaces of technological interest [1]. Depending on misorientations, these interfaces can be incommensurate and thus more difficult to solve than periodic ones. We focus here on a grain boundary resulting from a 90° rotation between two Si crystals around a common $[1 \bar{1} 0]$ direction. The interface contains this common direction, which is thus a commensurate direction, and two directions parallel to each other: $[0 0 1]$ of the first crystal and $[1 1 0]$ of the second one. The resulting 90° $\langle 1 1 0 \rangle$ tilt boundary is incommensurate along these parallel directions, since the ratio of the respective periodicities facing each other is the irrational number $\sqrt{2}$ [2,3].

The theoretical background to describe incommensurate interfaces was provided as an extension of the quasicrystal one [4,5]. Recent advances in high-resolution electron microscopy now allow us to resolve such a structure, taking incommensurate nature fully into account, as done for instance in gold [6].

In this work, we show how to associate high resolution results with state-of-the-art calculations [7,8] and the unit model [5] to solve the structure of Si 90° $\langle 1 1 0 \rangle$ tilt boundary (see Fig. 1). In particular we introduce a general two-step energy minimization to extract the 3D atomic coordinates from the 2D image spots, done here for silicon.

- [1] F. Fournel et al, Applied Physics Letters, **80** (2002) 793.
- [2] E. Toyoda et al, Thin Solid Film, **517** (2008) 323; Jap. J. of Applied Physics, **48** (2009) 021208.
- [3] J.-L. Rouvière et al, J. of Physics : Conference Series **209** (2010) 012041.
- [4] D. Gratias et al, Phil Mag. Letters, **57** (1988) 63.
- [5] A. Sutton, Acta metall., **36** (1988) 1291; Progress in Materials Science, **36** (1992) 167.
- [6] A. Gautam et al, Acta Materialia, **61** (2013) 5078.
- [7] L. Genovese et al, BigDFT code, **v1.8** (2016) <http://bigdft.org>
- [8] K. Lejaeghere et al, Science, 351 (2016) 1415.

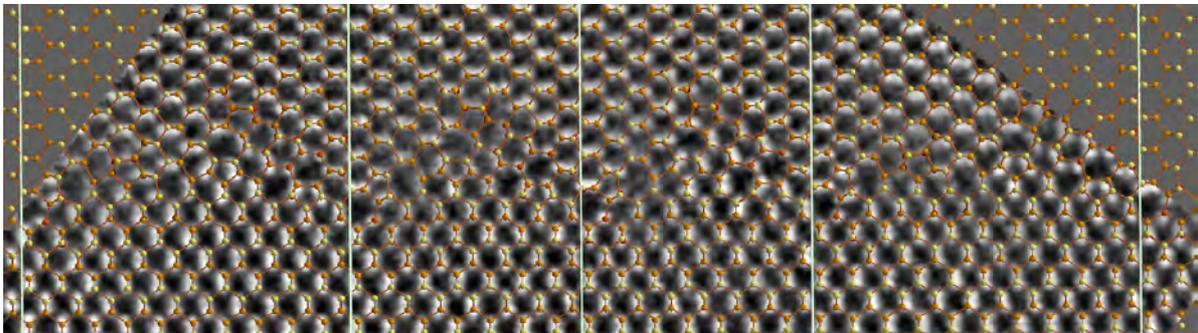


Fig. 1 – High-angle annular dark field (HAADF) scanning transmission electron microscopy image (STEM) illustrating the complexity of the incommensurate Si 90° $\langle 1 1 0 \rangle$ tilt boundary. The common $[1 \bar{1} 0]$ direction is perpendicular to the plane view. The experimental image is overlaid by a calculated structure. The vertical lines partition the structure into approximant units.

Grain boundary structure in high entropy alloys

Diana Farkas ¹

Diana@vt.edu

¹ Department of Materials Science and Engineering
Virginia Tech, Blacksburg, VA 24061, USA

We report atomistic simulation studies of grain boundary structure in a high entropy FCC alloy. The simulations are based on empirical interatomic potentials and use massively parallel molecular dynamics techniques at the atomistic level to study the local structure. The studies address a series of grain boundaries with random misorientations around the [110] crystallographic axis. We analyze the relaxed structures using various models and visualization techniques, ranging from the structural unit model to analyzing the dislocation content of the boundary region. A main focus is the role that the local composition in the random alloy plays in the structure and energy of the boundaries. The implications for the overall properties of high entropy alloys are discussed.

On the temperature dependence of grain boundary and surface energies in tungsten

Daniel Scheiber¹, Oliver Renk², Maxim Popov¹, and Lorenz Romaner¹

lorenz.romaner@mcl.at

¹ Materials Center Leoben Forschung GmbH, Roseggerstrasse 12, 8700 Leoben, Austria.

² Erich Schmid Institute of Materials Science, Jahnstraße 12, 8700 Leoben, Austria.

A good understanding of the temperature-dependence of material properties is of strong relevance for design of materials. While for many bulk properties the temperature dependence has been well investigated, for grain boundary and surface energies the picture is still rather incomplete. Large discrepancies exist between experimental values of interface energies, which are typically carried out at elevated temperatures, and corresponding ab-initio simulations based on density function theory (DFT), which are commonly performed at 0K. To close the gap either experiments need to be extrapolated to low temperatures or DFT calculations extended to finite temperatures.

In this study, we investigate the temperature dependence of interfaces energies in tungsten. We rely on the quasi-harmonic approximation and DFT to calculate phonons for different grain boundaries and surfaces. Based on that, the corresponding Helmholtz free energies as a function of temperature are obtained. Our simulations show considerable reduction in interface energy with temperature for all investigated interfaces grain boundaries and surfaces. Furthermore, we show how changes in grain boundary structure can occur upon heating for certain boundaries. With these results, we can provide close comparison to available experimental data, including in particular equilibrium crystal shapes of small tungsten particles and pores as a function of temperature. Furthermore, we discuss the implications of our findings for related phenomena such as segregation or cohesive properties of grain boundaries.

Nano-scale mapping of the electron density at Al grain boundaries and correlation with grain-boundary energy

Proloy Nandi¹, Xiahan Sang², Eric R. Hoglund¹, Raymond R. Unocic²,
Dmitri A. Molodov³ and James M. Howe^{1*}

*jh9s@virginia.edu

¹Department of Materials Science & Engineering, University of Virginia, Charlottesville, VA 22904, USA

²Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

³Institut für Metallkunde und Metallphysik, RWTH Aachen, Kopernikusstraße 1452056, Germany

Grain boundary (GB) structures and energies are often calculated and such calculations have revealed correlations between GB energy and a change in electron density at the GB [1]. In this work, the plasmon peak in valence electron energy-loss spectroscopy (VEELS) was used to directly determine the variation in electron density across four well-characterized GBs in Al, spanning a range of known GB energies from about 60 to 600 mJ/m² [2]. The results show that the plasmon energy, E_p , is lower at the GB than in the adjacent grains due to a decrease in the electron density (Figs. 1a,b), and that the change in GB energy increases in proportion to the decrease in electron density, ΔE_p (Fig. 1c). The decrease in electron density extends further, $\Delta x E_p$, into the adjacent grains with increasing GB energy (Fig. 1d). Plasmon damping also increases with increasing GB energy, providing a secondary means of assessing GB properties. These results demonstrate that VEELS can be used to provide insight into the fundamental origin and properties of GBs in metals, and potentially determine the magnitude of the GB energy, even for a low-energy (~ 60 mJ/m²) coherent S3 GB in Al.

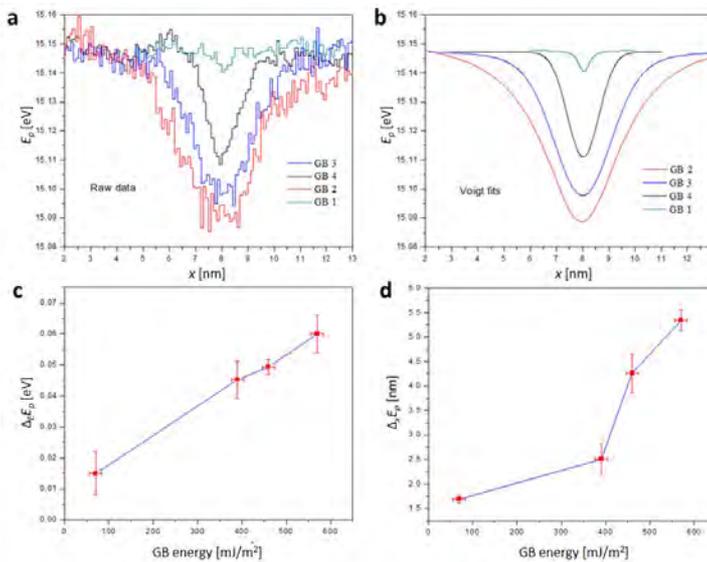


Figure 1: (a) Comparison of raw plasmon energy profiles experimentally obtained across all four GBs. (b) Voigt fits, which better depict the change in plasmon peak energy ΔE_p and width $\Delta x E_p$ of the four GBs. (c) Variation of ΔE_p as a function of GB energy, and (d) dependence of $\Delta x E_p$ with GB energy.

[1] A. F. Wright and S. R. Atlas, *Phys. Rev. B*, 50 (1994) 15248.

[2] P. Nandi, et al., *Micros. Microanal.* 23(S1) (2017) 414.

Acknowledgments Authors JMH, PN and ERH are grateful for partial funding under NSF Grant DMR-1106230. The authors thank Drs. E. Stach and D. Su for help with research conducted in part at CFN-BNL supported by the U.S. DOE-BES under Contract DE-SC-00112704, and acknowledge research supported as part of a user proposal at ORNL-CNMS, which is a U.S. DOE Office of Science User Facility (XS and RRU).

Grain Boundary Thermodynamics: Segregation

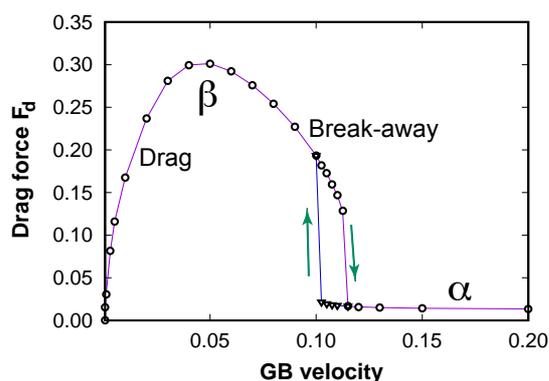
Interaction of moving grain boundaries with solutes

Yuri Mishin

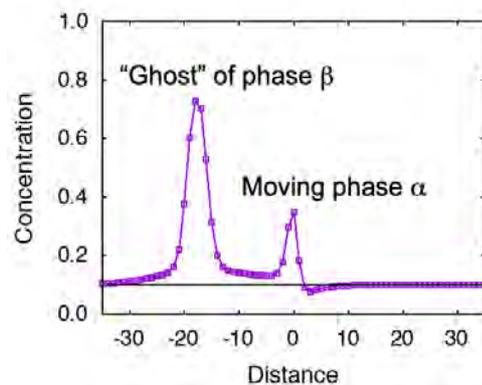
*ymishin@gmu.edu

Department of Physics and Astronomy, George Mason University, Fairfax, Virginia, USA

Solutes can strongly interact with grain boundaries (GBs) and impact their thermodynamic and kinetic properties. Some of the most interesting effects of solute segregation include the segregation-induced GB phase transformations and the solute drag/pinning effect. An even more interesting is the effect of GB motion on GB phase transformations. Studying these effects by molecular dynamics is highly problematic due to the limited time scale of the method. The talk will present several alternative methods for studying phase transformations in moving GBs. One method is based on a semi-analytical discrete GB model in a binary solid solution. The regular solution model predicts first-order phase transformations in GBs, which can be shown by a GB phase coexistence line and GB spinodals of the bulk phase diagram. The model overcomes the time-scale limitation and treats both GB thermodynamics and GB dynamics within a unified framework. It gives direct access to the solute drag force and the GB free energy, which are difficult to compute by atomistic simulations. GB migration can be modeled on different timescales and over a wide range of velocities in both the transient and steady-state regimes. The simulations reveal interesting effects, such as kinetic stabilization of metastable or even unstable GB phases, dynamic GB phase transformations, and the dynamic GB hysteresis. Other interesting effects include the break-way events in which the GB leaves the segregation atmosphere behind and forms a new segregation. This new segregation atmosphere can represent the same of a different GB phase. It is shown how the discrete model reduces to phase-field model in the limit of wide segregation region. The phase-field simulations within this model yield similar results as the discrete model but have certain computational advantages. A new kinetic Monte Carlo model will also be analyzed. This model includes thermal fluctuations and phase separation phenomena in the segregation atmosphere. The results of this study can be broadly interpreted in terms of extremum principles of non-equilibrium thermodynamics, which predict dynamic stabilization of thermodynamically unstable but kinetically favored phases. Extension of the models to 2D and 3D systems and more accurate thermodynamic treatments will be discussed.



Solute drag force versus the grain boundary velocity. The boundary motion starts in the phase β and exhibits the drag dynamics at small velocity and break-away dynamics at large velocity. As the velocity increases, the boundary undergoes a dynamic transformation to the low-segregation phase α . The transformation is accompanied by the dynamic hysteresis shown by the arrows.



Composition profile across a moving grain boundary undergoing the α - β dynamic phase transformation. The boundary breaks away from the segregation atmosphere of phase β and forms a new atmosphere corresponding to phase α . The atmosphere left behind creates a "ghost" grain boundary.

A generalization of McLean's segregation formula using a low temperature expansion

Thomas Schuler^{1,2*}, Frédéric Christien², Patrick Ganster², Krzysztof Wolski²

*thomas.schuler@cea.fr

¹ DEN-Service de Recherches de Métallurgie Physique, CEA, Université Paris-Saclay,
F-91191 Gif-sur-Yvette, France

² Mines Saint-Etienne, Université de Lyon, CNRS, UMR 5307 LGF, Centre SMS, F-42023 Saint-Etienne, France

Abstract

The widely used McLean segregation isotherm formula corresponds to a mean-field approach of segregation phenomena. With modern computing tools based on density functional theory, we now have access to precise information on various segregation sites at an interface. A more rigorous approach based on statistical physics tools is required to take full advantage of all the data that can be computed at the atomic scale. We use the low-temperature expansion formalism to derive new expressions to compute the amount of segregated solutes at an interface. Within the same formalism, we also compute embrittlement potencies (as defined in the Rice and Wang theory) taking into account the details of each segregation site, both in the canonical and grand-canonical ensemble. We apply this formalism to P and H co-segregation at Fe twin boundaries.

Low-temperature expansion

The low-temperature expansion formalism requires a reference state (e.g. the pristine interface, with no segregated elements) from which we perform the expansion of the system's free energy. To this end, we consider excited states, each corresponding to a segregated solute (or a collection of segregated solutes) at a specific interface site. Finally, we compute the concentration of segregated elements at each site, either by imposing the total concentration of a given chemical species (canonical ensemble) or its chemical potential (grand-canonical ensemble). The generalization of this approach to compute embrittlement potencies is straightforward but raises new questions on how to define this quantity, related to the competition between fracture time and equilibration time. In the limit where only one type of solute segregates at one type of boundary site with no interaction among segregated solutes, we recover the McLean segregation isotherm.

P-H co-segregation at Fe twin boundaries

As an example, we apply this formalism to the study of P and H co-segregation at body-centered cubic Fe twin boundaries. We computed P-H binding and segregation energies in the bulk, at a twin boundary and at the corresponding free surface. All these calculations were done ab initio using the PWSCF code. We were then able to determine in which conditions having both impurities (P and H) at the same time leads to the embrittlement of the twin boundary, compared to the case where both impurities are considered separately (i.e. they have no interaction).

Mechanism of grain-boundary segregation of 3d transition-metal solutes in bcc Fe: *ab initio* local-energy analysis

Zhuo Xu, Shingo Tanaka, and Masanori Kohyama*

*m-kohyama@aist.go.jp

Research Institute of Electrochemical Energy, Department of Energy and Environment, National Institute of Advanced Industrial Science and Technology, 1-8-31, Midorigaoka, Ikeda, Osaka 563-8577, Japan

For iron and steel, it is crucial to understand the interactions of transition-metal (TM) solutes with grain boundaries (GBs) in bcc Fe. Recently, the interactions between 3d-TM solutes and a screw dislocation core in bcc Fe were investigated by density-functional theory (DFT) calculations [1], while detailed mechanisms are not yet clarified. In the present study [2], we deal with 3d-TM solute segregation at typical coincidence GBs, $\Sigma 11(332)$ and $\Sigma 3(111)$, in bcc Fe by using DFT calculations combined with *ab initio* local-energy and local-stress schemes [3, 4]. In our previous studies using local-energy and local-stress calculations via QMAS code [5], the presence of *looser* and *tighter* sites in Fe GBs was found as GB sites with expansive and compressive local stresses, and relatively large and small atomic volumes, respectively [6]. The local-energy decomposition of the segregation energy provided novel insights into the mechanism of *sp*-element segregation at metallic GBs [7, 8], where the segregation energy is decomposed into four terms as 1) a local-energy change of a substituted Fe atom at a GB in becoming the bulk Fe atom, 2) a local-energy change of a segregated solute atom at a GB from the state in bulk Fe, 3) local-energy changes of surrounding Fe atoms at a GB due to the solute-atom segregation, and 4) local-energy changes of surrounding Fe atoms of the solute atom in bulk Fe by replacing the solute atom with a Fe atom. In the present study, we have examined 3d-TM solute segregation at *looser* and *tighter* sites of the Fe GBs, and obtained the following results: the early TMs (Sc, Ti and V) are preferentially segregated to *looser* sites antiferromagnetically, the late TMs (Co, Ni and Cu) are preferentially segregated to *tighter* sites ferromagnetically, and the middle TMs (Cr and Mn) are segregated antiferromagnetically to both sites. TMs at both ends of the 3d series show larger segregation-energy gains, while Mn shows a cusp at the center, which is similar to the 3d-TM solute-dislocation interactions [1]. By the local-energy decomposition combined with the local density of states analysis, the segregation of the early TMs is mainly attributed to the stabilization of surrounding Fe atoms by the TM solute at a *looser* site, and that of the late TMs is mainly attributed to the stabilization of a TM solute itself from bulk Fe to a GB site and the destabilization of Fe atoms around the TM solute in bulk Fe. The cusp at Mn is mainly caused by the destabilization of Fe atoms around the Mn solute in bulk Fe, due to nearly-localized high-spin *d* states of Mn in bulk Fe analogous to Hund's rules, in contrast to substantial Mn-Fe *d-d* hybridization for Mn at GBs.

- [1] M. Wakeda *et al.*, Acta Mater. **131**, 445 (2017)
- [2] Z. Xu, S. Tanaka and M. Kohyama, J. Phys. Condens. Matter **31**, 115001 (2019)
- [3] Y. Shiihara, M. Kohyama and S. Ishibashi, Phys. Rev. B **81**, 075441 (2010)
- [4] H. Wang *et al.*, J. Phys. Condens. Matter **25**, 305006 (2013)
- [5] S. Ishibashi *et al.*, Phys. Rev. B **76**, 153310 (2007)
- [6] S. Kr. Bhattacharya *et al.*, J. Phys. Condens. Matter **25**, 135004 (2013)
- [7] S. Kr. Bhattacharya, M. Kohyama, S. Tanaka and Y. Shiihara, *ibid.* **26**, 355005 (2014)
- [8] H. Wang, M. Kohyama, S. Tanaka and Y. Shiihara, J. Mater. Sci **50**, 6864 (2015)

Acknowledgement: This work was supported by MEXT as a social and scientific priority issue (CDMSI) to be tackled by using post-K computer. We greatly thank Prof. Y. Shiihara, Dr. S. Ishibashi, Dr. M. Wakeda, Dr. S. Kr. Bhattacharya, Dr. H. Wang, Mr. K. Ito and Dr. H. Sawada.

Solute segregation at the CSL $\Sigma 3(111)$ iron GB

A.S. Kholobina^{1,2}, W. Ecker¹, R. Pippan³, D. Scheiber¹, V.I. Razumovskiy¹.

Anastasiia.Kholobina@mcl.at

¹Materials Center Leoben Forschung GmbH, Roseggerstrasse 12, 8700 Leoben, Austria

²Department Materials Physics, Montanuniversität Leoben, Jahnstrasse 12, 8700 Leoben, Austria

³Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Jahnstrasse 12, 8700 Leoben, Austria

Abstract

Hydrogen embrittlement (HE) is a latent problem for structural materials, which still requires a better understanding at the fundamental level. One of the possible and well-described in literature HE mechanisms is related to hydrogen enhanced decohesion (HEDE). In this work, we have investigated the effect of some impurities on HEDE in Fe using density functional theory calculations. The results show that some of impurities can reduce or enhance the decohesion of Fe caused by H. The effects of co-segregation and site competition using the McLean segregation isotherm have been investigated and the impact of alloying on HEDE in Fe has been established in a systematic manner.

Impurity segregation to a special CSL GB in Fe

We have used the CSL $\Sigma 3(111)[1\bar{1}0]$ GB that has been chosen according to the modified embedded-atom method (MEAM) calculations [1] in order to study the effect of some impurities on HEDE in Fe. In Fig. 1, we show segregation profiles of one interstitial (C) and one substitution (Nb) impurities as well as of H interstitial as an example. These as well as other elements selected for the current investigation strongly segregate to the representative GB. According to the strengthening energy (η) calculated within the framework of Rice-Wang theory, hydrogen tends to embrittle the selected GBs in iron. In contrast to H, carbon and niobium can strengthen the GB and have a similar positive effect on the decohesion resistance of the bulk Fe calculated using the partial cohesive energy concept (χ) [2]. The segregation profiles have been also used to evaluate GB impurity using the McLean[3] segregation isotherm and to estimate a possible grain size effect [4].

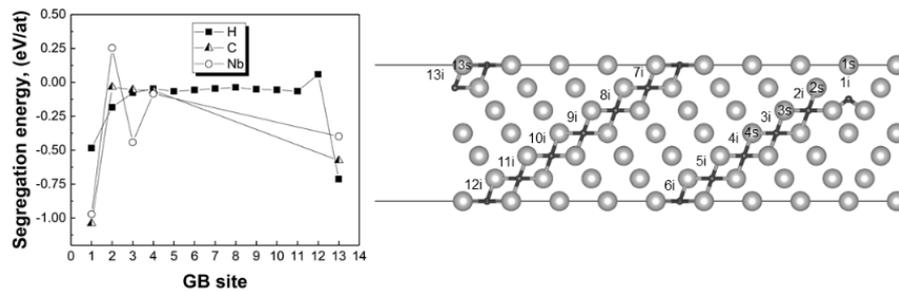


Fig. 1 H, C and Nb segregation profiles at $\Sigma 3(111)$ iron GB.

[1] D. Scheiber et. all, Model. Simul. Mater. Sci. Eng. **24**, 35013 (2016).

[2] V.I. Razumovskiy et. all, Acta Mater. **82**, 369 (2015).

[3] V.I. Razumovskiy et. all, Acta Materialia **147**, 122-132 (2018).

[4] D. Scheiber et. all, Scripta Materialia **150**, 110-114 (2018).

Solute segregation at (100) and (110) tilt grain boundaries in Fe at the atomic scale

C. Paré^{1,2,3}, C. Domain^{1,3*}, J. Vidal^{1,3}, C.S. Becquart^{2,3}

**christophe.domain@edf.fr*

¹ EDF-R&D, Département Matériaux et Mécanique des Composants, Les Renardières,
F-77250 Moret sur Loing, France

² Univ. Lille, CNRS, INRA, ENSCL, UMR 8207, UMET, Unité Matériaux et Transformations,
F-59000 Lille, France

³ EM2VM, Joint laboratory Study and Modeling of the Microstructure for Ageing of Materials

In many alloys and for instance in the steels used as structural materials in nuclear power plant pressurized reactors, solute can segregate to grain boundaries under thermal ageing or irradiation. These solute segregations can affect the mechanical properties of the materials, by either reinforcing the grain boundary cohesion (like carbon) or reducing it (like phosphorous). In order to predict the segregation of these solutes, models such as the ones derived by Mac Lean [1] for binary systems or Guttman for multi-component systems [2], require the knowledge of solute – grain boundary energies, which depend on the grain boundary characteristics. These data can be obtained by simulation at the atomic scale and are currently known only for few high symmetry tilt grain boundaries (e.g. Sigma3, Sigma5). In this work, many different (100) and (110) tilt grain boundaries, that span low to high angle disorientations generated in [3] for Fe have been investigated. Their interaction with different solutes present in steels (e.g. Cr, Cu, Mn, Mo, Ni, Si, P, C) have been calculated using DFT. The results will be presented and compared to available experimental data as well as to the prediction of EAM potentials when available, i.e. for C and P.

[1] D. McLean, Grain boundaries in metals. 1957.

[2] M. Guttman, Equilibrium segregation in a ternary solution: A model for temper embrittlement. Surf Sci 1975;53:213

[3] O. Kapikranian, H. Zapolsky, C. Domain, R. Patte, C. Pareige, B. Radiguet, P. Pareige, Atomic structure of grain boundaries in iron modeled using the atomic density function, *Phys. Rev. B.*, 89 (2014) 014111

A combined effect of vacancies and segregated impurities at grain boundaries in nickel

Martina Mazalová^{1*}, Monika Všíanská^{2,3,1}, Jana Pavlů^{1,2,3}, Mojmír Šob^{1,3,2}

*394206@mail.muni.cz

¹ Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, CZ-611 37 Brno, Czech Republic

² CEITEC - Central European Institute of Technology, Masaryk University, Kamenice 753/5, CZ-625 00 Brno, Czech Republic

³ Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Žitkova 22, CZ-616 62 Brno, Czech Republic

This work presents a detailed ab initio study of interactions between grain boundary (GB), impurities X (X = Al, Si) and vacancies (Va) in fcc ferromagnetic nickel. As a basis of our calculations, supercells containing 60 or 120 atoms, complemented by the tilt S5(210) GB, were used. The calculations were performed within the density functional theory using the VASP code [1–3] with projector-augmented plane wave (PAW) potentials [4, 5]. Two possible approaches to equilibration of structure (full relaxation and relaxation with fixed lattice parameters in the GB plane) are presented and discussed.

In our study the following GB configurations were investigated (superscripts (i) or (s) mean an impurity atom in an interstitial or substitutional position, respectively): GB Ni₁₂₀Si₂⁽ⁱ⁾, GB Ni₆₀, GB Ni₁₂₀, GB Ni₁₁₈Al₂^(s) and GB Ni₁₁₈Si₂^(s). By addition of a vacancy to the above-mentioned structures, it was found that vacancies at this GB may lose their open volume in the most stable configurations, which results in a change of the GB structure. The energy of formation of the structures with GB, vacancy and impurity is positive. The binding energy of a vacancy to a combined defect GB+X is negative for all structures. The inclusion of an X+Va pair into the structure containing GBs is energetically favourable, if calculated with respect to two reference states: “structure with GB, but without any vacancy and impurity” and “impurity in the standard element state”.

As fcc Ni is a ferromagnetic metal, the change of the distribution of magnetic moments on particular atoms caused by impurities, vacancies and GBs was also studied. It was found that Al and Si impurities gain a magnetic moment with antiparallel orientation and the magnetic moment of neighbouring nickel atoms decreases. On the other hand, the presence of a vacancy causes an increase of magnetic moments of neighbouring Ni atoms. However, the “magnetic-moment-decreasing” effect of an impurity with a negative induced magnetic moment is usually larger than the “magnetic-moment-increasing” effect of a vacancy. It was concluded that the distance from the impurity has the dominating influence on the magnetism of Ni atoms in comparison to the distance from the vacancy or GB. As there is very little experimental information on interaction between impurities, vacancies and GBs in fcc nickel, most of the present results are theoretical predictions which may motivate future experimental work.

This research was supported by the Grant Agency of the Czech Republic (Project No. GA16-24711S), by the Ministry of Education, Youth and Sports of the Czech Republic [Project CEITEC 2020 (LQ1601)], by Masaryk University [Project „Research and development in analytical and physical chemistry” (MUNI/A/1375/2018)] and by the Academy of Sciences of the Czech Republic (Institutional Project No. RVO:68081723). Computational resources were provided by the Ministry of Education, Youth and Sports of the Czech Republic under the Projects CESNET (Project No. LM2015042), CERIT-Scientific Cloud (Project No. LM2015085) and IT4Innovations National Supercomputing Center (Project No. LM2015070).

- [1] Kresse G, Hafner J. Phys Rev B 1993;48:13115.
- [2] Kresse G, Furthmüller J. Phys Rev B 1996;54:11169.
- [3] Kresse G, Furthmüller J. Comput Mater Sci 1996;6:15.
- [4] Blöchl PE. Phys Rev B 1994;50:17953.
- [5] Kresse G, Joubert D. Phys Rev B 1999;59:1758.

Compositional analyses at interfaces using atom probe tomography

L. Liliensten^{1*}, D. Palanisamy¹, J. He¹, P. Kontis¹, S.K. Makineni¹, D. Raabe¹, B. Gault^{1,2}

**l.liliensten@mpie.de*

¹ Max-Planck-Institut für Eisenforschung, Max-Planck Straße 1, 40237 Düsseldorf, Germany

² Department of Materials, Imperial College, South Kensington, London SW7 2AZ, UK

Due to the specific properties of interfaces, such as a high chemical activity or a change in the local electronic properties, they are often the loci of significant solute segregation, which can further lead to the formation of complexions or the precipitation of secondary phases. Although critical to the control of the material's properties, understanding the chemical processes at interfaces is extremely challenging, as it implies to characterize at the relevant scale with near-atomic resolution. Atom probe tomography is emerging as the perfect complement to electron microscopy to provide the details of the distribution of species, including light elements, at interfaces and crystalline defects.

In this presentation, several systems will be presented to cover various effects occurring at interfaces. I will illustrate how atom probe tomography can help build a more holistic understanding of interfacial processes so as to rationalize the future design and use of engineering materials.

I will start by discussing grain boundary phases forming during creep tests of Ni-based superalloys. These materials have a very high chemical and microstructural complexity, and their use in high temperature applications often results in the segregation of specific elements and hence the formation of new phases. Anticipating alloys' fracture requires to understand how and where solutes are dragged, and how can they be used at interfaces to enhance the mechanical properties. In particular, the role of boron will be investigated. It is added to superalloys to reinforce the grain boundaries, where it can be formed as solid solution or borides. It is characterized by APT, and the interaction with the neighboring phases by solute drag on dislocations crossing interfaces is analyzed. The ductilizing role of boron at interfaces is reinforced based on the obtained results.

Results on Mn segregation at twin boundaries in a Mn/Al Heusler alloys, with bears great potential as rare-earth-free magnetic material, will also be presented. The metastable τ phase can be obtained from the high temperature equilibrium ϵ -phase (hcp) and may further decompose into the β and γ_2 phases, which are detrimental to the magnetic properties. The magnetic properties of the τ phase are also affected by defects that form during the $\epsilon \rightarrow \tau$ phase transformation, such as $\Sigma 3$ nanotwins. Correlated TEM and APT analyses evidenced a strong Mn segregation at the twin boundaries, with low or no compositional change in the twinned region. Evidencing such segregation helps understand the link between the magnetic properties and the microstructure of the alloy.

Comparison of different ways to evaluate interfacial excess atomic areal density from atom probe data of grain boundaries

Thomas Walther

**t.walther@sheffield.ac.uk*

Department of Electronic & Electrical Engineering, University of Sheffield, UK

Grain boundary segregation is an important phenomenon both in metallurgy and semiconductor technology. For comparison between different experimental methods as well as for setting up appropriate computer models for atomic-scale simulations it is important to measure the interfacial excess of atoms segregated to grain boundaries or incorporated at interfaces between thin films highly accurately.

Some recent studies by tomographic atom probe tomography claim to have measured the interfacial excess of atoms segregated to grain boundaries with ultra-high precision, down to 0.01 [1] or 0.02 [2] atoms/nm² although the experimental scatter from repeated measurements is typically 1-2 orders of magnitude higher, cf. figure 4 in [3].

This study critically evaluates these claims, analysing compositional profiles of simulated interfaces in three different ways, namely by

- i) standard line profile integration,
- ii) the ladder approach developed by Krakauer & Seidman [4],
- iii) the conceptEM approach developed originally for TEM [5] and STEM [6] by the author.

[1] M Herbig, M Kuzmina, C Haase, RKW Marceau, I Gutierrez-Urrutia, D Haley, DA Molodov, P Choi & D Raabe. *Acta mater* 83 (2015) 37-47

[2] Y Ohno, K Inoue, K Fujiwara, K Kutsukake, M Deura, I Yonenaga, N Ebisawa, Y Shimizu, K Inoue, Y Nagai, H Yoshida, S Takeda, S Tanaka & M Kohyama. *Appl Phys Lett* 110 (2017) 062105

[3] M Herbig, D Raabe, YJ Li, P Choi, S Zaefferer & S Goto. *Phys Rev Lett* 112 (2014) 126103

[4] BW Krakauer & DN Seidman. *Phys Rev B* 48:9 (1993) 6724-6727

[5] T Walther. *J Microsc* 215:2 (2004) 191-202

[6] T Walther. *J Microsc* 223:2 (2006) 165-170

Investigation of grain boundary solute segregation behavior using atomic-resolution STEM-EDS

Bin Feng^{1*}, Nathan R. Lugg¹, Akihito Kumamoto¹, Naoya Shibata^{1,2}, Yuichi Ikuhara^{1,2}

*feng@sigma.t.u-tokyo.ac.jp

¹ Institute of Engineering Innovation, The University of Tokyo, Tokyo, 113-8656, Japan

² Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, 456-8587, Japan

Abstract

In this study, we investigated grain boundary (GB) chemistry in yttria-stabilized zirconia (YSZ) using atomic-resolution scanning transmission electron microscopy (STEM) and energy-dispersive x-ray spectroscopy (EDS). We found that Y segregate in the GBs along with the segregation of O, while these Y atoms prefer to segregate in some specific atom sites. Based on these results, GB solute segregation behavior will be discussed in detail.

Introduction

GB segregation is an important topic in materials science, which has been widely studied so far. With the recent development of aberration-corrected STEM and spectroscopy, direct observation of GB dopant segregation is possible at atomic resolution. As a result, GB segregation mechanisms has been revealed for many materials. However, most of these studies were focused on the case of non-solute segregations, of which the dopant atoms can not be soluble inside grain interior. On the other hand, little is reported for GB solute segregation behavior, of which the dopants can reside both at the grain interior and GBs. In this study, GB solute segregation phenomena in YSZ was studied by direct observation of the local GB chemistry using atomic-resolution STEM-EDS.

Experimental procedure

Five types of YSZ bicrystals (10 mol% Y_2O_3 doped ZrO_2) with different GB characters were fabricated by diffusion bonding of two single crystals. STEM-EDS were performed using JEOL JEM-ARM200CF, with an accelerating voltage of 200 kV. We have also combined with electron dynamical scattering theory and atomic site-exchange Monte-Carlo simulations to further interpret the experimental results.

Results and discussion

The atomic structures of these GBs were first determined by high angle annular dark-field (HAADF)-STEM imaging. From the STEM-EDS analysis, we found that Y segregate to the GB core accompanied with increased O concentration. These results suggest that the equilibrium GB chemical distribution is dominated by the long-range electric interactions between charged GB core and charged point defects. Further atomic-resolution EDS maps indicate that Y preferentially segregate to some specific atomic sites. Combining with the theoretical calculations, we demonstrate that the structural factor of GB strain relaxation also affects the Y segregation in the GB. Our results provide a fundamental understanding of GB solute segregation behavior in ionic oxide materials.

Impact of misorientation at symmetric grain boundaries on segregation ability for $\Sigma 3\{111\}$ tilt boundaries in Si

Y. Ohno^{1*}, K. Kutsukake¹, T. Tamaoka², S. Takeda², Y. Shimizu¹, N. Ebisawa¹, K. Inoue¹, Y. Nagai¹, N. Usami³

*yutakaohno@imr.tohoku.ac.jp

¹Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

²Institute of Scientific & Industrial Research, Osaka University, Osaka 567-0047, Japan

³Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan

Grain boundaries (GBs) are inevitably introduced in polycrystalline silicon (Si) ingots for solar cells, and they have substantial influences on electronic properties such as carrier recombination activity, via the segregation of impurity atoms. Especially, asymmetric GBs with higher GB energy are frequently introduced in Si ingots, and they severely affect the overall material properties even when their density is very low. Therefore, a comprehensive knowledge of the recombination activity of the GBs, as well as their segregation ability of impurity atoms depending on their atomistic structure, is indispensable to produce cost-effective high-efficiency solar cells by controlling the formation of detrimental GBs.

In the present study, we examined asymmetric $\Sigma 3\{111\}$ GBs with the $\langle 110 \rangle$ tilt axis, in which the tilt angle and the GB plane orientation were off from their ideal values, in a high-performance Si ingot for commercial solar cells. The photoluminescence (PL) contrast, that is related to the recombination activity, was high for the asymmetric $\Sigma 3\{111\}$ GBs even when the degree of misorientation was small. The PL contrast was as high as ~ 0.6 for an asymmetric $\Sigma 3\{111\}$ GB whose tilt angle was $+7^\circ$ off from the ideal angle of 70.5° . High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) revealed that, most parts of the asymmetric GBs were composed of arrays of GB dislocations lying on the symmetric $\Sigma 3\{111\}$ GB segments. Those dislocations were edge-type with the Burgers vector of $1/3\langle 111 \rangle$. Atom probe tomography (APT) revealed that oxygen atoms would segregate at the atomic sites under tensile stress above about 2 GPa, which were introduced along the GB dislocations [1]. Small amount of carbon atoms also segregated, while they would locate only nearby the dislocation cores. The recombination activity is almost zero for the ideal symmetric $\Sigma 3\{111\}$ GBs [2], and dislocation cores locating at GBs scarcely influence the recombination activity [3]. Considering that the effect of oxygen atoms segregating at GBs on the recombination activity is rather small [3], carbon atoms segregating at GB dislocations would severely influence the recombination activity. We also found an asymmetric $\Sigma 3$ GB whose GB plane was off from $\{111\}$; it was composed of nanofacets on $\{111\}$ and $\{112\}$. Even though the faceted GB would have a high segregation ability due to strains around the edges of the nanofacets [4], its PL contrast of ~ 0.3 was smaller in comparison with dislocated GBs. This suggests that the misorientation in the tilt angle, rather than that in the GB plane orientation, would impact on the recombination activity, as well as on the segregation ability of GBs.

[1] Y. Ohno, *et al.*, J. Microsc. **268** (2017) 230.

[2] Y. Ohno, *et al.*, S. Takeda, Appl. Phys. Lett. **103** (2013) 102102.

[3] Y. Ohno, *et al.*, Appl. Phys. Lett. **109** (2016) 142105.

[4] C. L. Liebscher, *et al.*, Phys. Rev. Lett. **121** (2018) 015702

Acknowledgments: This work is supported by JST/CREST (Grant No. JPMJCR17J1,2017-2023).

Sintering of yttrium aluminum garnet (YAG) for laser applications: role of additives on the subsequent (micro-)structural evolution

Camille Perrière^{1,2*}, Rémy Boulesteix^{1,2}, Alexandre Maître^{1,2}, Lucie Chrétien^{2,3}, Christian Salle^{2,3}

*camille.perriere@unilim.fr

¹ IRCER, UMR CNRS 7315, Univ. Limoges, F-87068 Limoges, France

² LCTL, F-87068 Limoges, FRANCE

³ CILAS, F-45063 Orléans, FRANCE

Yttrium Aluminum Garnet (YAG, $Y_3Al_5O_{12}$) is an excellent host for high power solid state lasers due to its high mechanical and optical properties [1]. This matrix allows incorporation in solid solution of luminescent ions such as rare-earth elements (*e.g.* Nd^{3+} , Yb^{3+} , Ho^{3+} ...) or transition metals (*e.g.* Cr^{4+}). Nevertheless, the optical quality of transparent ceramics can be damaged by the presence of residual microstructural defects (residual porosity, secondary phase). A drastic control of the ceramic process including the sintering is essential of the optical quality required for laser applications.

Sintering aids are used in ceramics to enhance densification kinetics and to achieve full density. More specifically, controlling the relative velocities of grain boundaries and pores during sintering is crucial to the production of a pore-free material. These phenomena can be overcome by using additives [2]. They modify the mass transport kinetics at the grain boundary through either changes in ionic diffusivity or the addition of drag force. Their choice is particularly critical for the manufacturing of transparent ceramics: they should be effective for fully densification without forming any undesired color center or secondary phase, which may alter optical properties by introducing absorbing or scattering centers, respectively [3]. Thus, doping at levels lower than the solubility limit is necessary to avoid uncontrolled enrichment of the grain boundaries and secondary phase precipitation.

The purpose of the present work is to determine the influence of different additives (*e.g.* Ca^{2+} , Mg^{2+} , Si^{4+}) on YAG ceramics microstructure (*i.e.* porosity, grain size, secondary phase, grain boundary composition) to identify sintering mechanisms and, in particular, the rate-limiting elementary step like mass transport process by solid-state or liquid-phase diffusion. First, this work will be focused on the determination of their limit of solubility as a function of the sintering temperature. Then, chemical composition and the location of secondary phases which are issued from the reaction of additives with YAG phase at high temperature will be identified by combining Transmission Electron Microscopy (TEM or HRTEM) and nanoSIMS methods. The corresponding thin slices will be prepared using a focused ion beam (FIB). Special attention will be paid on the characterization of grain boundaries where various phenomena like atomic segregation, precipitation and/or liquid phase formation could occur. At the end, a correlation between used additives, ceramic microstructure and optical properties (*i.e.* transmittance) will be established.

[1] A. Goldstein et A. Krell, « Transparent Ceramics at 50: Progress Made and Further Prospects », *Journal of the American Ceramic Society*, vol. 99, n° 10, p. 3173-3197, oct. 2016.

[2] R. L. Coble, « Sintering Crystalline Solids. I. Intermediate and Final State Diffusion Models », *J. Appl. Phys.*, vol. 32, n° 5, p. 787-792, 1961.

[3] L. Bonnet, R. Boulesteix, A. Maître, R. Belon, L. Chrétien, et C. Sallé, « Influence of (Nd+Y)/Al ratio on sintering behavior and optical features of $Y_{3-x}Nd_xAl_5O_{12}$ ceramics for laser applications », *Optical Materials*, vol. 77, p. 264-272, mars 2018.

Segregation assisted grain boundary precipitation in a model Al-Zn-Mg-Cu alloy

Huan Zhao^{1,*}, Frédéric de Geuser², Alisson Kwiatkowski da Silva¹, Agnieszka Szczepaniak¹,
Baptiste Gault¹, Dirk Ponge¹, Dierk Raabe¹

*h.zhao@mpie.de

1. Max-Planck-Institut für Eisenforschung, Max-Planck-Str. 1, 40237 Düsseldorf, Germany
2. Univ. Grenoble Alpes, CNRS, Grenoble INP, SIMaP, F-38000 Grenoble, France

Understanding the composition and structure evolution of grain boundaries and grain boundary precipitation at near-atomic scale in aluminum alloys is crucial to tailor mechanical properties and to increase resistance to corrosion and stress corrosion cracking. Here, using atom probe tomography and scanning transmission electron microscopy, we elucidate the sequence of precipitation on grain boundaries in comparison to the bulk in a model Al-Zn-Mg-Cu alloy [1,2]. The process starts with solute enrichment on grain boundaries due to equilibrium segregation accompanied by solute depletion in their vicinity, the formation of Guinier-Preston (GP) zones in the solute-enriched grain boundary regions, and GP zones growth and transformation. The equilibrium segregation of solutes to grain boundaries during aging accelerates this sequence compared to the bulk. Analysis of the ~10 nm wide precipitate-free zones adjacent to the solute-enriched grain boundaries shows that the depletion zones are determined by (i) interface equilibrium segregation; (ii) formation and coarsening of the grain boundary precipitates and (iii) the diffusion range of solutes in the matrix.

- [1] H. Zhao et al., *Acta Materialia*, 156, (2018), 318-329.
[2] H. Zhao et al., *Scripta Materialia*, 154, (2018), 106-110.

Acknowledgements H. Zhao acknowledges China Scholarship Council for the PhD scholarship granted to support this work. The authors are grateful for the Max-Planck Society and the BMBF for the funding of the Laplace and the UGSLIT projects respectively.

An atom-probe tomography study of the temporal evolution of concentration retention excesses and depletions at $\gamma(\text{F.C.C.})/\gamma'(\text{L1}_2)$ interfaces in a Ni-Al-Cr-Re superalloy

Sung-Il Baik^{1,2}, Zungang Mao^{1,2}, Ronald D. Noebe³, David N Seidman^{1,2*}

**d-seidman@northwestern.edu*

¹Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA

²Northwestern University Center for Atom Probe Tomography (NUCAPT), Evanston, IL 60208, USA

³NASA Glenn Research Center, 21000 Brookpark Rd, Cleveland, OH 44135, USA

The coarsening kinetics of coherent $\gamma'(\text{L1}_2)$ -precipitates in a quaternary Ni–10Al–8.5Cr–2Re (at.%) alloy aged at 973 K (700 °C) from 0 to 1024 h are studied utilizing atom-probe tomography (APT). The temporal evolutions of concentration retention excesses and depletions, of each element, at $\gamma(\text{f.c.c.})/\gamma'(\text{L1}_2)$ interfaces, are discussed in detail. The measured compositional trajectories of both phases are presented in the quaternary Ni-Al-Cr-Re phase-diagram, which utilizes a tetrahedron for their display. The $\gamma'(\text{L1}_2)$ -precipitates are nucleated in the $\gamma'(\text{L1}_2)$ -phase-field and they have a composition trajectory that evolves toward the $\gamma'(\text{L1}_2)$ -solvus surface, which is curved. While the composition trajectory of the $\gamma(\text{f.c.c.})$ -phase commences in the $[\gamma(\text{f.c.c.}) \text{ plus } \gamma'(\text{L1}_2)]$ -phase-field, at the mean-composition of this quaternary alloy, which moves along a line that evolves toward the $\gamma(\text{f.c.c.})$ -solvus surface, which is also curved. The composition trajectory of the $\gamma'(\text{L1}_2)$ -precipitate-phase encompasses nucleation, growth and coarsening, while the composition trajectory of the $\gamma(\text{f.c.c.})$ -phase reflects changes in the matrix's composition. The tie-line between the $\gamma(\text{f.c.c.})$ - and $\gamma'(\text{L1}_2)$ -phases is determined by the end-point compositions of the two-phases on the two conjugate solvus surfaces. Furthermore, the composition trajectories of both phases are curvilinear. Additionally, we have also observed compositional trajectories of the $\gamma(\text{f.c.c.})$ - and $\gamma'(\text{L1}_2)$ -phases in two binary Ni-Al alloys [1] and three ternary Ni-Al-Cr alloys [2,3,4], which demonstrates that this is an important phenomenon associated with phase separation (phase decomposition or precipitation). To explain the common phenomena in these binary, ternary and quaternary alloys it is necessary to include the off-diagonal terms in the diffusivity matrix, which gives rise to solvent-solute and solute-solute flux couplings.

[1] Submitted for publication, 2018

[2] C. Booth-Morrison, J. Weninger, C. K. Sudbrack, Z. Mao, R. D. Noebe, and D. N. Seidman, "Effects of Solute Concentrations on Kinetic Pathways in Ni-Al-Cr Alloys," *Acta Materialia*, **56** (2008)3422-3438.

[3] Z. Mao, C. K. Sudbrack, K. E. Yoon, G. Martin, and D. N. Seidman, "The Mechanism of Morphogenesis in a Phase Separating Concentrated Multi-Component Alloy," *Nature Materials* **6** (2007) 210-216.

[4] Z. Mao, C. Booth-Morrison, C. K. Sudbrack, G. Martin, and D. N. Seidman, "Kinetic Pathways for Phase Separation: An Atomic-Scale Study in Ni-Al-Cr Alloys," *Acta Materialia*, **60** (2012) 1871–1888.

Acknowledgements: This research was supported by the National Science Foundation, Division of Materials Research (DMR) grant number DMR-1610367 001, Profs. D. Farkas and G. Shiflet, grant officers. Atom-probe tomography was performed at the Northwestern University Center for Atom-Probe Tomography. The LEAP tomograph at NUCAPT was purchased and upgraded with grants from the NSF-MRI (DMR-0420532) and ONR-DURIP (N00014-0400798, N00014-0610539, N00014-0910781, N00014-1712870) programs. NUCAPT received support from the MRSEC program (NSF DMR-1720139) at the Materials Research Center, the SHyNE Resource (NSF ECCS-1542205), and the Initiative for Sustainability and Energy (ISEN) at Northwestern University. We also thank research associate professor Dr. Dieter Isheim for managing NUCAPT.

Grain Boundary Dynamics: Diffusion, Embrittlement

Grain boundary phase transitions probed by tracer diffusion measurements

Sergiy Divinski

divin@wwu.de

Institute of Materials Physics, University of Münster, Germany

Abstract

The existence of grain boundary phase transitions can sensitively be probed via tracer diffusion measurements. The examples for structure phase transitions in low-sigma boundaries of pure Cu and pre-wetting phase transitions in Cu-Bi alloys are presented and discussed.

Results

Grain boundary diffusion is strongly affected by both, interface structure and segregation of residual impurities and represents, thus, an extremely sensitive tool to probe grain boundary phase transitions. Recently, the existence of temperature-induced transitions in the grain boundary structure were revealed by high-precision radiotracer diffusion measurements in low sigma Cu bicrystals [1,2]. An existence of critic temperatures, which corresponds simultaneously to specific "kinks" in the temperature dependences of the grain boundary diffusivity and the disappearance of the grain boundary diffusion anisotropy, is discovered and related to the temperature-induced phase transitions [3].

Segregation-induced grain boundary phase transitions in the Cu-Bi system were investigated by the radiotracer measurements and explained in terms of a pre-wetting phase transition [4]. Measurements of Ag grain boundary diffusion in the same Cu-Bi alloys highlight an intrinsic heterogeneity of the grain boundary phase transitions when the pre-melted and almost segregation-free high-angle grain boundaries co-exist in the polycrystalline Cu-Bi alloy in a broad range of volume concentration of Bi.

[1] H. Edelhoff, S. I. Prokofjev, S.V. Divinski, *Scr. Mater.* 64 (2011) 374-377.

[2] S.V. Divinski, H. Edelhoff, S. Prokofjev, *Phys. Rev. B* 85 (2012) 144104.

[3] T. Frolov, S.V. Divinski, M. Asta, Y. Mishin, *Phys Rev Lett* 110 (2013) 255502.

[4] S. V. Divinski, M. Lohmann, Chr. Herzig, B. Straumal, B. Baretzky, W. Gust, *PRB* 71 (2005) 104104

Experimental evidence for anomalous grain boundary diffusion of Fe in Cu and Cu-Fe alloys

Vladimir A. Esin^{1*}, Daria Prokoshkina², Sergiy V. Divinski²

*vladimir.esin@mines-paristech.fr

¹ MINES ParisTech, PSL Research University, Centre des Matériaux, Evry, France

² Institute of Materials Physics, University of Münster, Münster, Germany

Grain boundary diffusion in the Cu-Fe system is still an issue despite a well-developed methodology of grain boundary diffusion measurements. Different results obtained for this system by different authors have been published so far [1-4] and they are contradictory to some extent.

The aim of the present study is to complete the published previously measurements and to clarify the specific behaviour of Fe in Cu. Fe grain boundary diffusion is studied in 99.995 wt.% pure Cu and the Cu-Fe alloys with iron contents of 0.18, 0.45, 0.6 and 0.8 wt. % using the radiotracer technique. A series of isothermal experiments at 1000 K reveals that the triple product of iron grain boundary diffusion is almost independent on the iron content excepting the alloy containing 0.8 wt. % of Fe where the triple product is increased by three orders of magnitude. Additional experiments at 1100, 900 and 717 K using this alloy confirm the anomaly observed at 1000 K, namely the triple product is continuously increasing following the Arrhenius dependence from 717 K to 1100 K except the temperature of 1000 K, where the triple product is anomalously high.

The obtained results are analyzed applying thermodynamic calculations of Fe and S solubility in Cu. It is suggested that the observed anomalies are related to a change of the grain boundary structure associated with a phase transition occurring in the Cu-Fe alloys [5].

[1] J. Bernardini, C. Girardeaux, A. Rolland, Def. and Dif. Forum 249 (2006) 161-166.

[2] J. Ribbe, G. Schmitz, S.V. Divinski, Def. and Dif. Forum 289-292 (2009) 211-217.

[3] D. Prokoshkina, A. Rodin, V. Esin, Def. and Dif. Forum 323-325 (2012) 171-176.

[4] J. Ribbe, V.A. Esin, S.V. Divinski, Acta Mat. 165 (2019) 431-443.

[5] D. Prokoshkina, V.A. Esin, S.V. Divinski, Acta Mat. 133 (2017) 240-246.

The effect of grain boundary segregation on embrittlement: current advances, challenges and problems

Pavel Lejček¹, Mojmír Šob^{2,3,4*}

**mojmir@ipm.cz*

¹ Laboratory of Nanostructures and Nanomaterials, Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic

² Masaryk University, Faculty of Science, Department of Chemistry, Brno, Czech Republic

³ Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Brno, Czech Republic

⁴ Central European Institute of Technology, CEITEC MU, Masaryk University, Brno, Czech Republic

Intergranular brittle fracture is closely related to the chemistry of grain boundaries and to the difference of the segregation energies of the grain boundaries and the free surfaces (Rice–Wang model). To elucidate the effect of individual solutes on embrittlement of various base materials such as steels and nickel-base superalloys, grain boundary and surface segregation was extensively studied in many laboratories. As a result, numerous data on surface and grain boundary segregation have been gathered in literature. They were obtained in two main ways, by computer simulations and from experiments. These results are frequently applied to quantify the embrittling potency of individual solutes. Unfortunately, the values of the segregation energy of a solute at grain boundaries as well as at the surfaces obtained by various authors sometimes differ by more than one order of magnitude: such a difference is unacceptable as it cannot provide us with representative view on the problem of material temper embrittlement. In some cases it seems that these values do not reflect physical reality or are incorrectly interpreted. Here we summarize the available data on interfacial segregation and embrittlement of various solutes in nickel and bcc iron and critically discuss their reliability, assessing also limitations of individual approaches employed to determine the values of segregation and strengthening/embrittling energies. We demonstrate that theoretical approaches are limited by the size of the computational repeat cell used for the calculations of the segregation energy. On the other hand, even when using repeat cells that are not sufficient for reliable evaluation of the segregation energy, the change in the grain boundary cohesion (strengthening/embrittling energy) may be obtained with a reasonable accuracy. For many impurities, there is lack of experimental segregation data. Therefore, many calculated results are theoretical predictions which may motivate future experimental work.

Physical metallurgy of segregation and its impact on embrittlement and austenite reversion in medium Mn steels

Alisson Kwiatkowski da Silva¹, Dirk Ponge^{1*}, Zirong Peng¹, Margarita Kuzmina¹, Baptiste Gault¹, Dierk Raabe¹

**d.ponge @mpie.de*

¹ Max-Planck-Institut für Eisenforschung GmbH, Germany

Microstructures of medium manganese steels can be tailored to provide superior combinations of high strength, ductility and toughness. Due to their relative low alloying and production costs these steels are candidates for future high strength steels in automotive production. During the heat treatment, equilibrium segregation of solutes like Mn to grain boundaries and dislocations are essential to trigger desired phase transformations like austenite reversion. But segregation can also lead to grain boundary embrittlement. Over the years, MPIE has developed extensive research in order to understand the segregation phenomena in Mn steels, embrittlement and the reversion of austenite. More recently, we start to develop a new approach in order to quantitatively and qualitatively describe the Mn segregation in the BCC structure. This approach couples thermodynamic data from Calphad with the Gibbs model of segregation what allows a more precise description of the segregation behavior observed by atom probe tomography than the more typical Langmuir-McLean segregation model. The most important consequence of this model is that the presence of a spinodal region for the Fe-Mn BCC free-energy will lead to a first order transition of the grain boundary interface. This first order transition is typically represented in equilibrium segregation calculations as a discontinuous jump in the composition of the grain boundary. From the kinetics viewpoint, it implies the formation of metastable spinodal fluctuations that tend to grow further with time at the segregated region, as observed by atom probe tomography. By one hand, this increase in Mn content at the grain boundary leads to an increase of the overall enthalpy of the boundary and embrittlement at lower temperatures. By another hand, these low-dimensional spinodal fluctuations on the grain boundary act as a precursor to the nucleation of austenite when they become strong enough in composition and wavelength. Once austenite is formed, the amount of Mn segregated to the grain boundaries is drastically reduced and the toughness of the grain boundary is increased.

Grain Boundary Dynamics: Corrosion, Wetting

Grain boundary wetting by a second solid phase in the iron-based alloys

B.B. Straumal^{1-4*}, O.A. Kogtenkova¹, A.A. Mazilkin^{1,4}, A.B. Straumal^{1,3},
Yu.O. Kucheyev¹, B. Baretzky⁴

*straumal@issp.ac.ru

¹ Institute of Solid State Physics, Russian Academy of Sciences, Institutskaya str. 2, 142432 Chernogolovka, Russia

² Chernogolovka Scientific Center, Russian Academy of Sciences, Lesnaja str. 9, 142432 Chernogolovka, Russia

³ National University of Science and Technology «MISIS», Leninskii prosp. 4, 119049 Moscow, Russia

⁴ Karlsruher Institut für Technologie (KIT), Institut für Nanotechnologie, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

Abstract

A fundamentally new phenomenon has recently been discovered, namely the wetting phase transitions of the of grain boundaries (GBs) by layers of the second solid phase. This implies that the second solid phase in the two phase regions of phase diagrams can be located at grain boundaries of the initial phase, both in the form of equilibrium thin or thick layers and as separate lenticular particles. The second phase morphology is determined by the ratio of the energies of the grain bound arias and the interphase borders, and can depend on temperature and pressure, or on the concentration of alloying constituents.

Grain boundary wetting by a second solid phase

The transition from incomplete to the complete wetting of grain boundaries by the liquid phase proceeds always with increasing temperature. It is because the temperature dependence of a GB energy in a solid phase intersects $\sigma_{GB}(T)$ with the temperature dependence of the energy of two solid/liquid interphase boundaries $2\sigma_{SL}(T)$. $2\sigma_{SL}$ always decreases with increasing temperatures stronger than the GB energy σ_{GB} since liquid phase has higher entropy in comparison with a solid one. In some cases the transition from incomplete to the complete GB wetting by a second solid phase also proceeds with increasing temperature like in Zn–Al and Fe–C systems. It is because GB energy in the α -phase $\sigma_{\alpha\alpha}$ becomes lower than the energy of two solid/ solid α/β interphase boundaries $2\sigma_{\alpha\beta}$. However, the wetting is also solid, and there is no simple reason, why $\sigma_{\alpha\alpha}(T)$ should decrease with increasing temperature stronger than $2\sigma_{\alpha\beta}(T)$. Indeed, we observed that the GBs can become completely wetted by a second solid phase with decreasing temperature. Moreover, the dependences $\sigma_{\alpha\alpha}(T)$ and $2\sigma_{\alpha\beta}(T)$ can intersect twice. In this case the GB dewetting transition would follow the GB wetting transition.

Grain boundary wetting in the iron-based alloys

In this work we investigated the GB wetting transitions in the technologically important Fe-based alloys, namely the Fe-Nd-B-based hard magnetic alloys and Fe-Cr-based CROFER alloys used for the high-temperature applications like solid oxide fuel cells. Authors thank the Allianz Industrie Forschung (grant 19838), Ministry of Education and Science of the Russian Federation in the framework of the Program to Increase the Competitiveness of NUST “MISIS” and Russian Foundation for Basic Research for the financial support.

Wetting of grain boundaries by intermetallic compounds in an industrial magnesium alloy

K.V. Tsoy*, I.A. Mazilkin, A.B. Straumal

*Key_tsoy@issp.ac.ru

Laboratory of Internal Boundaries in Metals, the Institute of Solid State Physics RAS, Chernogolovka, Russia

The alloy EZ33A is a magnesium alloy widely used in industry. This alloy in the cast state demonstrates low microporosity, good weldability, and creep resistance up to 250 °C. Unfortunately, the magnesium EZ33A alloy has low plasticity at ambient temperatures. The reason for low plasticity is the formation of intermetallic compounds at the grain boundaries. In order to improve the structure of this alloy and its mechanical properties, the goal was set: to experimentally investigate the grain boundary wetting phase transition of α -Mg/ α -Mg grain boundaries by the second phase.

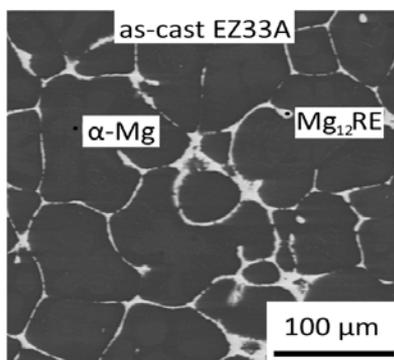


Fig. 1. Microstructure of the initial sample

Using the method of scanning electron microscopy (SEM), we obtained micrographs of the structure of each sample (for example, Fig. 1) selected using light microscopy. Due to the fact that there were a lot of samples, the measurements were made on two scanning electron microscopes - CamScan from Tescan and VegaII from the same company. Using the electron-dispersive x-ray spectroscopy (EDS), a chemical analysis was carried out and the structures of the samples were obtained, along which the two-phase composition is visible, as well as the grain size and the number of completely wetted boundaries. Using these micrographs, the average contact angles and fractions of wetted boundaries were calculated. X-ray diffraction spectra were obtained on a Siemens D-500 diffractometer. Spectra were taken for three representative samples: initial and annealed at 530 °C and 550 °C. According to the data obtained, the phase composition and the change in the amount of the second phase were visible. Phase analysis and calculation of the lattice parameters were performed using the PowderCell 2.4 program. On the RMS-3 instrument, the hardness of the components of the structure was measured.

As a result of the study, the existence of a grain boundary wetting phase transition of α -Mg/ α -Mg grain boundaries with the second liquid phase was shown. After a series of annealing, the temperature of the eutectic transformation of the magnesium alloy EZ33A and the temperature of the onset of the wetting phase transition were determined. In order to increase the plasticity of the alloy at room temperature, an optimal heat treatment sequence was suggested. Also, measurements were made of the hardness of the second phase, the intermetallic compound, which acquired a value of - 210 HV, provided that the α -Mg phase is 41.5 HV.

Acknowledgments The work was performed with the financial support of the Russian Science Foundation (project # 18-72-00243).

Influence of the grain boundary structure on the wetting transition in EZ33A cast alloy

A.B. Straumal^{1,2*}, K.V. Tsoy¹, I.A. Mazilkin^{1,2}, Eggeler G.³

*a.str@issp.ac.ru

¹Laboratory for Interfaces in Metals (LIM), Institute for Solid State Physics (ISSP) RAS, Chernogolovka, Russia

²Laboratory for Hybrid Nanostructured Materials, National University for Science and Technology (NITU MISiS), Moscow, Russia

³ Chair for Materials Science and Engineering, Ruhr-Universität Bochum, Bochum, Germany

Abstract

In this work, the EZ33A Mg-cast alloy was investigated by the electron backscattering diffraction method (EBSD) after isothermal annealing at different temperatures and quenching. Under annealing, the Mg/Mg grain boundaries in the polycrystalline samples become wetted by the liquid phase (the Mg₁₂RE intermetallic phase in the quenched state). As a result, the authors evaluated the whole angular spectrum of grain boundaries found in this alloy in a stable state concerning the wetting temperatures of these grain boundaries and their crystallographic structure. The biggest fraction of the spectrum with the low grain boundary wetting temperatures contains the random grain boundaries with high misorientation angle. The special grain boundaries with low energy have high wetting temperatures and occupy a narrow fraction of the spectrum.

Materials and Methods

The EZ 33A alloy is a magnesium cast alloy that used in aerospace, medical and other industries. Low microporosity, good weldability and creep resistance up to 250 °C are the most important properties of this alloy highly valued in production. Nevertheless, the ductility of this alloy at ambient temperature is very poor and limits the range of machining method applicable in production.

The samples of EZ33A were annealed at different temperatures between solidus and liquidus to obtain different wetting states of the system. After metallographic preparation, the samples were investigated in the scanning electron microscope (SEM) with the electron backscattering diffraction method (EBSD). The EBSD data was analyzed. The spectrum of the grain boundaries found in the system and the wetting temperatures data show the differences in the surface energies of the different types of grain boundaries qualitatively.

Acknowledgments The work was performed with the financial support of the Russian Science Foundation (project # 18-72-00243).

Grain boundary wetting correlated to the grain boundary properties: a laboratory-based multimodal X-ray tomography investigation

Jun Sun^{1,2*}, Yubin Zhang², Allan Lyckegaard¹, Florian Bachmann¹, Erik Lauridsen¹, Dorte Juul Jensen²

*jsun@xnovotech.com

¹ Xnovo Technology ApS, 4600, Køge, Denmark

² Department of Mechanical Engineering, Technical University of Denmark, Denmark

The penetration behavior of liquid gallium in aluminum is characterized using laboratory X-ray attenuation tomography and related to grain boundary properties obtained from 3D grain maps reconstructed by laboratory diffraction contrast tomography (LabDCT). The data is unique with more than 100 grain boundaries analyzed with regards to their misorientation and plane inclination. It is suggested that it is the grain boundary energy which determines if a boundary is wetted or not: low energy boundaries are much more resistant to liquid gallium than higher energy ones. The potentials of using laboratory diffraction contrast tomography for statistical studies of grain boundaries are thereby demonstrated.

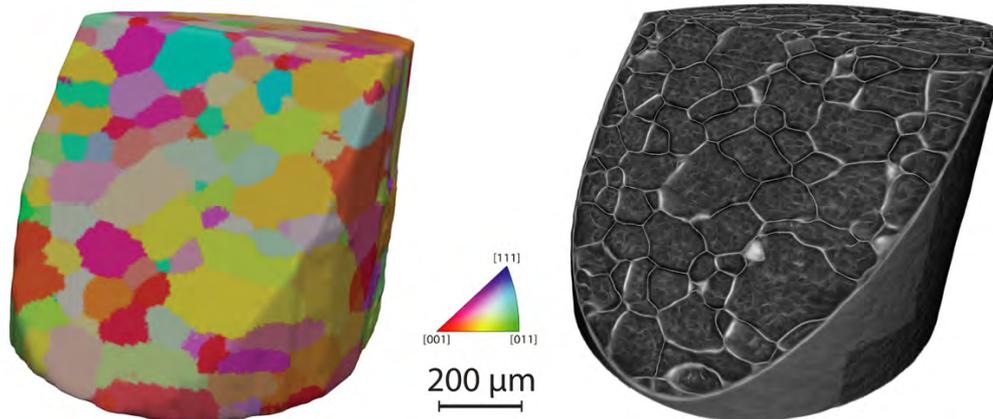


Figure: Correlative analysis of same sample volume imaged from diffraction contrast tomography and absorption contrast tomography [1]. Left: 3D grain map reconstructed from laboratory diffraction contrast tomography, with inverse pole figure coloring of the grains. The five macro-parameters for describing the grain boundary can be calculated from the 3D grain map. Right: Reconstructed sample volume at a similar position in the sample, determined by attenuation contrast tomography using edge enhancement: bright lines reveal the Ga-decorated grain boundaries.

[1] J. Sun, Y. Zhang, A. Lyckegaard, F. Bachmann¹, E.M. Lauridsen, D. Juul Jensen, Scripta Materialia, Vol. 163, 2019, pp77-81. (DOI: <https://doi.org/10.1016/j.scriptamat.2019.01.007>)

Intergranular corrosion modelling: a cellular automata approach

Simone Guiso^{1,2*}, Dung di Caprio², Jacques de Lamare¹, Benoit Gwinner¹

*simone.guiso@cea.fr

¹ *Den-Service de la Corrosion et du Comportement des Matériaux dans leur Environnement (SCCME), CEA, Université Paris-Saclay, F-91191, Gif-sur-Yvette, France*

² *Chimie ParisTech, PSL Research University, CNRS, Institut de Recherche de Chimie Paris (IRCP), F-75005 Paris, France*

Intergranular corrosion (IGC) is one of the attacks that a material may suffer. It is characterized by a preferential attack to grain boundaries, which induces an acceleration of the material degradation. As an example, it can concern stainless steels (SS), when exposed to oxidizing media (e.g. HNO_3), as in the chemical industry [1] or in the nuclear fuel reprocessing industry [2]. Fully understand the degradation mechanism is an important challenge.

IGC is characterized by the formation of triangular grooves at grain boundary level. Their progression leads, with a certain periodicity, to grain dropping, which causes an acceleration of the corrosion phenomenon [3]. From a quantitative point of view, the description of IGC kinetics is still incomplete: in particular, the IGC evolution at bulk level, is quite uneasy to access by experiments. Numerical simulations can, in this case, provide more information and improve the knowledge.

Cellular Automata (CA) can model any complex reality through simple rules and space-time discretization, and are particularly suitable to model IGC [4-5]. The goal of this work is to simulate with CA the kinetics of degradation by IGC, to match as accurately as possible the experimental results in [3]. A hexagonal close-packed (HCP) grid is chosen for the simulations. The granular material structure is modeled through the Voronoi algorithm, while two corrosion probabilities (for grain and grain boundary species) drive the time evolution. With appropriate time and space equivalences, CA simulations are then able to reproduce accurately the experiments in terms of corrosion propagation velocity. The surface morphology reflects the same pattern as in the experiments : after the first transitory phase, grains start detaching from the material and accelerate the IGC process. The material-solution interface is then studied through the time evolution of the solution-grain boundary distribution. Results show an important dependence on the choice of the two corrosion probabilities.

[1] Corrosion in the chemical processing industry - Corrosion by acid nitric. Corrosion in the petrochemical industry, ASM International members (1994) 184-186.

[2] Fauvet, P., Corrosion issues in nuclear fuel reprocessing plants. Nuclear corrosion science and engineering. D. Feron, Woodhead Publishing. 22 (2012) 679-728.

[3] B.Gwinner et al., Towards a reliable determination of the intergranular corrosion rate of austenitic stainless steel in oxidizing media. Corrosion Science 107 (2016) 60-75.

[4] D.Di Caprio et al., 3D cellular automata simulations of intra and intergranular corrosion. Corrosion Science 112 (2016) 438-450.

[5] C.F. Perez-Brokate et al., Cyclic voltammetry simulations with cellular automata. Journal of Computational Science 11 (2015) 269-278.

Grain Boundary Dynamics: Migration, Phase Transformation

The how and why of grain boundary dynamics: a disconnection perspective

David J Srolovitz^{1,2,3,4*},

Jian Han³, Kongtao Chen³, Spencer L Thomas^{3,5}, Chaozhen Wei^{6,7}, Yang Xiang^{6,7}

**srol@cityu.edu.hk*

¹Department of Materials Science & Eng., City University of Hong Kong, Hong Kong SAR, China

²Hong Kong Institute for Advanced Study, City University of Hong Kong, Hong Kong SAR, China

³Department of Materials Science & Eng., University of Pennsylvania, Philadelphia, PA USA

⁴Department of Mechanical Eng. & Applied Mechanics., University of Pennsylvania, Philadelphia, PA USA

⁵Department of Materials Science & Eng., North Carolina State University, Raleigh, NC USA

⁶Institute for Advanced Study, Hong Kong University of Science and Technology, Hong Kong SAR, China

⁷Department of Mathematics, Hong Kong University of Science and Technology, Hong Kong SAR, China

The motion of grain boundaries (GB) is most commonly controlled by the formation and motion of line defects within the boundary (assuming that there is not amorphous phase at the GB). These line defects, known, as disconnections have both a finite step height h and Burgers vector \mathbf{b} . The set of all possible combinations of h and \mathbf{b} are set by the bicrystallography (DSC lattice) – h or \mathbf{b} equals zero is possible in some situations. The dynamics of GBs (including low and high Σ , non- Σ or general, symmetric, asymmetric, and mixed GBs) are determined by the set of operable disconnections and their characters [1]. These dynamics include GB migration, GB shear coupling, GB sliding,.. (e.g., see [1-3]). We present a quantitative approach to understanding GB dynamics as a function of GB type, temperature and driving force based upon a model for disconnection nucleation and migration [1-3]. We parameterize this model based upon atomistic measurements of disconnection nucleation and migration barriers and validate these predictions against molecular dynamics simulations and experimental observations. Finally, we compare and contrast GB migration in bicrystals to that in polycrystalline materials; i.e., the effects of triple junctions [4,5], grain rotation [2], and defect emission during GB motion [5].

[1] J Han, SL Thomas, DJ Srolovitz, “Grain-Boundary Kinetics: a unified approach,” *Progress in Materials Science* **98**, 386-476 (2018).

[2] SLThomas, KT Chen, J Han, PK Purohit, DJ Srolovitz, “Reconciling grain growth and shear-coupled grain boundary migration,” *Nature Comm* **8**, 1764 (2017).

[3] KT Chen, J Han, SLThomas, DJ Srolovitz, “Grain boundary shear coupling is not a grain boundary property,” *Acta Materialia*, in press (2019).

[4] LC Zhang, J Han, Y Xiang, DJ Srolovitz, “Equation of Motion for a Grain Boundary,” *Physical Review Letters* **119**, 246101 (2017).

[5] SL Thomas, CZ Wei, J Han, Y Xiang, DJ Srolovitz, “A Disconnection Description of Triple Junction Motion”, *Nature Comm.*, in press (2019).

Visualizing grain boundary properties with octonions

Ian Chesser^{1,*}, Toby Francis², Marc De Graef¹, and Elizabeth A. Holm¹

*ichesser@andrew.cmu.edu

¹Department of Materials Science and Engineering, Carnegie Mellon University, USA

²Materials Department, University of California Santa Barbara, USA

We develop a method to visualize interface properties that accounts for anisotropy in the full 5-D space of macroscopic crystallographic parameters. This method leverages the recently developed octonion metric [1] to define distances between grain boundaries. Multidimensional scaling is used to learn the structure of grain boundary space from a matrix of N^2 pairwise octonion distances computed from a list of N grain boundaries. A low dimensional representation of grain boundary space is proposed and its connectivity is found to be consistent with existing grain boundary literature. Grain boundary energies and mobilities computed from molecular dynamics simulations are visualized in 2D and 3D for a wide range of grain boundaries, including general boundaries. Energy and mobility are found to be smooth almost everywhere in the reduced grain boundary space. Interpolation and regression are discussed in the space of grain boundaries.

[1] Francis, Toby, et al. "A geodesic octonion metric for grain boundaries." *Acta Materialia* 166 (2019): 135-147.

Direct imaging of atomistic grain boundary migration

J. Wei^{1*}, B. Feng¹, R. Ishikawa¹, N. Shibata^{1,2}, Y. Ikuhara^{1,2}

*wei@sigma.t.u-tokyo.ac.jp

¹ Institute of Engineering Innovation, the University of Tokyo, Tokyo 113-8656, Japan

² Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya 456-8587, Japan

Abstract

In the presentation, we will discuss the atomistic mechanism and related grain boundary (GB) structural evolutions of GB migration. By designing an experiment to control the motion of the GB, we observed the GB migration by atomic-resolution scanning transmission electron microscopy (STEM). We experimentally show that the GB migration is processed by correlated shuffling of atoms at GB ledges, with the GB passing through several low energy stable/metastable structures.

Introduction

Grain boundary (GB) migration is crucially important for the microstructure evolutions of polycrystalline materials. Although numerous efforts have been made to understand the atomistic mechanism of the GB migration, there are still lack of atomic-scale experimental observations of GB migration. In the presentation, we will discuss the atomistic mechanism and related GB structural evolutions during GB migration based on atomic-resolution STEM imaging.

Experiments and results

Our experiments started from the model GB of $\Sigma 7$ [0001] / {2-310} in α -Al₂O₃, which was fabricated by bicrystal method. By using electron beam, we designed an experiment to introduce interstitials from one of the grains to the GB, which enables us to drive the motion of the GB. As shown in Fig. 1, the $\Sigma 7$ GB migrated from the dotted straight line in (a) to the solid curved line in (b). We then imaged this migration process step-by-step by annular dark-field (ADF) STEM. The details about the experimental set-up and the related atomistic mechanism of GB migration will be discussed in the presentation.

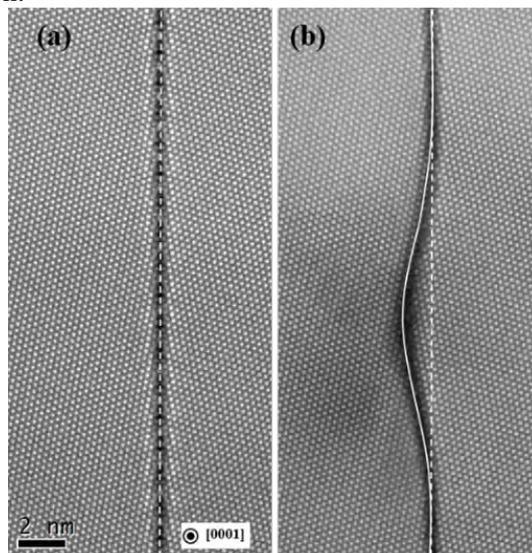


Fig 1. ADF-STEM images of the $\Sigma 7$ GB before (a) and after (b) migration.

Dislocation mediated shear coupled migration of (112) tilt grain boundary in α -Fe

Anna Serra, Napoleon Anento

a.serra@upc.edu

Dept. Civil & Environmental Engineering, Universitat Politècnica de Catalunya (UPC), Campus Nord, Mòdul C-2, Gran Capità s/n, Barcelona 08034. Spain

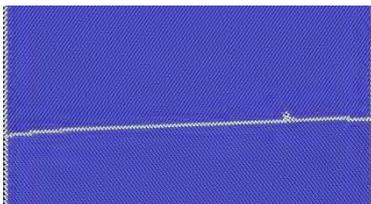
Abstract

The interaction of lattice dislocations of Burgers vector $\vec{b} = \frac{1}{2} \langle 111 \rangle$ with the $\langle 1-10 \rangle (112)$ symmetric tilt grain boundary in bcc Fe produces disconnection dipoles under an applied shear stress. The reaction of the incident dislocation with the produced disconnections facilitates either the transmission of the dislocation or a shear-coupled grain boundary migration depending on the dislocation character. Edge dislocations act as continuous sources of disconnections that follow the grain boundary facilitating the shear-coupled grain boundary migration. Mixed dislocations are transmitted to the adjacent grain by the recombination with disconnections. In both cases, the process is conservative, namely, without atomic diffusion.

Introduction

The plastic deformation associated to the GB migration in the stress driven regime involves the creation and glide of intrinsic GB dislocations. Therefore, the efficiency of the shear coupled migration mechanism depends on the existence of sources of GB dislocations with step character, namely, disconnections. The creation of disconnection dipoles may occur in pristine boundaries at high stresses but the presence of a source of disconnections at the interface reduces significantly the resolved shear stress associated to the migration of the grain boundary. We show that the reaction of a $\frac{1}{2} \langle 111 \rangle$ edge dislocation with the (112) GB provides such source.

Results



The interaction of a $\frac{1}{2} \langle 111 \rangle$ dislocation with the $\{112\}$ GB in bcc Fe produces, under an applied shear stress, dipole pairs of disconnections. Depending on the character of the dislocation, the same GB accommodates plastic deformation by two different ways:

- i) Shear coupled GB migration induced by an edge dislocation that acts as a source of disconnections that moves together with the GB.
- ii) Full transmission to the adjacent grain of the mixed dislocation by adding two disconnections. The GB is displaced by two planes due to the motion of the second disconnection of each dipole. All these processes are conservative, i.e. no need of atomic diffusion.

An attempt to connect grain boundary migration to their atomic structure by mean of molecular dynamics

Sylvain Queyreau^{1,*}, Zakaria El Omari¹, Charlie Kahloun¹ and Brigitte Bacroix¹

**sylvain.queyreau@cnrs.fr*

¹Université Paris 13, Sorbonne Paris Cité, Laboratoire des Sciences des Procédés et des Matériaux, LSPM, CNRS, UPR 3407, 99 avenue Jean-Baptiste Clément, F-93430 Villetaneuse, France

Grain boundary migration is one of the mechanisms at the origin of microstructure evolutions occurring in crystalline materials subjected to thermomechanical treatments. Despite an extensive literature on the subject, many aspects remain unsolved and a unified formalism capable of predicting the evolution of microstructure has yet to be formulated. One of the many challenges in understanding GB motion is related to vast panel of GB atomic configurations or the existence of several motive forces operating simultaneously in experimental samples [1,2]. In this context, atomistic simulations have proven to be particularly useful as GB migration can be investigated under well defined conditions, and large scale systematic investigations are now possible.

In this work, we report a Molecular Dynamics investigation of the migration of a large panel of CSL GB in fcc Ni as described by EAM potentials [3,4]. In order to construct lesser known GB with mixed tilt+twist or asymmetric character, a house-made tool is developed to orient and constrain the simulation domain to the CSL lattice defined by the two crystal orientations, in a fashion very similar to the approach proposed in [5]. GB motion may be initiated by a synthetic driving force as defined in [6]. For the set of studied GBs, very different temperature behaviour are observed ranging from athermal, to thermally activated and non monotonous thermal behaviour. Different behaviours are sometimes observed for very similar GBs, confirming the important rôle of the GB atomic structure over the macroscopic geometrical parameters describing GB.

In an attempt to rationalize these results, we also developed an automated post-processing of the atomic configurations into a discrete modeling of GB in terms of intrinsic dislocations and disconnections, when present. This analysing tool based on the construction of Frank circuits is applied to a dozen of simple GB and a correlation is made when possible between elementary migration mechanisms - atomic shuffling or disconnection motion- and discrete structure of GB. Our findings are also compare to classical model of the literature [7,8,9].

[1] Gottstein, G and Shvindlerman, LS, 1999. Grain Boundary Migration in Metals: Thermodynamics, Kinetics, Applications. CRC Press.

[2] Beucia, B et al., International Journal of Plasticity, 115 (2019) 29.

[3] Foiles, SM et al., Physical Review B, 33 (1986) 7983.

[4] Foiles, SM and Hoyt JJ, Acta Materialia, 54 (2006) 3351.

[5] Banadaki, AD and Patala, S. Journal of Applied Crystallography, 48 (2015) 585.

[6] Janssens, KGF et al., Nature Materials, 5 (2006) 124.

[7] Bollmann, W. 1970. Crystal Defects and Crystalline Interfaces. Springer Berlin Heidelberg, Berlin, Heidelberg.

[8] Frank, FC, Acta Metall., 1 (1953) 15.

[9] Bilby, BA, et al., Proc. R Soc. A, 231 (1955) 263.

A regularized phase field model for anisotropic motion-by-curvature

Thomas Philippe*

**thomas.philippe@polytechnique.edu*

Physique de la Matière Condensée, Ecole Polytechnique, CNRS, France

For realistic interfacial energy, the equation of anisotropic motion-by-curvature exhibits backward-parabolic behavior over portions of its domain and needs to be regularized to model phenomena such as the formation of facets and wrinkles. In the classical theory, the ill-posedness of the dynamic equations is removed by adding a curvature-dependent term to the surface energy, which introduces a bending length. In this work, we adopt a diffuse description of an interface and present a phase-field model for strongly anisotropic surface energy that is regularized using an approximation of the Willmore energy and model kinetically controlled interface motion. Using the method of matched asymptotic expansions, it is shown that the phase-field model converges to the sharp-interface theory. Coarsening dynamics of the faceting instability is also investigated, as an illustration.

Atomic-scale observations of step structure and migration mechanisms in interfaces

U. Dahmen^{1,*}, T. Radetic² and F. Lançon³

*udahmen@lbl.gov

¹NCEM/Molecular Foundry, LBNL, Berkeley, Ca, USA

² Faculty of Technology and Metallurgy, University of Belgrade, Serbia

³ Univ. Grenoble Alpes, CEA, Mem, F-38000 Grenoble, France

The atomic displacements involved in the motion of steps and facets are of key importance for our understanding of microstructural evolution in materials. Faceted interfaces move via the nucleation and propagation of steps. This mechanism can change the rate of interface migration by many orders of magnitude.

Using high resolution electron microscopy, we have made direct observations of the atomic structure and dynamics of steps in interfaces. This talk will present an up-to-date review of these observations, focusing mainly on the migration of high-angle interfaces bounding island grains in $90^\circ \langle 110 \rangle$ and $60^\circ \langle 111 \rangle$ bicrystals of gold. Some of these observations are supported by atomistic simulations on model structures extracted from experimental images.

Step motion is found to be erratic in nature and involves the collective motion of groups of atoms, which can be visualized from the difference between atomic resolution images before and after a migration event. It is observed that short stacking faults similar to those found in the 9R dissociation of many grain boundaries in low-stacking-fault materials are an important feature of the step structure. Numerical simulations reproduce the observed structures well and reveal that the mechanism of step motion involves the constriction and expansion of a stacking fault [1].

This analysis is directly linked with observations of grain boundary migration during shrinkage of island grains under capillary forces. Dynamic in-situ experiments show that the process is controlled by characteristic steps for each facet, step motion is erratic and the rate of shrinkage is non-parabolic. These experiments reveal a distinct variety of steps and facets, moving stochastically and at different rates until the island grain vanishes. Although the general behavior of grains in $90^\circ \langle 110 \rangle$ bicrystals is similar to that of grains in $60^\circ \langle 111 \rangle$ bicrystals, the stronger anisotropy in the latter system leads to greater stability of fully faceted island shapes just before the final shrinkage event.

From a broader perspective, the role of steps and facets in the migration of grain boundaries will be compared briefly with the same effect in solid-liquid interfaces, using in-situ observations of the random thermal motion of nanosized liquid Pb inclusions in Al [2]. In both cases, interfaces are found to be incapable of moving unless enabled by defects, which usually preexist, or which can nucleate when allowed by size effects and proximity to a roughening transition.

[1] Bowers et al., Physical Review Letters, 116(10) (2016) 106102.

[2] Radetic et al., Acta Materialia. 141 (2017) 427

Acknowledgments Work at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Grain boundaries interacting with the diffusion-controlled growth of alloys

Silvère Akamatsu^{1,*} and Sabine Bottin-Rousseau¹

**silvere.akamatsu@insp.jussieu.fr*

¹Sorbonne Université, CNRS UMR 7588, Institut des Nanosciences de Paris, 4 place Jussieu, 75005 Paris, France

We present a study of the coupling of the growth trajectory of grain boundaries in polycrystals with the diffusion-controlled solidification dynamics of nonfaceted alloys [1]. We performed in situ experiments with real-time optical observation during thin-sample directional solidification [2]. At low solidification velocity, an anisotropic grain boundary, typically a low-misorientation subboundary, commonly adopts a low-energy inclination in the solid. It grows tilted at an angle that remains essentially equal to its value determined at rest by the equilibrium at the grain1-grain2-liquid trijunction. When the solidification velocity is increased and approaches the cellular threshold, the subboundary tilt angle decreases, and vanishes when a cellular morphology forms. Therefore, for low growth velocities, the motion of a subboundary groove is slaved to the grain-boundary anisotropy, whereas at high velocity it is slaved to the diffusion-controlled dynamics. Our findings are in good agreement with a recent linear-stability analysis of the problem [3]. Phase-field numerical simulations (collaboration with S. Ghosh, M. Plappa and A. Karma) also clearly evidence that the absence of mobility of subboundaries, at least on micrometric scales, is key to this dynamics [1].

[1] S. Ghosh et al., arXiv:1901.06705.

[2] S. Bottin-Rousseau et al., Phys. Rev. B, Vol. 66 (2002) 054102.

[3] G. Faivre et al., Compte Rendus de Physique, Vol. 14 (2013) 149.

Grain Boundary Spinodal and Transient Spinodal in FeMn System: Phase-Field and Experimental Study

Reza Darvishi Kamachali*, Alisson Kwiatkowski da Silva, Eunan McEniry, Dirk Ponge, Dierk Raabe

*kamachali@mpie.de

Max-Planck-Institut für Eisenforschung, Max-Planck-Str. 1, 40237 Düsseldorf, Germany

Segregation-assisted grain boundary (GB) phase transition can strongly alter the GB and therefore the mechanical properties of polycrystalline materials. This depends on the both thermodynamics and kinetics of solute migration to the GB region. In this study, a new phase-field model has been proposed that employs a relative density parameter, coupled to the concentration field, to distinguish and study the GB region. The model is equipped with available thermodynamics data and atomistic simulations for studying Fe-3Mn, Fe-4Mn and Fe-9Mn (at.%) alloys, that are studied experimentally as well. For an Fe-3Mn at 450 °C, a first-order spinodal transition was predicted and confirmed by atom-probe tomography measurements. Furthermore, it was shown that for compositions beyond the spinodal point (at a given temperature), a transient spinodal transition occurs at the GB that is followed with high segregation of Mn. Figure 1 below demonstrates the evolution of composition field within the GB plane. The current model is applicable for studying and design of microstructures based on GB segregation and phase separation in polycrystalline materials.

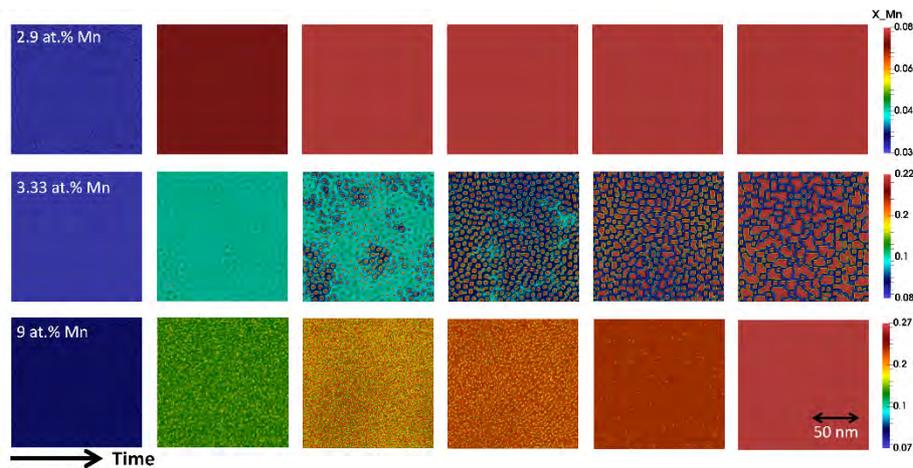


Figure 1: Evolution of GB segregation of Mn for three compositions (below, at and above the spinodal point) are shown.

Theory and modeling of the austenite-martensite interface structure and glissile transformation in steels

Francesco Maresca^{1*}, William A. Curtin¹

*francesco.maresca@epfl.ch

¹ Laboratory for Multiscale Mechanics Modeling (LAMMM)
École Polytechnique Fédérale de Lausanne, Switzerland

The austenite-martensite (fcc-bcc) transformation controls the formation of microstructures in a wide range of high strength steels. Recent progress in the physical metallurgy of steels has shown that nanolaminate austenite/martensite microstructures contribute to high material toughness and resistance to hydrogen-embrittlement [1,2]. Despite its relevance for applications, there is no established theory for the transformation capable to predict the contribution of the austenite-martensite phase transformation to ductility.

To clarify the mechanism of transformation, we have performed atomistic simulations of the interface reproducing the major experimental TEM and HRTEM observations in Fe alloys. The atomistic model reveals for the first time the structure and motion of the athermal and glissile fcc austenite/bcc martensite interface in steels [3]. The interface structure consists of $[-101](111)_{\text{fcc}}$ screws, as envisioned by previous theories, and $[1-11](-101)_{\text{bcc}}$ screws with kinks, which was not envisioned before.

The atomistic findings have guided the formulation of a new, parameter-free double-shear predictive theory of martensite crystallography. Theory predictions show that the fcc/bcc lattice parameter ratio is the key factor controlling the shape deformation (i.e. the in-situ transformation strain), which can achieve more than 90%, namely three times the existing experimental estimates. The theory can thus be used for guiding design of novel and tougher advanced high-strength steels.

- [1] E. De Moor, S. Lacroix, A. Clarke, J. Penning, J.G. Speer (2008), “Effect of retained austenite stabilized via quench and partitioning on the strain hardening of martensitic steels”, *Metall. Mater. Trans. A* **39**, 2586-2595.
- [2] D. Raabe, S. Sandlöbes, J. Millán, D. Ponge, H. Assadi, M. Herbig, P.-P. Choi (2013), “Segregation engineering enables nanoscale martensite to austenite phase transformation at grain boundaries: A pathway to ductile materials”, *Acta Mater.* **61**, 6132-6152.
- [3] F. Maresca, W.A. Curtin (2017), “The austenite/lath martensite interface in steels: Structure, athermal motion, and in-situ transformation strain revealed by simulation and theory”, *Acta Mater.* **134**, 302-323.

Migration of fcc/bcc interfaces — in situ TEM study and MD simulation

Juan Du¹, Zhi-Peng Sun¹, Frederic Momprou², Fu-Zhi Dai¹, Ben Xu¹, Wen-Zheng Zhang^{1*}

*zhangwz@tsinghua.edu.cn

¹ School of Materials Sci. & Eng., Tsinghua University, China

² CEMES-CNRS, Toulouse, 31055, France

Abstract

An investigation has been made on the migration of semicoherent fcc/bcc interfaces using in situ TEM study and MD simulation. Both experimental and simulation results indicate that some fcc/bcc interfaces are glissile and their motion is associated with a long-range strain.

Introduction

Fcc/bcc phase transformation lays the basis for designing heat treatment processes of numerous technically important steels. In contrast to its importance, the details of the phase transformation are still not fully clear. To explore the details, it is essential to clarify how the fcc/bcc interfaces migrate during the phase transformation. This work focused on lath- or plate-shaped transformation products, in so called a Widmanstätten structure. Such a structure has a reproducible crystallographic feature and is often associated with a puzzling surface relief effect. The long-range strain field associated with interface migration is crucial to a quantitative understanding of this effect, which is also a basis for understanding the aggregates of the product phase in a Widmanstätten structure.

Results

Experimental study of the long-range strain field associated with migration of interfaces using in situ TEM is challenging. Existing interfaces between austenite (fcc) and ferrite (bcc) in a duplex stainless steel were mostly immobile. The observations were mainly made from growing of new austenite needles formed in TEM foil, with the crystallography different from the previous austenite due to the foil effect, as quantitatively explained. Both normal motion and ledge motion of interfaces were observed, and continuous motion of semicoherent interfaces is confirmed. Interaction of dislocations in the matrix with moving interfaces was frequently observed. Dislocations were often observed to be generated from the moving interface and emitted to the matrix, suggesting a strong strain field generated in the front of the transformation interface.

The MD simulation of typical semicoherent interfaces between fcc and bcc iron reveals different modes of interface migration, varying with the dislocation structures. It clarifies a quantitative relationship between the dislocation motion, atomic displacement, and macroscopic deformation in a phase transformation. The motion of these interfaces is usually associated with the migration-shear coupling effect. The mobile dislocations always glide in the slip plane defined by the line direction and the Burgers vector, regardless whether the slip plane is a low index plane or not. If the slip systems is in accord with the phenomenological theory of martensite crystallography (PTMC), both the direction and magnitude of the shear is roughly consistent with the prediction of the PTMC. The simulation results also suggest the rules on anisotropic migration of coherent interfaces and on the evolution of variants.

Grain boundaries in solar cells: structure-property correlations

Chen Li*

*lichen0320@gmail.com

EMAT, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerpen, Belgium

Solar energy is a promising means of addressing global warming and the ever-increasing demand for energy. Thin film polycrystalline solar cells have the advantages of low-cost, high-efficiency and flexibility that allows them to be coated on bending substrates. Interestingly, until now the efficiencies of polycrystalline cells including CdTe and Cu(In,Ga)Se₂ (CIGS) exceed that of their single crystal counterparts, indicating exciting defect physics, especially at grain boundaries (GBs). Electron microscopy is a powerful tool for understanding the physics behind the structure-property relationships of solar materials [1-3]. A typical example is shown in Fig. 1. In order to understand how Cl-treatment dramatically improves the cell efficiency of CdTe, electron beam induced current (EBIC) in a scanning electron microscope (SEM) has been applied to map the local carrier collection efficiency on CdTe samples with and without Cl-treatment. Then we determined the atomic structure and chemical compositions of GBs using scanning transmission electron microscopy (STEM). The atomic structure of the GBs does not show clear changes after Cl-treatment, however, electron energy loss spectroscopy (EELS) revealed a distinct change of elemental distribution in GBs: after Cl-treatment all the GBs (apart from twin boundaries) become Cl-rich and Te-poor. Based on these results, we built atomic models and calculated the energy band structure. Combining all the results, the intrinsic physics of the electrical behavior was revealed: Cl doping causes p-n-p junctions at GBs, making GBs and grain interiors separated transport passageways for electrons and holes, respectively. Therefore GBs become efficient at collecting current. Such a systematic workflow shows the power of electron microscopy for elucidating the physical principles behind the electrical behavior of individual defects in solar materials. Moreover, *in-situ* heating microscopy allows us to directly probe growth-structure correlations [4]. STEM imaging and simultaneous EELS elemental mapping during the *in-situ* growth of CuInSe₂ (CIS) solar material show that planar defects and GBs play very important role in recrystallization during growth: GBs always migrate towards grains with high-densities of planar defects. Further atomic structure investigation and atomic EELS mapping show a secondary phase of antiferroite Cu_{2-x}Se (CS) at GBs. Theoretical calculations show that such a CS phase is super-ionic conducting, and hence assists GB migration. Combining all these techniques,

growth-structure-property correlations can be understood, which will open new doors to achieving high performance low cost solar cells.

[1] C. Li, et al. Phys. Rev. Lett. **111** (2013) 096403

[2] C. Li, et al. Phys. Rev. Lett. **112** (2014) 156103

[3] C. Li, et al. Materials Science in Semiconductor Processing **65** (2017) 64-76

[4] C. Li, et al. to be submitted

Acknowledgments Research supported by US DOE Sunshot Project, EU Marie Curie grant No. 656378 – Interfacial Reactions, and the Max Planck Society. Collaborators will be acknowledged in the corresponding slides during the presentation.

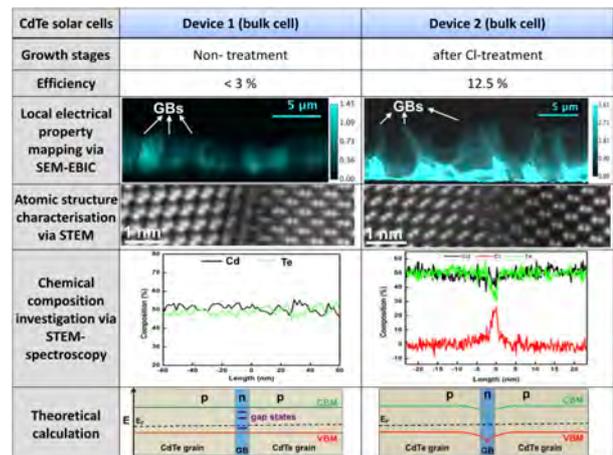


Fig. 1. Combining different microscopy techniques is powerful for determining the fundamental physics of defects. Cl-treatment improves the efficiency of CdTe solar cells, because Cl replaces Te at GBs forming p-n-p

Functional Properties and Low Dimensional Systems

Universal dynamic response in polycrystals of advanced superionic conductors

A.V. Andreeva*, A.L. Despotuli

*andreeva@ipmt-hpm.ac.ru

Institute of microelectronics technology and high purity materials RAS, Chernogolovka, Russia

The aim is to reveal distinctive properties of grain boundaries (GB) in advance superionic conductors (AdSICs) and on this basis to explain the absence of the universal dynamic response (Jonsher's law) in AdSIC polycrystals at 300K in the range of frequencies up to $\sim 10^{10}$ Hz. The AdSICs have the best ion-transport properties, such as a high ionic conductivity $\sigma_i > 10^{-1}$ S/cm at room temperature (RT) and low activation energy of ions movement $E_i \approx 0.1$ eV. Such properties are connected with the special crystal structure of AdSIC monocrystal, optimum for fast ion transport. According to Sunandana's definition [1], a fast ionic conductor = frame sublattice + partial basis + disordering. It is shown that AdSIC structure presents a close-packed cubic lattice of motionless ions penetrated by a 3D-network of topology homogeneous tunnels in which mobile ions move by hopping mechanism. The certain relations between the sizes and polarization of mobile and immobile ions exist in the FIT-tunnels to achieve a homogeneous barriers distribution and a low value of E_a . The geometry of FIT-tunnels in a rigid lattice presents a chain of deformed atomic tetrahedrons conjugated by faces. The preliminary estimates of possible deformations of FIT-tunnels elements are made. GBs of real polycrystalline samples of AdSICs can essentially influence the value σ_i .

A new distinctive (anomalous) property of AdSICs is the absence of the universal dynamic response ($\text{Re}\sigma^*(\omega) \propto \omega^n$ ($n < \approx 1$)) in these polycrystalline materials at 300K in the range of frequencies up to $\sim 10^{10}$ Hz. This power law is usually used in materials science as the standard method of the characterization of solid-state ionic materials. The mechanism of the Jonsher's law origin and its anomalous behavior in AdSICs have been explained on the basis of structure-dynamic approach (SDA) of nanoionics (proposed by the authors) - theory of ion transport in non-uniform on nanoscale potential landscape [2]. According to SDA, the Jonsher's law holds for solid-state ionic conductors in the frequency range depending on the heights η and the heights difference ($\Delta\eta$) of potential barriers in the crystal structure. At sufficiently high values of η and $\Delta\eta$ always, there are spatial areas with the local Maxwell displacement currents (j_D) through potential barriers and ionic hopping currents (j_i) over the same potential barriers, which have comparable values, that leads to the universal response. The absence of the universal dynamic response in AdSICs at RT indicates that in a frequency range up to $\sim 10^{10}$ Hz the inequality $j_D \ll j_i$ holds. It is determined by the synergy processes of structural self-organization and formation of low energy special GBs in AdSICs. Therefore, the values $\Delta\eta$ do not exceed ~ 0.1 eV on GBs, and the response has an ohmic character, i.e., does not depend on ω . An important role of the GB - coherence is emphasized. For AdCICs, the coherence of GBs means not only a continuity of lattice planes at interface intersection but also a continuity of FIT-tunnels at GB intersection and a slight increase of barriers heights η on a boundary in comparison with those in the bulk crystal. Structural models of some special GBs in AdSICs are presented. This research was financially supported by the State Task # 075-00475-19-00.

[1] Sunandana C.S. 2015. Introduction to solid state ionics: phenomenology and applications. Boca Raton: Taylor & Francis.

[2] Despotuli A.L., Andreeva A.V. // Ionics. 2015. V.21. P. 459–469.

Atomic structure and Li-ion conductivity at (La,Li)TiO₃ high-angle tilt grain boundaries

Shun Sasano^{1*}, Ryo Ishikawa^{1,2}, Hiromichi Ohta³, Naoya Shibata^{1,4}, and Yuichi Ikuhara^{1,4}

* sasano@sigma.t.u-tokyo.ac.jp

¹ Institute of Engineering Innovation, The University of Tokyo, Bunkyo, Tokyo 113-8656, Japan

² Japan Science and Technology Agency, PRESTO, Kawaguchi, Saitama 332-0012, Japan

³ Research Institute for Electronic Science, Hokkaido University, Kita, Sapporo 001-0020, Japan

⁴ Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, Aichi 456-8587, Japan

A rechargeable lithium-ion battery (LIB) is a standard power source for modern society because of high energy density and excellent cycle characteristics. Although currently used liquid-state electrolytes show relatively high lithium-ion conductivity, they have some serious problems such as liquid-leakage and firing, so much safer nonflammable solid-state electrolytes have attracted much attention [1]. Lithium lanthanum titanate (LLTO): (Li_{3-x}La_{2/3-x})TiO₃ (0 < x < 0.16) [2] is one of the good candidates for solid-state Li-ion electrolytes because it shows high Li-ion conductivity in the bulk (1×10^{-3} S cm⁻¹). However, Li-ion conductivity of LLTO is largely reduced at grain boundaries (GBs), which prevents the practical application of LLTO to all-solid-state Li-ion battery. Conventional electrochemical impedance spectroscopy is useful method to measure the conductivity, but it has been impossible, only by this method, to reveal what types of GBs reduce Li-ion conductivity in LLTO. The purpose of this study is, therefore, to elucidate the origin of Li-ion resistivity at individual grain boundaries. In general, for polycrystal ceramics, it is difficult to observe GB structures at atomic scale because of their random crystal orientations. In this study, we fabricate the orientation controlled LLTO coincidence site lattice high-angle tilt GBs ($\Sigma 5$, $\Sigma 13$) by bicrystal method combined with pulsed laser deposition (PLD). We then investigate the relationship between atomic structures, chemistry and local Li-ion conductivity at the LLTO GBs by scanning transmission electron microscopy (STEM), electron energy loss spectroscopy (EELS), and electrochemical strain microscopy (ESM) in atomic force microscopy [3, 4].

LLTO thin film was hetero-epitaxially grown on SrTiO₃ (STO) bicrystal substrate by PLD. To obtain an electron transparent sample for STEM and EELS experiments, STO substrate was removed by mechanical polishing and the LLTO film was subsequently thinned by Ar ion milling. The atomic structures and chemistry at the GBs were investigated by STEM and EELS. The local Li-ion conductivity at the GB was measured by ESM. STEM and EELS results show the enrichment of La-ions at the GB and ESM result shows the reduction of Li-ion conductivity around the GB. These results indicate that the local enrichment of La-ions at the GB cores may be related to the reduction of Li-ion conductivity.

[1] N. Kamaya, et al., Nat. Mater. 10 682 (2011) 682-686.

[2] Y. Inaguma, et al., Solid State Commun. 86 (1993) 689-693.

[3] S. Jesse, et al., MRS Bull. 37 (2012) 651-658.

[4] S. Sasano, et al., Appl. Phys. Exp. 10 (2017) 061102.

Ab-initio investigation of structure, chemistry and electronic properties of doped grain boundaries in ZnO

Jürgen Spitaler^{1,*}, Daniel Scheiber¹ and Peter Supancic²

*juergen.spitaler@mcl.at

¹Materials Center Leoben Forschung GmbH, Roseggerstr. 12, 8700 Leoben, Austria

²Institut für Struktur- und Funktionskeramik, Montanuniversität Leoben, Peter-Tunner-Strasse 5, 8700 Leoben, Austria

Doped ZnO grain boundaries are the functionally active parts in varistors, electronic components used as overvoltage protection. In doped ZnO used for varistors, the grain boundaries play a crucial role for the functional behavior: They act as a trap for doping elements and in consequence give rise to charged layers, which eventually lead to the peculiar highly non-linear current-voltage characteristics. We investigate different grain boundaries in terms of structure and energetics. For the S7 grain boundary we study the segregation of doping elements (Pr, Bi) to the grain boundary and how they facilitate the creation of Zn vacancies, which are considered to be crucial for the varistor behavior. Moreover, we study the influence of dopants on the formation energy of inversion boundaries. Using ab-initio calculations we explain why certain dopants (Sb, Fe) enable twinning, while other dopants do not show this phenomenon.

Acknowledgments

We acknowledge financial support from the COMET program within the K2 Center *Integrated Computational Material, Process and Product Engineering (IC-MPPE)* (Project No 859480). This program is supported by the Austrian Federal Ministries for Transport, Innovation and Technology (BMVIT) and for Digital and Economic Affairs (BMDW), represented by the Austrian research funding association (FFG), and the federal states of Styria, Upper Austria and Tyrol.

AgNWs heat-treatment at low temperature (60°C): a combined scanning transmission electron microscopy and molecular dynamic investigation

Arastoo Teymouri¹, Esmail Adabifiroozjai^{2*}, Richard F. Webster³, Hongyang Ma⁴, Xiaojing Hao¹, Martin A. Green¹, Supriya Pillai^{1&5}

**adabifiroozjai.e@nims.go.jp*

¹School of Photovoltaic and Renewable Energy (SPREE), University of New South Wales (UNSW), Sydney 2052, Australia

²Research Centre for Functional Materials (RCFM), National Institute for Materials Science (NIMS), Tsukuba 305-0047, Japan

³Electron Microscope Unit (EMU), University of New South Wales (UNSW), Sydney, 2052, Australia

⁴School of Materials Science and Engineering, University of New South Wales (UNSW), Sydney 2052, Australia

⁵School of Engineering, Macquarie University, Sydney 2109, Australia

It has been a while that silver nanowires (AgNWs) have been introduced as an alternative of indium tin oxide (ITO) for transparent conductive layers in solar cells. In order to make an optimized network with high electrical conductivity, AgNWs are conventionally heat treated at ~200°C. However, one of the requirements of newly developed non-Si based solar cells is the heat-treatment at lower temperature. In the present work we investigate the joining process of AgNWs at temperature as low as 60°C. Tomographic images of the joints are provided by angular scanning transmission electron microscopy (STEM) and early stages of the joining of 17 nm thick nanowires (two million atoms) are explored using molecular dynamic (MD) simulation. The results show careful optimization of parameters as well as proper preparation of AgNWs pave the way for reaching to an optimized conductive network at low temperatures (*e.g.* 60°C). Additionally, our combined characterization and simulation study indicates that old-fashioned technique such as scanning electron microscopy is not capable of revealing the initial steps of joining that occur at nanoscale.

Higher temperatures yield smaller grains in a thermally stable phase-transforming nanocrystalline alloy

Dor Amram^{1,2*}, Christopher A. Schuh²

**dor.amram.da@gmail.com*

¹ Department of Materials Science and Engineering, Technion - Israel Institute of Technology, Haifa, Israel

² Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA

As methods of stabilizing nanocrystalline alloys by grain boundary segregation continue to advance, the number of material systems in which this effect manifests – solely and clearly – remains small. Even in stabilized systems, increasing the annealing temperature always causes grains to grow, even if briefly. Many interesting questions arise, however, when interface-generating phenomena are at play during annealing at high temperatures.

Here we study thermal stability across the allotropic $\alpha \leftrightarrow \gamma$ phase transformation – an interface-generating process – in several nanocrystalline binary Fe alloys. The evolution of phases and grain sizes is tracked in-situ by annealing during x-ray diffraction, while cycling through the transformation. Post-annealed microstructures are characterized by electron microscopy. We explain some striking differences between these alloys in the framework of the regular nanocrystalline solution model.

Extended crystal defects in layered chalcogenide materials: atomic scale structural investigations

Douglas L. Medlin¹

dlmedli@sandia.gov

¹Sandia National Laboratories, Livermore, California 94550, USA

The layered chalcogenides comprise a broad class of materials characterized by functional layer units that are separated by extremely weak bonding, often van der Waals-like, between the double-layers of chalcogen atoms (i.e., S, Se, Te). Such materials play important roles in thermoelectric devices and are of growing interest in the context of emerging functional materials such as topological insulators. The weak interfacial bonding between the functional layers gives rise to strongly anisotropic thermal, electronic, and mechanical properties, but also provides tremendous flexibility for tailoring different combinations of functional units.

In this presentation, our work applying electron microscopy to investigate layered chalcogenides, focussing in particular on the nature of extended crystallographic defects and interfaces in these materials. I will begin with a brief overview of the diversity of structures possible with the layered chalcogenides. Next, I will discuss HAADF-STEM observations of the atomic structure of dislocations in Bi₂Te₃. I will focus on two very different types of dislocation: one with Burgers vector of type $(1/3)\langle 2 -1 -1 0 \rangle$, which lies parallel with the basal plane, and the other with Burgers vector of type $(1/3)\langle 0 1 -1 -1 \rangle$, which has a large dislocation component normal to the basal plane of $c/3$, or one full quintuple unit. The first type possesses a stoichiometric core that is glissile on the basal plane. Here, measurements of the dislocation core-widths provide insight concerning the nature of the gamma surface at the so-called van der Waals gap. The second type of dislocation possesses a much more complex core consisting of bismuth-rich faulted region consistent with Bi₃Te₄, which can be understood as forming through a climb dissociation process.

Climb-dissociated dislocations also arise in the zirconium telluride (ZrTe₅) system, an orthorhombic material with a puckered double-chalcogen layer. Here, our observations have shown that [001] dislocations, which have a large Burgers vector of 1.37 nm, dissociate by climb into two $(1/2)[001]$ dislocations separated by a complex stacking fault region.

Finally, I will discuss our microscopy work on multi-layer di-chalcogenide thin films. In these systems very weak interlayer bonding allows for relatively easy in-plane rotation giving rise to a variety of in-plane defects. Additional defects arise due to stacking errors and incomplete layer growth. Electron microscopic observations drawing on HRSTEM, atomically-resolved EDS, and nanoprobe diffraction provide insight concerning the configurations of the interfaces and defects in these systems.

Acknowledgments Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

Fast mass transportation of metastable AgCu alloys in confined AlN/AgCu/AlN nanolayer sandwiches

Luchan Lin^{1*}, Sebastian Siol¹, Marta D. Rossell¹, Rolf Erni¹, Jolanta Janczak-Rusch¹, Lars P.H. Jeurgens¹

*luchan.lin@empa.ch

¹ Empa, Swiss Federal Laboratories for Materials Science and Technology, 8600 Dübendorf, Switzerland

Nanostructured thin films are usually known to be metastable in their as-deposited state [1]. An increase in temperature may kinetically activate a microstructural transformation of the thin film/substrate system to minimize its total Gibbs energy (including bulk, surface and interface terms). Such microstructural transformations can proceed by concurrent processes, such as grain growth, wetting/dewetting, phase separation and/or fast mass transportation [2]. The thermal response of the metastable thin film system will differ if it is put in confinement between chemically inert barriers, since then the free surface is replaced by an additional interface [3]. In this work, the phase stability of AgCu alloy nanolayers, as confined by inert AlN barrier layers (AlN/AgCu/AlN nanolayer sandwich), is investigated by in-situ heating STEM and HR-SEM. To this end, supersaturated AgCu nanolayers with a bulk eutectic composition of 60 at.% Ag / 40 at.% Cu were magnetron-sputtered at room temperature. It is found that the supersaturated AgCu alloy exhibits a selective fast mobility of Cu in the confinement structure upon heating, whereas Ag remains largely immobile. Depending on the thickness of the confined AgCu nanolayer and the processing atmosphere, very fast and extensive mass transport of Cu can occur at temperatures of 350 °C and even down to 150 °C (Fig. 1). *In situ* STEM observations show that the microstructural transformation with extensive Cu mass transport is finished within minutes at 350 °C. The respective diffraction patterns of pristine and annealed structures indicate that the size and interface coherency of the Ag domains increase upon heating. It is concluded that the much higher atomic mobility of Cu in the confined structure is dictated by the different atomic structures and energies of the Ag/AlN and Cu/AlN interfaces of the respective Ag and Cu domains, as formed by phase separation in confinement.

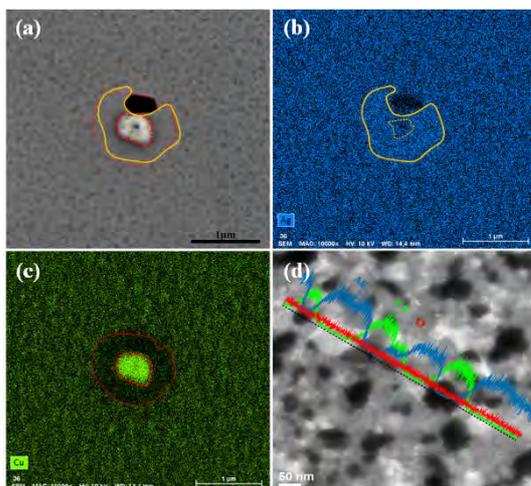


Fig.1 AlN/AgCu/AlN nanolayer sandwich after annealing at 350 °C for 5 min in air. Alloy thickness: 16nm. (a) SEM image of nanolayer sandwich on sapphire (Al₂O₃). (b)(c) Corresponding elemental maps of Ag and Cu. (d) STEM-EDX line profiles of a nanolayer sandwich on amorphous Si₃N₄.

[1] C.V. Thompson, *Annu. Rev. Mater. Res.* 2012, 42: 399-434.

[2] M. Chiodi, C. Cancellieri, and F. Moszner, et al. *J. Mater. Chem. C.* 2016, 4: 4927-4938.

[3] G. Kaptay, J. Janczak-Rusch, and L.P.H. Jeurgens, *J. Mater. Eng. & Perf.* 2016, 25: 3275–3284.

Anisotropic intermixing in Au-Fe bimetallic nanowhiskers

Yuanshen Qi^{1*}, Gunther Richter², Leonid Klinger¹, Eugen Rabkin^{1**}

*yuanshen.qi@campus.technion.ac.il **erabkin@technion.ac.il

¹ Department of Materials Science and Engineering, Technion – Israel Institute of Technology, 3200003 Haifa, Israel

² Max Planck Institute for Intelligent Systems, Heisenbergstrasse 3, 70569 Stuttgart, Germany

The classical laws of diffusion in metals fail at the nanoscale because of the steep concentration gradients and scarcity of vacancy sources. Here, we conducted a series of systematic diffusion measurements on Au-Fe bimetallic nanowhiskers. Defect-free $\langle 110 \rangle$ -oriented Au nanowhiskers having $\{001\}$ and $\{111\}$ side facets were grown by molecular beam epitaxy technique, followed by another deposition of Fe layers. The Fe layers deposited on $\{001\}$ and $\{111\}$ Au facets were single- and polycrystalline, respectively. Focused ion beam (FIB) milling and lift-out technique was used to harvest individual Au-Fe nanowhiskers for heat treatments and subsequent transmission electron microscopy (TEM) sample preparation in cross section geometry with the zone axis parallel to the nanowhiskers axis. Scanning transmission electron microscopy (STEM) with atomic resolution high-angle angular dark-field (HAADF) imaging and electron energy loss spectroscopy (EELS) scanning were carried out for the characterization of the atomic structure of interfaces and composition distribution in their vicinity. We uncovered anisotropic penetration of Fe in Au along $\langle 001 \rangle$ and $\langle 111 \rangle$ directions, even though the diffusion in cubic crystal should be isotropic. The penetration depth of Fe in Au along $\langle 001 \rangle$ was much shorter than it was along $\langle 111 \rangle$ direction and both were shorter than the values estimated from the literature data on bulk diffusion of Fe in Au. We attribute this anisotropic intermixing to the difference in mobility of single- and polycrystalline Fe-Au interfaces. We developed a kinetic model allowing determination of the interface mobilities from our interdiffusion data. The slow mobility of the Fe- $\{001\}$ Au interface was correlated with its atomic structure.

Generation of 2H polytype at an incoherent second-order twin boundary in a silicon nanowire

Zhanbing He¹, Jean-Luc Maurice^{2*}, Qikai Li¹ and Didier Pribat²

*jean-luc.maurice@polytechnique.edu

¹ State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, China

² LPICM, CNRS, École polytechnique, 91128 Palaiseau, France

Abstract

By using atomic resolution high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM), we evidence the coherent intergrowth of diamond cubic (3C polytype) and 2H hexagonal Si in a Si nanowire grown by the vapour-liquid-solid (VLS) technique. Nucleation of the 2H domains have taken place at an incoherent $\Sigma=9$ boundary: a model of the intergrowth of 3C and 2H Si is proposed and the reasons for the generation of 2H Si are discussed.

Some more details

Metastable 2H silicon, an hexagonal polytype of standard Si, may have interesting electro-optical properties [1]. This polytype has been observed in Si nanowires (NWs) grown by the VLS technique (for VLS, see [2]) using tin as catalyst and plasma enhanced chemical vapour deposition (PECVD) as a means to bring matter [3]. It has also been intentionally generated: by epitaxy on the walls of wurtzite GaP NWs [4], or by deformation of Si NWs [5]. Here, we observe it in the core of a Si NW, coherently intergrown with surrounding 3C Si. The coherent intergrowth would open up the way to new applications implying heterojunctions of 3C and 2H Si.

The nanowire studied was obtained by VLS-PECVD using In as catalyst; its characterization was performed using atomic resolution STEM (JEM-ARM200F equipped with a Cs-probe corrector and a Cs-image corrector), in the HAADF mode.

Multiple twinning occurs at a kink in the NW, when the growth direction is changing from $\langle 111 \rangle$ to $\langle 211 \rangle$. At this place, twin boundaries make a star-like shape in the centre of the NW. Those boundaries include first-order ($\Sigma=3$) twin boundaries and an incoherent second-order ($\Sigma=9$) twin boundary. Quite interestingly, this boundary, which probably formed the last during growth, follows an asymmetric and quite strained $\{111\}/\{220\}$ interface (those planes are normally 3.68° apart in a pure $\Sigma=9$ twin relationship). The core of this interface gives birth to 2H domains, that grow over long distances, parallel to the $\langle 211 \rangle$ NW growth direction.

[1] M. Amato, *et al.*, Nano Lett. **16**, 5694-5700 (2016).

[2] R. S. Wagner and W. C. Ellis, Appl. Phys. Lett. **4**, 89-90 (1964).

[3] J. Tang, *et al.*, Nanoscale **9**, 8113-8118 (2017).

[4] H. I. T. Hauge, *et al.*, Nano Lett. **15**, 5855-5860 (2015).

[5] L. Vincent, *et al.*, Nanotechnology **29**, 125601 (2018).

Axial strain relaxation in core-shell nanowires with a polyhedral core due to the nucleation of misfit prismatic dislocation loops

S.A. Krasnitckii^{1,2,3*}, A.M. Smirnov^{2,3}, Gutkin M.Yu.^{1,2,3}

* krasnitsky@inbox.ru

¹ Peter the Great St. Petersburg Polytechnic University, St.-Petersburg, Russia

² ITMO University, St.-Petersburg, Russia

³ Institute of Problems of Mechanical Engineering, Russian Academy of Sciences, St. Petersburg, Russia

Excellent functional properties of composite core-shell nanowires (NWs) make them attractive for designing optical and electronic modern devices [1, 2]. Reliability of the devices is largely determined by the state of interfaces in NWs including their shape, lattice mismatch and presence of defects [3, 4]. To predict and prevent the deterioration of NWs, it is important to create theoretical models describing the strain relaxation process. Among such models, the axisymmetric models of core-shell NWs prevail. They are widely used for defining the critical conditions of misfit dislocation generation [5-7]. The main disadvantage of this approach is the fact that real polyhedral shapes of core-shell interfaces are ignored. On the other hand, the effect of flat faces and sharp edges on the strain relaxation is well known [8].

Recently we have solved a boundary-value problem in the classical theory of elasticity for a cylinder that contains an inclusion in the form of a long polyhedral prism subjected to three-dimensional eigenstrain [9]. This has allowed us to consider the critical condition of misfit stress relaxation process in composite core-shell NWs with cores of polyhedral shapes. We have presumed the nucleation of rectangular prismatic dislocation loops (PDL) on both the free surface and interface in core-shell NWs with cores having the forms of long triangular, square hexagonal prisms and circular cylinders as well. We have calculated and analyzed the energy change due to the PDL nucleation in NWs, which contains the following terms: the strain energy of a rectangular PDL [10], the dislocation core energy [11] and the energy of elastic interaction between the PDL and the misfit stress field. It is shown that in the case when PDLs nucleate on the NW free surface and expand into the shell, the most stable with respect to the PDL generation are NWs with cores of triangular cross section, while those with cylindrical cores are the least stable. In contrast, when PDLs nucleate at the interface and expand into the core, the most stable are NWs with cylindrical cores, while those with cores of triangular cross section are the least stable.

- [1] N I Goktas, P Wilson, A Ghukasyan, D Wagner, S McNamee, R R LaPierre *Appl. Phys. Rev.* **5** (2018) 041305
- [2] G Ai, H Li, S Liu, R Mo, J Zhong *Adv. Funct. Mater.* **25** (2015) 5706
- [3] G Perillat-Merceroz, R Thierry, P-H Jouneau, P Ferret, G Feuillet *Appl. Phys. Lett.* **100** (2012) 173102
- [4] S Conesa-Boj, H I T Hauge, M A Verheijen, S Assali, A Li, E P A M Bakkers, A Fontcuberta i Morral *Nano Lett.* **15**, 5 (2005) 2974
- [5] M Yu Gutkin, I A Ovid'ko, A G Sheinerman *J. Phys.: Condens. Matter* **12** (2000) 5391
- [6] I A Ovid'ko, A G Sheinerman *Phil. Mag.* **84**, 20 (2004) 2103
- [7] J Colin *J. Appl. Mech.* **83** (2015) 021006
- [8] K L Kavanagh, Saveliev I, M Blumin, G Swadener, H E Ruda *J. Appl. Mech.* **111** (2012) 044301
- [9] S A Krasnitckii, D R Kolomoets, A M Smirnov, M Yu Gutkin *J. Phys.: Conf. Ser.* **816** (2018) 012043
- [10] M Yu Gutkin, I A Ovid'ko, A G Sheinerman *J. Phys.: Condens. Matter* **15** (2003) 3539
- [11] J P Hirth, J Lothe 1982 Theory of Dislocations Wiley, New York

The deformation mechanism of bi-crystalline twinned Au nanowires

Omer David¹, Christine Borchers², Cynthia A. Volkert², Dan Mordehai^{1,*}

*danmord@tx.technion.ac.il

¹ Department of Mechanical Engineering, Technion – Israel Institute of Technology, Israel

² Institute of Material Physics, Georg-August-Universität Göttingen, Niedersachsen, Germany

The basic mechanisms for nanoscale deformation of bi-crystalline Au nanowires, containing a single longitudinal twin boundary are investigated. A combined experimental-computational study, including in-situ transmission electron microscopy (TEM), in-situ scanning electron microscopy (SEM) and molecular dynamics (MD) simulations, is performed. Examination of the microstructure in the experiments reveals that pristine nanowires (without pre-existing twins) stored planar defects on two sets of (111), whereas in the twinned nanowires they were found to disappear during the deformation. Moreover, larger twinned regions were identified in the pristine nanowires. MD simulations shed light on the underlying dislocation mechanisms. The onset of plasticity was found to be controlled by the nucleation of dislocations at the edges of the nanowire. In pristine nanowires, consecutive nucleation events and the lack of pre-existing obstacles for dislocation motion formed twinned regions during tension. On the other hand, when a longitudinal twin boundary is introduced in the nanowire, it delays deformation twinning along the nanowire axis. The nucleated dislocations interact with the pre-existing twin during glide, resulting in different reactions that lead to the disappearance of the planar defect, to the motion of twin boundaries or to the formation of new grain boundaries within the nanowire. We discuss the different mechanisms in detail and relate them to the mechanical properties observed experimentally.



Figure: Twinned regions (dark gray) formed during tensile loading of a bi-crystalline Au nanowire.

Acknowledgments This joint research project was financially supported by the Research Cooperation Lower Saxony – Israel from the Ministry of Science and Culture of Lower Saxony and the Volkswagen Foundation, which is gratefully acknowledged.

Mechanical Properties

Stress concentration and distribution in ceramic composites with triple junction heterogeneities

A.B. Vakaeva^{1*}, S.A. Krasnitckii^{2,3,4}, A.M. Smirnov^{3,4}, M.A. Grekov¹ and M.Yu. Gutkin^{2,3,4}

**a.vakaeva@spbu.ru*

¹St. Petersburg State University, Universitetskaya nab. 7/9, St. Petersburg, 199034, Russia

²Peter the Great St. Petersburg Polytechnic University, Politekhnikeskaya 29, St. Petersburg, 195251, Russia

³ITMO University, Kronverkskii pr. 49, St. Petersburg, 197101, Russia

⁴Institute of Problems of Mechanical Engineering, Russian Academy of Sciences, Bolshoi 61, Vasil. Ostrov, St. Petersburg, 199178, Russia

Most of ceramics and ceramic composites contain heterogeneities (such as pores and inclusions), which are considered as one of the main features in the structure of ceramic materials [1, 2]. The type, size and distribution of heterogeneities in ceramics strongly depend on the technology used for their synthesis and further processing. The common place is the presence of heterogeneities at grain boundaries (GBs) and their triple junctions (TJs). In these cases, heterogeneities make a great contribution to the brittleness of ceramics because they play the role of stress concentrators and sources for intergranular cracking. Therefore, the study of stress concentration due to the presence of heterogeneities located at GBs and TJs is of primary importance for developing theoretical models of stress relaxation, plastic deformation and fracture in ceramics under external loading.

In the work [3], the perturbation method was used to solve the problem of a ceramic material with TJ pores of three-fold symmetry. These results can be extended to a more complex problem of stress distribution in the vicinity of a TJ inclusion. In the present work, we attack this problem by both the analytical and numerical means. In doing so, we assume that inclusion-matrix interface satisfies the ideal inseparability conditions [4] and use the Goursat – Kolosov complex potentials, the Muskhelishvili representations and the universal boundary perturbation technique as well. Following Muskhelishvili [5], the complex potentials are found out in terms of power series in small parameter. In each-order approximation of the boundary perturbation method, the problem is reduced to solving the two independent Riemann – Hilbert's boundary problems. An algorithm for finding any-order approximation expressed in elementary functions is suggested. The analytical results are given in an explicit form for the first-order approximation. To solve the described problem numerically, we use the finite-element method. The analytical and numerical results are compared and discussed in detail.

[1] Carter C.B., Norton M.G., Ceramic Materials: Science and Engineering, 2nd Edition (Springer, New York, 2013).

[2] Ragulya A.V., Advances in Applied Ceramics, Vol. 107, No. 3 (2008) 118.

[3] Vakaeva A.B., Krasnitckii S.A., Smirnov A.M., Grekov M.A., Gutkin M.Yu., Reviews on Advanced Materials Science, Vol. 57, No. 1 (2018) 63-71.

[4] Grekov M.A., Vakaeva A.B., Proceedings of the 7th International Conference on Coupled Problems in Science and Engineering, COUPLED PROBLEMS 2017, (2017) 963-971.

[5] Muskhelishvili N.I., Some Basic Problems of the Mathematical Theory of Elasticity (Noordhoff, Groningen, Holland, 1963).

Acknowledgements The research was supported by Russian Foundation for Basic Research under grant 18-01-00468 and Russian Science Foundation under grant 18-19-00255.

Crystal slip and grain sliding: a two-stroke engine driving ductile localization

Alexandre Dimanov^{1*}, Michel Bornert², Jean Raphanel¹, Eva Héripré³, Mathieu Bourcier¹, Ababacar Gaye²,
Alexandre El Sabbagh¹, Wolfgang Ludwig⁴, Andrew King⁵

* alexandre.dimanov@polytechnique.edu

¹LMS, CNRS-UMR7649, Ecole Polytechnique, Route de Saclay, 91128 Palaiseau, France.

²Laboratoire Navier, CNRS-UMR8205, ENPC, 6-8 Avenue Blaise Pascal, 77420 Champs-sur-Marne, France

³MSSMAT, CNRS-UMR8579, CentraleSupélec, 3 Rue Joliot Curie, 91190 Gif-sur-Yvette, France

⁴MATEIS, UMR5510, INSA Lyon, 345 Avenue Gaston Berger, 69100 Villeurbanne, France

⁵SOLEIL Synchrotron, Beam line Psiché, L'Orme des Merisiers, 91190 Saint-Aubin, France

Viscoplastic properties of polycrystalline materials condition many aspects of our everyday life, as for example, hot forming and durability of metallic structures at high temperature, glacier flow, or plate tectonics powered by convection of Earth's mantle rocks. In general, it is admitted that viscoplastic deformation of polycrystals is largely dominated by crystal slip plasticity (CSP). Interfacial mechanisms, as grain boundary sliding (GBS) are mostly invoked for superplastic behaviour, favoured at high temperatures, small grain sizes and low strain rates. However, numerous studies evidence that often both mechanisms coexist. Still, very few have focussed on their respective contributions to the global deformation process. Besides, the way these mechanisms interact remains unclear. These questions are the aim of the present work.

We have studied the viscoplastic response to uniaxial compression of two different classes of annealed and un-textured polycrystalline CFC materials: ionic NaCl and Aluminium, characterized by coarse and equilibrated polygonal grains (ca. 300 nm). Aiming specifically at the localization aspects and mechanisms identification, we realized 2D full strain field micromechanical characterization, based on *in situ* SEM multi-scale observations and digital image correlation (DIC, [1]). Additionally, NaCl samples were analysed by *in situ* synchrotron X-ray tomography, so that we obtained 3D full strain fields.

Our results clearly show that for both materials CSP and GBS coexist. Besides, their interactions are co-operative: CSP is undoubtedly the dominant strain cumulative mechanism. Though, GBS continuously acts as a secondary (but necessary) mechanism, allowing for accommodation of local grain-to-grain strain incompatibilities, resulting from the inherently anisotropic nature of crystal slip. Both mechanisms are absolutely necessary to ensure macroscopically homogeneous flow. For both materials, we show how a minor (but crucial) contribution of GBS allows the development of localization bands and ductile strain propagation throughout the microstructure.

[1] Bourcier et al., Journal of Geophysical Research, Vol. 118 (2013). doi.org/10.1002/jgrb.50065

Acknowledgments We warmly thank the ANR (ANR MicroNaSel) and the Fondation EDF (Chaire énergies durables) for the financial support of the PhD's of M. Bourcier, A. Gaye and A. El Sabbagh. We acknowledge Hakim Gharbi, Alexandre Tanguy and Simon Hallais for technical and experimental support.

Microstructural investigation of damage evolution at the intersection of shear bands

G. Gerstein^{1*}, F. Gutknecht², T. Clausmeyer², F. Nürnberger¹, Y. Estrin³, H.J. Maier¹

*gerstein@iw.uni-hannover.de

¹Institute für Werkstoffkunde (Materials Science), Leibniz Universität Hannover,
An der Universität 2, 30823 Garbsen, Germany

²Institute of Forming Technology and Lightweight Component (IUL)
TU Dortmund University Baroper Str. 303, 44227 Dortmund, Germany

³Department of Materials Science and Engineering, Monash University,
Clayton 3800 Victoria, Australia

Abstract

The nucleation and evolution of micro and nano damage in dual phase steel subjected to plastic strains is investigated. The focus of the electron-microscopic analysis is on the shear band formation in the material. Special methods of grinding, polishing and etching of the samples were employed to analyse the development of the voids. The voids are the main indicators for the development of damage in the plastically deformed samples and their evolution depends on the load path.

Electron microscopic examination of damage evolution

Analysis of the interaction between the resulting shear bands and the nanoscale voids that were generated at the intersection of the shear bands was performed by scanning electron microscopy and transmission electron microscopy.

Scanning electron microscopy and transmission electron microscopy measurements revealed the growth of nano-scale voids in regions with interacting shear bands. TEM investigations showed the presence of dislocation clusters in shear bands inside the grain and the presence of dislocation walls parallel to the shear direction. Apparently, the occurrence of shear bands was initiated by the presence of dislocation clusters.

Analysis of the load path dependency of damage evolution

The dependence of the 3D void distribution and the shape of the voids due to load path change in dual-phase steels on the amount of strain was investigated using metallographic analysis. The dependence of the damage evolution on the strain path change was analysed by EBSD. It was shown that the amount, shape and average size of nano voids are functions of strain and the orientation of the grains. The emergence of voids, their growth and shape is associated with the intersections of different shear bands, the development of moving dislocations in close packed lattice planes, and the characteristics of grain boundaries and triple junctions. The conducted studies allowed to estimate the magnitude of material damage, resulting from the development of shear bands, depending on the type and intensity of deformation.

Theoretical considerations on the initial of sizes were the original void upon formation - are also discussed.

Strengthening mechanisms in heavily cold-rolled stainless steels by heterogeneous nano-structures

H. Miura^{1*}, M. Kobayashi¹, Y. Todaka¹, C. Watanabe², Y. Aoyagi³

*miura@me.tut.ac.jp

¹Department of Mechanical Engineering, Toyohashi University of Technology, Toyohashi, Aichi, 441-8580 Japan

²Faculty of Mechanical Engineering, Kanazawa University, Kanazawa 920-1192, Japan

³Department of Finemechanics, Tohoku University, Sendai 980-8579, Japan

Various kinds of stainless steels were heavily cold rolled up to 95% at maximum. Mixed structures with nano-lamellar, shear bands and mechanical nano-twins were homogeneously developed. That is, all the component grain-boundaries are of low energy ones. Characteristic “eye-shaped” twin domains developed were surrounded by shear bands and embedded in the lamellar structure to form heterogeneous nano structure. The average boundary spacing of the lamellar and the twin domains was about 30 nm and 37 nm respectively. The width of the shear bands was approximately 90 nm [1]. The 90% rolled samples possessed high tensile strength over 1.5 GPa with ductility of 10% and high fatigue strength. These strengths were further raised by ageing. Ultrafine-grained structure and excellent mechanical properties could be achieved by simple cold rolling without severe plastic deformation. It was assumed that the achieved excellent mechanical properties were derived by the specific properties of the component low-energy grain boundaries.

[1] H. Miura, M. Kobayashi, Y. Todaka, C. Watanabe, Y. Aoyagi, N. Sugiura, N. Yoshinaga, *Scripta Mater.*, **133** (2017) 33.

Acknowledgments This research is financially supported by Japan Science and Technology Agency (JST) (20100115) under Industry-Academia Collaborative R&D Program "Heterogeneous Structure Control: Towards Innovative Development of Metallic Structural Materials", and the authors deeply appreciate this support.

Effect of interface character on the deformation behaviour of nanostructured metals

A case study on nickel

O. Renk^{1*}, V. Maier-Kiener²⁾, D. Kiener³⁾, R. Pippan¹

*Oliver.Renk@oeaw.ac.at

¹Erich-Schmid-Institute of Materials Science, Austrian Academy of Sciences, Jahnstrasse 12, 8700 Leoben, Austria

²Departement Physical Metallurgy and Materials Testing, Montanuniversität Leoben, Roseggerstrasse 12, 8700 Leoben, Austria

³Departement of Material Physics, Montanuniversität Leoben, Jahnstrasse 12, 8700 Leoben, Austria

High strength materials generally contain a large number of grain boundaries or interfaces which control their property spectrum. For instance, they are responsible for the enhanced strength of nanomaterials but also damage initiates most often from there, presumably linked to the creation of stress hotspots within the interface due dislocation-interface interactions. For this reason, it is necessary to understand these processes as well as the influence of interface character or chemistry in detail.

Findings from various nanocrystalline FCC materials obtained by high temperature nanoindentation jump tests, suggest that above some temperature strain rate sensitivity increases remarkably, presumably linked to a change of defect-interface interactions. Comparison of the transition temperatures with those obtained earlier in an in-situ TEM study on the same materials indicates, that the reason for the increased rate sensitivity is a change from mechanically to thermally induced motion and decomposition of lattice dislocations at the boundaries. This transition occurs for different FCC materials at different homologous temperatures, emphasizing an important role of the interface chemistry and type. We will not only focus on the impact of this transition on mechanical properties, but also how chemistry or interface type affect the deformation behavior. To understand these effects, we performed similar nanoindentation experiments on different nickel based samples with similar interface spacing but having different characters (low and high angle as well as twin boundaries) and chemistry.

Homogenization model accounting for the internal stresses induced in slip bands

Diogo GONCALVES^{1*}, Maxime SAUZAY², Bertrand SICAUD^{2,3}, Jérôme HAZAN^{2,3}

**diogo.goncalves@cea.fr*

¹ Service d'Études Mécaniques et Thermiques (SEMT), CEA, Université Paris-Saclay, F-91191 Gif-Sur-Yvette, France

² Service de Recherches Métallurgiques Appliquées (SRMA), CEA, Université Paris-Saclay, F-91191 Gif-Sur-Yvette, France

³ Sorbonne Université, Institut de Formation Doctorale, IFD, 15 Rue de l'École de Médecine, 75006 Paris, France

Abstract

Many observations show that slip is strongly localized at grain scale. Then, a new localization rule, accounting for the internal stresses induced in slip bands instead of in grains is proposed and validated, based on the comparison with experimental results. It is shown that the slip band features are strongly dependent on the stacking fault energy of FCC materials. Moreover, these models result in a better representation of the activation of slip systems in the different FCC polycrystals and of the evolution of the Hall-Petch coefficient as a function of the stack fault energy.

Results

In FCC polycrystals, SEM surface observations show the formation of slip lines or slip bands (SB), related to the high degree of hardening observed for these materials. The SB accommodate most of the plastic strain, resulting in the activation of a low number of slip system in the grains, depending on the stacking fault energy (SFE) of the material.

Most of the polycrystal homogenization schemes consider either ellipsoidal grains (mean-field approaches) or Voronoï polyedra (full-field approaches). They lead to predictions in disagreement with experimental observations. The activation of many slip systems in each grain is most often predicted, even at very low macroscopic plastic strain. A polycrystalline homogenization model based on the following hypotheses has therefore been proposed and implemented:

- i) each SB is embedded in an elastic matrix. The SB are characterized by a length (the grain size) and a thickness that is measured experimentally and therefore depends on the SFE. The shear stresses are transmitted to the inter-band elastic ligaments due to the low ratio between thickness and grain size;
- ii) each band obeys plasticity laws based on dislocation dynamics, with the grain size playing a second role, acting as obstacles for the mobile dislocations;
- iii) for high SFE materials, the multiplication of SB is considered with the plastic strain increasing, while the number of SB remains constant for low SFE materials, according to experimental observations [1,2].

The simulations predict polycrystalline tensile curves in agreement with the curves measured on planar materials (Cu30%Zn and 316L SS), with a more linear hardening, and "concave" hardening for metals with high SFE, as Cu and Al. The number of activated systems, depending on the SFE and the grain size, is in better agreement with experimental observations, comparing to other homogenization models. Finally, the model predicts dependence of the Hall-Petch constant on normalized SFE, in agreement with many experimental data.

[1] C. Kahloun et al. International Journal of Plasticity. 84 (2016) 277–298.

[2] M. Ménard. PhD Dissertation, Université Bordeaux I, 2005.

Experimental study on mechanisms of age-hardening in V-alloyed and V-free high-nitrogen steels

E.G. Astafurova*, G.G. Maier, M. Yu. Panchenko, S.V. Astafurov, I.A. Tumbusova, A.S. Mikhno, E.V. Melnikov, V.A. Moskvina, N.K. Galchenko

*elena.g.astafurova@gmail.com

Institute of Strength Physics and Materials Science, Siberian Branch of Russian Academy of Sciences, Akademichesky pr. 2/4, Tomsk, 634055, Russia

Abstract

Experimental investigation of the kinetics and mechanisms of age-hardening in high-nitrogen steels (HNS) with different concentrations of vanadium was carried out. Analysis of the mechanisms of age-hardening, mechanical properties and fracture micromechanisms of the steels shows that the precipitation of particles by the mechanism of continuous decomposition causes greater strengthening effects and smaller embrittlement of the specimens compared to those with discontinuous decomposition of austenite.

Results

A complex study on the kinetics and mechanisms of age-hardening in HNS Fe-23Cr-17Mn-0.1C-0.6N, Fe-19Cr-22Mn-1.5V-0.3C-0.9N and Fe-19Cr-19Mn-2.5V-0.3C-0.8N (wt.%) with different concentrations of vanadium was carried out for the different age-hardening regimes (at temperatures T_A of 600, 700 and 800 °C for 10 minutes to 50 hours).

Regardless on T_A value, the following sequence of phase transformations realizes in steel without vanadium: at the first stage of aging, a δ -ferrite decomposes with the formation of the σ -phase and austenite and the formation of discontinuous decomposition cells (particles based on Cr_2N and austenite depleted in interstitial atoms) occurs along the grain boundaries of austenite; at the second stage, the cells grow in austenitic grains; at the third stage, a homogeneous precipitation of Cr_2N in untransformed austenitic grains occurs, and the σ -phase particles grow near grain boundaries filled with Cr_2N plates. In V-containing HNS, a complex reaction of discontinuous and continuous decomposition takes place. Heterogeneous growth of Cr_2N cells starts on grain boundaries and, later, homogeneous nucleation of (V,Cr)(N,C) particles is realized in the bodies of austenitic grains. An increase in T_A and in the V-concentration up to 2.5% both promote the activation of continuous nucleation of (V,Cr)(N,C) carbonitrides and suppress discontinuous decomposition of austenite in V-containing steels.

Age-hardening is accompanied by an increase in a yield strength of the steels. A comprehensive analysis of the mechanisms of precipitation hardening, the mechanical properties and fracture mechanisms shows that the homogeneous precipitation of particles based on vanadium nitride causes higher strengthening effects and provides smaller embrittlement effects in specimens of HNS compared to those in age-treated specimens with discontinuous decomposition of austenite.

Acknowledgements

The research was supported by the Russian Science Foundation (project No. 17-19-01197).

Mechanical behaviour of nickel symmetric CSL grain boundaries under triaxial loading: from dislocation nucleation to decohesion

B. Sicaud^{1,3*}, L. Van Brutzel², M. Sauzay¹

*bertrand.sicaud@cea.fr

¹ DEN – Service de Recherches Métallurgiques Appliquées, CEA, Université Paris-Saclay, F-91191, Gif-sur-Yvette, France

² DEN – Service de la Corrosion et du Comportement des Matériaux dans leur Environnement, CEA, Université Paris-Saclay, F-91191, Gif-sur-Yvette, France

³ Sorbonne Université, UPMC ED 391 SMAER

The investigation of the mechanical behaviour of grain boundaries (GB) at the atomic scale is of particular interest for the prediction of intergranular microcrack initiation in metals and alloys. At the polycrystal scale, many experimental observations report the formation of plastic slip bands impacting grain boundaries, leading to different phenomena: slip band transmission, strong deformations in the neighbouring grain or GB crack initiation. Further analytical or numerical computations based on crystal finite element (FE) analysis or discrete dislocation dynamics reveal strong multiaxial intergranular stress fields in the vicinity of the corners of the impinging slip bands [Sauzay and K.Vor 2013, Sauzay and M.O Moussa 2013]. However, to our knowledge, few atomistic studies [M. Černý et al. 2010, M. Černý et al. 2016] consider grain boundaries subjected to multiaxial loadings, as only uniaxial loadings are generally applied.

In this study, the mechanical behaviour of various grain boundaries is investigated through molecular dynamics (MD) computations. Loadings consisting in normal straining to the grain boundary plane coupled with transverse straining, are applied to numerous CSL tilt symmetrical [1 0 0] and [1 1 0] grain boundaries in nickel using the EAM potential proposed by Mishin. For each grain boundary, several tensile loadings are carried out for different transverse/normal strain ratio values varying between -0.3 and 0.3.

Geometrical and mechanical parameters such as: thicknesses, axial elastic moduli, critical normal stresses triggering either GB fracture or dislocation nucleation and Griffith energies, are reported for the grain boundaries under study.

An increase of the strain ratio correlates with an increase of the normal critical stress as a progressive behaviour transition from the emission of Shockley partial dislocations to GB brittle decohesion is observed. For all the considered grain boundaries, it is found that as the strain ratio increases from one tensile test to another, the first occurrence of GB crack initiation occurs as the critical stress is saturated, which may correspond to a GB intrinsic parameter of fracture.

Such thorough characterizations provide necessary information at the atomic scale for a bottom-up approach considering a multi-scale analytical model for the prediction of an intergranular crack initiation with a double criterion [Leguillon 2002]. In conjunction, a top-down approach brings a consistency to this multi-scale modeling; this reversed approach is based on MD simulations using displacement fields provided by crystal FE simulations of slip bands/GB interactions, thus allowing us to apply realistic intergranular loadings to our atomistic GB models.

Cohesive stress heterogeneities and the transition from intrinsic ductility to brittleness

D. Tanguy¹

dome.tanguy@univ-lyon1.fr

¹ Institut Lumière Matière, Univ Lyon, Université Claude Bernard Lyon 1, CNRS, Villeurbanne F-69622, France

Nanoscale cavities may be involved in the cracking of metals in a wide range of conditions, such as: fatigue, hydrogen embrittlement, creep, irradiation... A study, based on atomistic simulations, of their impact on the fracture of an intrinsically ductile grain boundary is presented. The crystallography of the GB is chosen such that dislocation emission, directly from the tip of the crack, is easy (intrinsic ductility). Increasing the GB coverage leads to a transition from a ductile behavior to a brittle one. The cavity size and inter-cavity spacings are in good agreement with the experiments of the literature (Miura J. Nucl. Mat. 2015). Nevertheless, even at the highest coverage, the character of the crack is highly sensitive to the initial position of the tip with respect to the smallest cavities. This complexity cannot be accounted for by the Rice and Thomson criterion which considers that an increasing amount of damage in the GB would bring the critical stress intensity factors for brittle propagation below the stress intensity factor for emitting a dislocation, therefore giving sharp transition towards brittleness. Instead, it is shown that the cavities create heterogeneities in the cohesive stress along the interface which induce this complex mixture of brittle and ductile responses. A heterogeneous cohesive zone model, with parameters extracted from the atomistic simulations, gives a clear demonstration of the phenomenon. It also enables to generalize the results obtained on a specific grain boundary.

Reference: D. Tanguy Phys. Rev. B **96**, 174115 (2017)

First principles investigation of H interaction with a $\Sigma 5$ [100] twist grain boundary in the fcc Al during a uniaxial tensile test

F. J. H. Ehlers^{1,2}, M. Seydou², D. Tingaud^{2,*}, F. Maurel¹, Y. Charles², S. Queyreau²

**david.tingaud@univ-paris13.fr*

¹ University Paris Diderot, Sorbonne Paris Cité, ITODYS, UMR 7086 CNRS, 15 rue J.- A. de Baïf, F-75205 Paris cedex 13, France

² Université Paris 13, Sorbonne Paris Cité, Laboratoire des Sciences des Procédés et des Matériaux, LSPM, CNRS, UPR 3407, 99 avenue Jean-Baptiste Clément, F-93430 Villetaneuse, France

For the theoretical assessment of intergranular fracture, ab initio investigations of Grain Boundaries (GBs) subjected to loading play a central role. While the modelling of material failure is an inherently multi-scale task, a first principles framework often provides unmatched accuracy for the description of atomic rearrangements and bond breakage at the heart of the region of key interest. At the same time, it is crucial to a meaningful analysis that the atomistic traction-separation curve emerging from density functional theory (DFT) based studies be coupled self-consistently to the stress field of the surrounding bulk grain. The absence of a robust solution to this challenge has manifested itself as a “cell size convergence problem” for the computed atomistic GB properties.

In this talk, we first show how this obstacle may be entirely circumvented for the modelling of metal GBs within a standard DFT framework [1]. In the procedure, we delimit a GB “local region” outside which the system response to deformation bears no significant evidence of the presence of a nearby GB, and behaves mostly on an elastic manner.

Then, we show through the example of H decoration of the fcc Al $\Sigma 5$ 36.87° [100] twist GB how this platform may be used efficiently for quantifying the influence of impurities on a metal GB in a multi-scale modelling approach. We investigated the H formation energies at the various unequivalent sites - or structural units- and in the vicinity of the GB evolve differently with the increase of tensile strain. Finally, following the considerations discussed in [2], the H impact on the full TSL curve at the most stable sites during elongation is assessed assuming relatively fast or slow diffusion of H atoms with respect to mechanical loading.

[1] Ehlers, FJH et al., Comput. Mater. Sci., 139 (2017) 39

[2] Van der Ven A. And Ceder G. Acta Materialia 52 (2004) 1223.

Plasticity Mechanisms

Using in-situ TEM to probe interface related plasticity mechanisms

Frédéric Mompiau

mompiau@cemes.fr

¹ CEMES-CNRS and Université de Toulouse, 29 rue Marvig, 31055 Toulouse, France

Abstract

The role of interfaces on plasticity is manifold. On the one hand, they significantly interfere with intra-granular mechanisms by impeding dislocations motion. On the other hand, they can also efficiently carry plastic deformation by themselves, during stress/strain coupled-migration mechanisms (twinning, strain induced phase transformations...). In this presentation, we'd like to highlight the usefulness of in-situ Transmission Electron Microscopy (TEM) to probe the large variety of mechanisms occurring at interfaces in metallic materials and their dynamics during miniaturized mechanical tests.

Results

The scope of this presentation concerns the questions raised by plastic deformation mechanisms that occur in confined conditions, especially in small grained metals, where interfaces play a significant role in controlling mechanical properties such as hardening (size effect on the yield stress) or inelasticity (Bauschinger effect). To address these questions, we have performed several in-situ straining experiments and exploited the TEM imaging and diffraction capabilities to analyze qualitatively and quantitatively dislocation and interface motions. Such experiments require dedicated samples, controlled microstructures and sample holders operating in a large range of temperature. We thus have tested small grained Al (grain size between 100 nm and 1 μ m) on MEMS-supported polycrystalline thin films, bulk polycrystals or bicrystals.

In polycrystals, several inter- (dislocation emission from internal or grain boundary sources) and intra- granular mechanisms (i.e. grain boundary sliding, rotation and grain growth) are activated during plastic deformation in a complex manner that can be first qualitatively retrieved. Quantitative measurements on inelastic recovery during straining and unloading experiments or grain rotation and migration can be retrieved from these observations and linked to mechanisms, i.e. disconnection motions or dislocation pile-ups, respectively. In bicrystals, grain boundary migration under stress can be probed in a controlled manner and disconnection mechanisms in link with intra-granular plasticity can be examined.

Unconventional twin interfaces revealed by EBSD in a single crystal of magnesium

Cyril Cayron^{1*}, Roland Logé¹

*cyril.cayron@epfl.ch

¹ Laboratory of Thermo Mechanical Metallurgy (LTM), PX Group Chair, Ecole Polytechnique Fédérale de Lausanne (EPFL), Rue de la Maladière 71b, 2000 Neuchâtel, Switzerland

Abstract

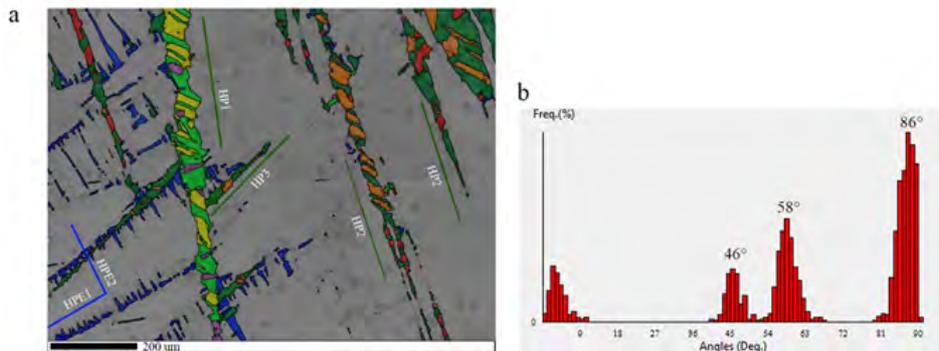
Some twins induced by deformation in a single crystal of magnesium have unconventional habit planes: the Miller indices of the interface referred in the twin are not the same as those referred in the parent matrix. This experimental result is in direct contradiction with the current opinion that assumes that deformation twinning is a simple shear mechanism.

Deformation twinning, simple shear and atom sizes

Theory of deformation twinning dates from the end of the 19th century and relies on the assumption that the lattice is transformed into an equivalent but misoriented lattice by simple shear. The interface between the twin and the matrix should be an invariant plane, i.e. the indices of the habit plane should be the same for the parent matrix and its twin $(hkl)_p = (hkl)_t$. This point of view ignores the atoms and their sizes. The continuous trajectories of the atoms during twinning are actually not compatible with a simple shear; the interface plane cannot be maintained fully invariant, and a slight increase of volume occurs during the transition. In order to take into account this steric effect, simple shear should be substituted by angular distortion. This new view allowed us to propose atomistic models for extension twinning and contraction twinning in magnesium, and also for martensitic transformations between fcc, bcc and hcp phases. However, proving the relevance of this approach is not easy; the classical theory of martensite crystallography (PTMC) is well established, and all the twins that have been observed till now are usual, with $(hkl)_p = (hkl)_t$.

The (58°, a+2b) twins in magnesium and its implications

Here we report an unconventional twin observed by Electron BackScatter Diffraction (EBSD) in a deformed single crystal of magnesium (figure below): its habit plane is $(01\bar{1}2)_t // (21\bar{3}2)_p$. This means that the habit plane of this type of twin is not restored when the distortion is complete. This experimental result comforts our efforts to shift the shear paradigm to take into account the atoms in the crystallographic models of deformation twinning and martensitic transformations.



On the interaction of a stacking fault with the $(10\bar{1}2)$ twin boundary in magnesium

A. Ostapovets^{1*}, A. Serra², R.C. Pond³

*ostapov@ipm.cz

¹ Central European Institute of Technology - Institute of Physics of Materials (CEITEC IPM), Academy of Sciences of the Czech Republic, Žitkova 22, 61662 Brno, Czech Republic

² Department of Civil & Environmental Engineering, Universitat Politècnica de Catalunya, Jordi Girona 1-3, 08034 Barcelona, Spain

³ College of Engineering, Mathematics and Physical Sciences, University of Exeter, Exeter, EX4 4QF, United Kingdom

Abstract

We analyze the interaction of a basal stacking fault with a $(10\bar{1}2)$ twin boundary in magnesium investigated using atomistic simulations. The defect delineating the interaction is characterised as an imperfect disconnection. In addition, we analyze the reaction which occurs between such defects and mobile twinning disconnections during twin growth.

Introduction

Magnesium and its alloys are prospective low weight materials. Deformation of such materials is often accompanied by twinning due to the significant plastic anisotropy of the hcp structure [1,2]. Consequently, the study of twin boundary migration mechanisms is important for a better understanding of the deformation behaviour of magnesium. Since a high density of basal stacking faults is often observed inside $(10\bar{1}2)$ twins [3,4], it is important to establish whether these serve as obstacles for twin growth, and thereby affect the mechanical properties of the material.

Results

The results of atomistic simulations are shown in Fig.1. Evidently, a stacking fault interaction with a $(10\bar{1}2)$ twin boundary produces a one-layer height step on the boundary, (a). It is demonstrated that this step also has dislocation nature. Growth of the twin by passage of twinning disconnections, (b), leads to the simultaneous extension of the stacking fault, (c).

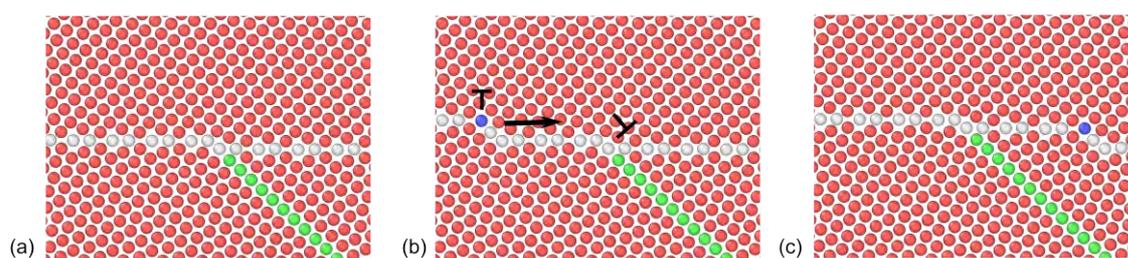


Fig. 1 Migration of a $(10\bar{1}2)$ twin boundary together with stacking fault extension. The projection direction is $[1\bar{2}10]$.

[1] S.G. Hong, S.H. Park, C.S. Lee, Acta Mater. 58 (2010) 5873–5885

[2] M.H. Yoo, S.R. Agnew, J.R. Morris, K.M. Ho, Mater. Sci. Eng. A319-321 (2001) 87-92

[3] F.L.Wang, S.R. Agnew, Int. J. Plast. 81 (2016) 63–86

[4] Q. Sun, X. Zhang, Y. Shu, L. Tan, Q. Liu, Mater. Lett. 185 (2016) 355–358

Deformation mechanisms of polycrystalline cobalt. A quantitative study by electron microscopy

Mayerling Martinez^{1*}, Eric Hug^{1*}

*eric.hug@ensicaen.fr

¹ Laboratoire de Cristallographie et Sciences des Matériaux, Normandie Université, CNRS UMR 6508, 6 Boulevard Maréchal Juin, 14050 Caen, France

Work hardening of polycrystalline hexagonal closed-packed (hcp) metals is characterized by two distinct stages: dislocation gliding and deformation twinning [1]. Among all hcp metals, cobalt is one of the less studied in terms of plasticity mechanisms. In this work, polycrystalline cobalt of high purity was plastically strained by monotonous tensile tests and work hardening stages were depicted by acoustic emission measurements [2]. The microstructures representative of strain mechanisms were studied by scanning and transmission electron microscopy. The analysis shows that during the first stage of work hardening, plasticity is driven by planar and single glide of dislocations in the basal plane, leading to well defined pile-up configurations against grain boundaries. In the second work hardening stage, twinning is the most active deformation mechanism. Electron backscattered diffraction technique (EBSD) was used to acquire an important quantity of data, allowing a statistical analysis as performed recently in others hcp metals [3]. The results show that the main twinning mode belongs to the $\{10\bar{1}2\}$ compression type and that multiple twin variants of this mode can be present inside a grain. EBSD data allowed the establishment for polycrystalline cobalt of new relationships between grain orientation, grain size, twin volume fraction, twinning modes and twin variants.

[1] T.B. Britton, F.P.E. Dunne, A.J. Wilkinson, Proc. Royal Soc. London A 471 (2015).

[2] M. Martinez, G. Fleurier, F. Chmelík, M. Knapek, B. Viguier, E. Hug, Mater. Charact. 134 (2017) 76-83.

[3] Y. Cui, Y. Li, Z. Wang, X. Ding, Y. Koizumi, H. Bian, L. Lin, A. Chiba, Int. J. Plast. 91 (2017) 134-159.

Effect of anisotropic elasticity on dislocation pile-ups and stress-induced slip transmission at grain boundaries

Xiaolei Chen* ^{[1][2]}, Stéphane Berbenni ^[1], Christian Motz ^[2], Thiebaud Richeton ^[1]

* xiaolei.chen@univ-lorraine.fr

[1] Université de Lorraine, CNRS, Arts et Métiers ParisTech, LEM3, F-57070 Metz, France

[2] Department of Materials Science and Technology, Saarland University, Germany

This study deals with an analytical approach based on the Stroh formalism [1-3] which provides the elastic fields of single straight dislocations and different dislocation pile-ups in anisotropic homogeneous media, half-spaces, bi- and tri-materials[4] while considering (or not) free surface effects [5]. The tri-material configuration allows considering a non-zero thickness in the nanometer range and a specific stiffness for the grain boundary (GB) region. The configuration with two free surfaces could be used to study size effects. The effects of anisotropic elasticity, crystallographic orientation, GB stiffness and free surfaces are first studied in the case of a single dislocation in a Ni bicrystal. Image forces may arise because of both dissimilar grain orientations, the presence of a finite grain boundary region and the presence of free surfaces. In particular, it is shown that the Peach-Koehler force projected along the dislocation glide direction can exhibit a change of sign with the dislocation position. For pile-ups, the dislocation positions are calculated by an iterative relaxation scheme minimizing the Peach-Koehler force on each dislocation. Both GB stiffness and grains misorientation influence pile-up length and induced resolved shear stress, but the effect of misorientation is clearly seen to be predominant. In parallel, in-situ micromechanical tests of micron-sized bi-crystals and observations coupling SEM, AFM and EBSD are performed. Different FCC bi-crystals are obtained from FIB (focused ion beam) machining. Step height spatial variations due to localized slip bands terminating at GB are measured by AFM (Atomic Force Microscopy) to determine the Burgers vector distribution in the dislocation pile-up. Hence, the driving force for slip activation in the neighboring grain can be computed and compared to the observed GB resistance to slip transmission.

[1] Hirth, J. P., Lothe, J., 1982. Theory of Dislocations (2nd ed.). Wiley, New York.

[2] Stroh, A. N. Philos. Mag. 3, 625–646 (1958).

[3] Ting, T. C. T. Anisotropic Elasticity. Theory and Applications. Oxford University Press 1996.

[4] Choi, S. T. & Earmme, Y. Y. Int. J. Solids Struct. 39, 943–957 (2002).

[5] H.Y. Wang, M.S. Wu, H. Fan. Int. J. Solids Struct. 44, Issue 5, 1563-1581 (2007)

Dislocation/coherent twin boundary interactions: new insights from quantitative in-situ TEM tensile testing

Hosni Idrissi^{1,2*}, Vahid Samaee², Dominique Schryvers²

*hosni.idrissi@uclouvain.be

¹Institute of Mechanics, Materials and Civil Engineering, Université catholique de Louvain (UCLouvain) – Place Sainte Barbe 2, bte L5.02.02, 1348 Louvain-la-Neuve, Belgium

²Electron microscopy for Materials research (EMAT), University of Antwerp (UA) – Groenenborgerlaan 171 2020 Antwerpen, Belgium

Ultra-fine grained materials often exhibit an outstanding strength, but unfortunately a detrimental low ductility. One exceptional case are nano-twinned materials which combine both, high strength and ductility [1]. This is associated with the presence of twin boundaries (TBs) though the underlying mechanisms of increased ductility are still not fully understood. Efforts have been devoted in the past to investigate dislocation-TB interactions using conventional static and dynamic TEM, MD simulations and more recently quantitative in-situ compression of pillars inside SEM and TEM [2]. However, tracking the intrinsic dislocation/TB mechanisms with quantitative in-situ TEM tensile testing remains absent in the literature. In this study, very clean small bi-crystal Ni samples with preselected single $\{111\}$ coherent TB (CTB) have been prepared using an original preparation method [3], see Fig. 1a. These samples were deformed in tension in-situ using the PI-95 TEM picoindenter holder and the Push-to-Pull (PTP) device (Bruker.Inc), see Fig. 1b. The interactions between dislocations nucleated from single arm sources with the CTB have been observed and quantified in-situ. For screw dislocations interacting with the CTB, the results revealed transition from slip transmission across the CTB to dislocation absorption inside the boundary. The absorption process involves the dissociation of the incoming screw dislocations into pairs of twinning/anti-twinning dislocations that glide in the same direction leading to CTB sliding. Image force of the CTB was measured by observing repulsive interactions between non-screw dislocations with the CTB. Finally, fracture of the sample at steps at TB was observed. The method used here open windows for more accurate characterization of the fundamental mechanisms controlling the interaction between dislocations and other types of GBs.

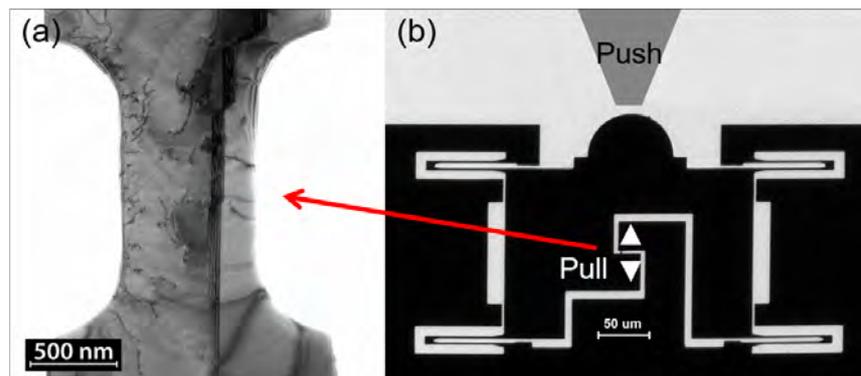


Figure 1: (a) Small-sized tensile sample with single CTB. (b) The Push-To-Pull device used for quantified in-situ TEM tensile testing. The compression of the semicircular end induces uniaxial tension in the middle gap where the sample is fixed with Pt using the FIB/SEM dual-beam instrument. This allows one-to-one relationship between tensile stress-strain curves and defects behaviour.

[1] L. Lu et al., *Science*, 304. (2004) 422-426.

[2] P.J. Imrich et al., *JOM*, 67.8. (2015) 1704-1712.

[3] V. Samaee et al., *Sci.Rep.*, 8 (2018) 12012 (1-11)

Atomistic simulation on nonequilibrium grain boundaries

Ayrat A. Nazarov*, Ramil' T. Murzaev

*AANazarov@imsp.ru

Institute for Metals Superplasticity Problems of the Russian Academy of Sciences, Ufa, Russia

Abstract

Molecular dynamics simulations of nonequilibrium grain boundaries (NE GBs) containing extrinsic grain boundary dislocations (EGBDs) in columnar nanocrystals of nickel are carried out, their atomic structure, long-range stress fields and energies, relaxation under cyclic stresses are studied.

Introduction

Interaction of GBs with lattice dislocations during plastic deformation results in the formation of EGBDs. The GBs containing EGBDs are referred to as NE GBs. The nonequilibrium state of GBs plays an important role in their mechanical properties, kinetics and thermodynamics and is particularly important for nanostructured materials processed by severe plastic deformation (SPD). So far, no atomistic studies of NE GBs have been carried out.

Description of the model and main results

We study columnar f.c.c. nanocrystals with [112] column axis containing four hexagonal grains per computation cell. Basing on an original method, lattice dislocations as precursors of EGBDs are introduced into selected GBs and the initial structures are relaxed using special protocols to keep these precursors in the GBs. This allowed us to construct, relax and study geometrically similar nanocrystals with different grain sizes and varying level of GB nonequilibrium (density of EGBDs). Also, the behavior of NE GBs under cyclic stresses simulating the effect of ultrasonic treatment was studied.

Based on the results of simulations, we have directly demonstrated that NE GBs induce long-range distortions of the crystal lattice in the grains and possess an enhanced energy, which increase with the density of EGBDs. The excess energies of NE GBs calculated from the results of molecular dynamics simulations and earlier developed disclination model agree fairly well. A combined action of internal stresses induced by EGBDs and applied oscillating tension-compression stresses results in an asymmetric process of the generation of lattice dislocations by NE GBs and their glide across the grains. This process leads to an effective elimination of EGBDs from the GBs and relaxation of their structure, energy and long-range stress fields. This relaxation has a threshold character: it occurs at sufficiently high amplitudes of the periodic stresses. The higher the stress amplitude, the shorter is the time of full relaxation. The process of lattice dislocation generation by NE GBs can be considered as one of the possible underlying mechanisms of the effect of ultrasonic treatment on the structure and properties of ultrafine grained materials processed by SPD methods. The proposed atomistic model of NE GBs can be used for studies of the effect of nonequilibrium state on kinetic properties of GBs.

The role of interface diffusion in deformation of metal nanostructures

A. Sharma, N. Gazit, L. Klinger, E. Rabkin

erabkin@technion.ac.il

Department of Materials Science and Engineering, Technion – Israel Institute of Technology, 3200003 Haifa, Israel

An assembly of hemispherical Ag nanoparticles is prepared by solid-state dewetting of thin Ag film deposited on the sapphire substrate. The in-situ nanomechanical compression testing of the particles with a flat diamond punch inside the scanning electron microscope demonstrates the deformation behavior typical for the nucleation-controlled plasticity: high elastic deformation followed by an abrupt particles collapse. The latter is associated with the dislocations nucleation in otherwise pristine particle. The average contact pressure in the contact zone at the onset of dislocation-controlled plasticity is about 8 GPa, and does not depend on particle size. This observation supports the hypothesis that the pseudoelasticity of much smaller Ag nanoparticles observed by Sun et al. [1] is intrinsically related to their ultrahigh strength. A stress-induced diffusion along the particle-substrate and particle-punch interfaces is identified as a factor controlling the pseudoelastic deformation. The corresponding diffusion model allows estimating the room-temperature self-diffusion coefficient of Ag along the Ag-W and Ag-Zirconia interfaces, which was quite close to the estimated value of the grain boundary self-diffusion coefficient in Ag. Based on this finding, the map of pseudoelastic deformation of several metals is proposed [2]. The physical reasons behind the accelerated diffusion along the metal-metal and metal-ceramic interphase boundaries are discussed [3].

- [1] J. Sun, L. He, Y.-C. Lo, T. Xu, H. Bi, L. Sun, Z. Zhang, S.X. Mao, J. Li, Liquid-like pseudoelasticity of sub-10 nm crystalline silver particles, *Nature mater.* 13 (2014) 1007.
- [2] A. Sharma, N. Gazit, L. Klinger, E. Rabkin, Pseudoelasticity of metal nanoparticles is caused by their ultra-high strength, *Advanced Functional Materials*, in press (2019).
- [3] A. Kumar, H. Barda, L. Klinger, M.W. Finnis, V. Lordi, E. Rabkin, D.J. Srolovitz, Anomalous diffusion along metal/ceramic interfaces, *Nature Communications* 9 (2018) 5251.

Unveiling metal-insulator transition in vanadium oxides

Junwoo Son¹, and Daesu Lee², and **Si-Young Choi**¹

youngchoi@postech.ac.kr

¹Department of Materials Science and Engineering, POSTECH, Pohang 37673

²Department of Physics, POSTECH, Pohang 37673

The metal-insulator transition attracts the crystallographic issues because the phenomena are coupled to a symmetry-lowering structural phase transition. Structural phase transition is accordingly related with various types of emergent functional properties, implying that the atomic modification and control can promise the new paradigms for electronics and photonics. Amongst them, vanadium dioxide (VO₂), an archetypal correlated oxide, show a metal-insulator transition (MIT) near room temperature and thus it can be regarded as a potential material to realize the metal insulator transition in our real life. In the recent effort in our group, the variety of VO₂ model experiments has been revealed through the intensive collaborations. Most of results were carried out through the combination of thin-film synthesis, structural and electrical characterizations, and theoretical modeling, in order to reveal the controllable parameters affecting metal insulator transition in VO₂, such as strain, composition, electronic coupling, structural coupling, and so on. In this talk, I will summarize and introduce four papers in VO₂ system that we have recently published.

Interphase Boundaries

Influence of interphase boundary anisotropy on lamellar eutectic solidification microstructures

Mathis Plapp^{1*}, Supriyo Ghosh¹

**Mathis.plapp@polytechnique.fr*

¹ Laboratoire de Physique de la matière condensée, Ecole Polytechnique, CNRS, 91128 Palaiseau, France

It is well documented in many experiments that crystallographic effects play an important role in the generation of two-phase patterns during the solidification of eutectic alloys. In particular, in lamellar composites, large patches of almost perfectly aligned lamellae are frequently observed. Moreover, the growth direction of the lamellae often markedly differs from the direction of the temperature gradient. Both of these effects cannot be explained either by the standard theory or the available numerical models of eutectic growth, which all assume the interfaces to be isotropic. We have developed a phase-field model in which the anisotropy of each interface (solid-liquid and solid-solid) can be separately controlled, and we have investigated the effect of interface anisotropy on the growth dynamics. We have found that anisotropy of the solid-solid interphase boundary free energy dramatically alters the growth dynamics. Tilted lamellae result from the modified equilibrium condition at the triple lines, in good agreement with a theoretical conjecture proposed recently. Moreover, in three dimensions, the interphase boundaries tend to align with directions of minimal energy. We have also performed simulations in which two grains with different anisotropies are in competition. In all cases, the grain containing the boundaries with the lowest energies was selected after a transient. These results shed new light on the selection of growth patterns in eutectic solidification.

Atom probe tomography study of austenitic transformation interfaces in high-formability dual-phase steels

A. Marceaux dit Clément^{1,2*}, K. Hoummada¹, J. Drillet², V. Hébert², P. Maugis¹

*arthur.marceauxditclement@arcelormittal.com

¹ Aix Marseille Univ, CNRS, IM2NP, Marseille, France

² ArcelorMittal Maizières Research SA, Maizières-lès-Metz, France

Automotive manufacturers aim to reduce their vehicles weight without jeopardizing the passenger's safety. To reach that goal, higher strength steels are being developed [1]. These steels must however show good formability properties to be used. The way the intercritical austenite decomposes upon cooling is directly responsible for the microstructure of the final product, and therefore for its mechanical and in-use properties (fracture toughness, corrosion resistance, weldability, etc.). The resulting phases of this decomposition indeed depend on both the chemistries of the intercritical austenite and the grain boundaries, among other parameters. The austenite formation from a cold-rolled ferrite-martensite microstructure is hereby studied in order to determine its properties (morphology, localization, chemistry).

Atom probe tomography (APT) allows for quasi-atomic characterization of the steel phases and of their interfaces. It has however scarcely been used to study the austenitic transformation during intercritical annealing. We used APT to analyse the transformation interfaces at different temperatures by gathering informations on the atomic distribution of solutes (Mn, Cr, Si) at these heterophase interfaces. Our attention is focused on ferrite-cementite, ferrite-austenite and austenite-austenite interfaces to cover the initial, on-going and final steps of austenite transformation. The obtained results are compared to growth and solute-partitioning models to understand the way austenite forms in the recrystallized microstructure.

[1] O. Bouaziz, H. Zurob, and M. Huang, « Driving force and logic of development of Advanced High Strength Steels for automotive applications », *Steel Research International*, p. 937-947, june 2013.

Effect of austenite stability on the competition between ductile and interfacial fracture in a medium-Mn, ultra-fine-grained steel for automotive applications

Quentin Tonizzo¹, Matthieu Mazière¹, Astrid Perlade², Anne-Françoise Gourgues-Lorenzon^{1*}

*anne-francoise.gourgues@mines-paristech.fr

¹ MINES ParisTech, PSL Research University, MAT-Centre des Matériaux, UMR CNRS 7633, B.P. 87, 91003 Evry cedex, France

² ArcelorMittal Global R&D - Maizières, Voie Romaine, 57283 Maizières-lès-Metz, France

Abstract

This work focuses on the fracture resistance of interphase interfaces in an ultrafine-grained, duplex (austenite + ferrite) medium-Mn steel under development for automotive applications. For the first time, a double transition in both fracture energy and fracture mechanisms was evidenced, from ductile dimples nucleated from inclusions ($T \geq 20^\circ\text{C}$) to interfacial microcracking followed by void growth (-40°C up to -5°C) and to fully interfacial fracture ($T \leq -60^\circ\text{C}$). This transition appears to be driven by the mechanical stability of austenite.

Material and microstructure

A 0.2C-5Mn-0.012P-0.004S (wt.%) laboratory steel was used as 1.2-mm-thick sheets obtained by cold rolling then intercritical annealing at 760°C for about 2 min leading to a fine-grained (0.3-1 μm) mixture of 63% of ferrite and 37% of austenite and a M_s temperature under -60°C .

Uniaxial tensile behaviour

At room temperature, a Lüders plateau was followed by significant work hardening, with significant transformation-induced plasticity (only 5% of austenite was found right before necking). At $+150^\circ\text{C}$, both austenite transformation and work hardening vanished. At -50°C , the yield strength decreased by 38% but strong work hardening occurred due to early transformation of austenite into fresh martensite, leading to earlier necking and dimpled fracture, with interfacial (ferrite/transformed martensite) microcracks at the origin of voids.

Impact testing behaviour

Under Charpy impact testing, ductile, slant fracture originated from inclusions in the upper shelf domain (90J/cm², $T \geq +20^\circ\text{C}$, thickness reduction 30%). In the lower shelf domain (7J/cm², $T < -60^\circ\text{C}$, thickness reduction 7%) flat interfacial fracture between ferrite and transformed austenite occurred, together with some secondary cleavage cracks originated from interphase interfaces. At intermediate temperatures (-40 to -10°C , thickness reduction 20%) a plateau in energy (40J/cm²) was found with dimpled fracture originated from interfacial microcracks. The length of these microcracks increased with decreasing test temperature. From this work, in this steel family, the appearance of interfacial decohesion with decreasing the test temperature could originate both from an evolution in mechanical properties of individual phases with temperature, and from the temperature-dependent, strain-induced transformation of austenite into fresh martensite that could increase stress concentration at interphase interfaces. Understanding the physical origin of such smooth interfacial decohesion, however, still needs further investigation.

Twin-interface interactions in bimetallic systems: molecular dynamics study

Romuald Béjaud^{1*}, Julien Durinck² and Sandrine Brochard²

**romuald.bejaud@polytechnique.edu*

¹ LSI, CEA-CNRS, École polytechnique, UP-Saclay & NewUni, 91128 Palaiseau

² INSTITUT P', Université de Poitiers, CNRS, ISAE ENSMA & SP2MI, 86962 Futuroscope

At the nanoscale, nanostructured materials can induce surprising mechanical properties when compared to bulk behaviour. Nanolayered or nanotwinned metals, for example, are known to have ultra-high mechanical strength, thermal stability and radiation resistance. Under mechanical stress, the plastic response of such materials is generally controlled by the interfaces. This trend is true for metallic nanolayered composites obtained by severe plastic deformation processes where mechanical twinning seems to be promoted by the heterophase interfaces [1]. In such materials, interfaces may act as partial dislocation and deformation twin sources on the one hand, on the other hand, others demonstrated that the interface structures have a key role for twin propagation [2].

In this study, we investigate how these bimetallic interfaces can influence deformation twin nucleation, propagation and thickening. Because of the small length and times scales at which the elementary plasticity mechanisms involved occur, molecular dynamics simulations prove to be relevant and efficient tools.

A thin bimetallic Cu/Ag film is examined. Some particular crystallographic orientations are used to introduce the most common interfaces observed in these multilayered systems and to allow the introduction of specific surface defects, which can act as dislocation sources under mechanical stress. We found that deformation twins are smaller for thin films containing "heterotwin" heterophase interface which is consistent with the low permeability of this interface to dislocations. But twins are more numerous in these systems, which is correlated to a recurring mechanism: Lomer dislocation nucleation. For the Cu/Ag films containing a "cube on cube" type interface, our simulations reveal the specific role of the misfit dislocation mesh for the nucleation of twinning partials directly from the interface [3].

[1] S. Zheng, I. J. Beyerlein, J. S. Carpenter, K. Kang, J. Wang, W. Han and N. A. Mara. Nature Communications, 4 (2013).

[2] X. H. An, S. M. Zhu, Y. Cao, M. Kawasaki, X. Z. Liao, S. P. Ringer, J. F. Nie, T. G. Langdon and Y. T. Zhu. Applied Physics Letters, 107 (2015).

[3] R. Béjaud, J. Durinck and S. Brochard. Acta Materialia, 144 (2018).

Numerical and experimental evidences of matrix slip across complex precipitate interfaces

Julien Guéno^{1*}, Fatim-Zahra Mouhib¹, Muhammad Zubair¹, James Gibson¹, Stefanie Sandlöbes¹, Sandra Korte-Kerzel¹

*guenole@imm.rwth-aachen.de

¹ Institute of Physical Metallurgy and Metal Physics, RWTH Aachen University, Germany

Abstract

The strengthening mechanisms in magnesium alloys are strongly related to the complex intermetallic precipitates that spread all over the microstructure, in particular the hard and brittle Laves phases. Here, we present numerical and experimental evidences of slip transfers across the interface between the matrix and complex precipitates.

Basal slip in Laves phases

The strengthening mechanisms in magnesium alloys are strongly related to the complex intermetallic precipitates that spread all over the microstructure. In particular, the hard and brittle Laves phases [1] commonly observed in such alloys exhibit a complex atoms stacking with largely unknown plasticity mechanisms [2].

We propose here a numerical atomistic approach at the cross-road of experiments and *ab initio* simulations, to shed light on the mechanisms responsible for the plasticity in hexagonal Mg₂Ca (C14) Laves phases. Elastic and plastic properties of bulk Laves phase are investigated by both first principle and classical atomistic simulations. Molecular dynamics/statics simulations with a robust MEAM interatomic potential are performed to study the propagation of dislocations, by a combination of nudge-elastic-band (NEB) methods and nano-mechanical tests. In particular, the propagation of <a> dislocations in the basal plane by the so-called synchroshear mechanism [3,4] are investigated at the atomic scale [5]. All these results are finally correlated and discussed by considering experimental findings, especially from micro-pillar compression tests. Our goal is to improve the understanding of the largely unknown plasticity of Laves phases.

Slip across Laves phase interface

After ensuring a deeper understanding of the plasticity in Laves phase, the transfer of slip from the Mg matrix to the Laves phase precipitate will be evidenced by both numerical and experimental methods. In particular, while nano-mechanical experiments combined with SEM and TEM observations demonstrate slip transfer at Laves phases interfaces, molecular dynamics/statics are performed to highlights the mechanisms underlying such a slip transfer, like dislocations pile-up and Burgers vector changes.

[1] F. Laves and H. Witte, Metallwirtsch. Metallwiss. Metalltech. **15**, 840 (1936).

[2] M.F. Chisholm, *et al.*, Science **307**, 701 (2005).

[3] P.M. Hazzledine *et al.*, MRS Proceedings **288**, 591 (1992).

[4] P.M. Hazzledine and P. Pirouz, Scripta metallurgica et materialia **28**, 1277 (1993).

[5] J. Guéno¹ *et al.*, arXiv preprint, arXiv: 1902.01646(2019).

Zr-Cr interface stability of irradiated chromium-coated Zircaloy-4 alloy

Joël Ribis^{1*}, Jean-Christophe Brachet¹, Benoît Arnal¹, Elodie Rouesne¹, Stephane Urvoy¹, Françoise Barcelo¹, Aurélie Gentils², Cédric Baumier², Frédéric Leprêtre³, Jérémy Bischoff⁴, Edouard Pouillier⁵

**Joel.ribis@cea.fr*

¹ DEN-Service de Recherches Métallurgiques Appliquées, CEA, Université Paris-Saclay, F-91191, Gif-sur-Yvette, France

² Centre de Sciences Nucléaires et de Sciences de la Matière, Université Paris-Sud-CNRS-IN2P3, Université Paris-Saclay, 91405 Orsay Campus, France

³ DEN-Service de Recherches de Métallurgie Physique, Laboratoire JANNUS, CEA, Université Paris-Saclay, Gif-sur-Yvette

⁴ FRAMATOME, 10 rue Juliette Récamier, F-69456 Lyon, Cedex 06, France

⁵ EDF R&D, Department of MMC, avenue des Renardières, F-77818 Moret-Sur-Loing, France

In Light Water Reactors, under hypothetical LOss of Coolant Accident (LOCA) scenario, zirconium alloy nuclear fuel claddings undergo significant steam oxidation at high temperatures. In such accidental situation, decreasing the oxidation rate of nuclear fuel claddings is a key issue to improve the accident tolerance of the nuclear fuel sub-assembly. Hence, CEA has engaged specific studies on chromium-coated zirconium alloys in the framework of CEA-FRAMATOME-EDF collaborative program on Enhanced Accident Tolerant Fuel (E-ATF) cladding materials.

Beyond the LOCA issues, the adhesion strength of the Cr coating has to be assessed under irradiation. Thus, the purpose of the study is to determine the stability of the Zr/Cr interface of a Cr-coated Zircaloy-4 alloy after irradiations by means of Transmission and Scanning Electron Microscopy.

On a first type of Zr/Cr interface, it is reported the formation of a few tenths nanometers thick Zr(Fe,Cr)₂ polytype structured Laves phase displaying both C14 and C15 lattice symmetry. After ion irradiation up to 10 dpa at 400°C, only the C14 phase is observed while the destabilization of the C15 phase could be attributed to some segregation of iron at the interface. For a second interface, obtained under different deposition conditions, only the C15 phase is observed at the interface. The in-situ ion irradiation at 400°C up to 20 dpa showed a partial dissolution of the C15 phase accompanied with a sharpened distribution of the Zr and Cr atoms. In all cases, the semi-coherent atomic structure of the interface observed before and after irradiation may explain the good residual adhesion properties of the coating to the substrate.

Metal/ceramic interfaces: a new class of high-diffusivity paths

Aakash Kumar^{1*}, Hagit Barda², Amit Shrama², Leonid Klinger², Michael W. Finnis³, Vincenzo Lordi⁴, Eugen Rabkin², David J. Srolovitz^{1,5,6}

*aakashk@seas.upenn.edu

¹ Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104, USA

² Department of Materials Science and Engineering, Technion – Israel Institute of Technology, 3200003 Haifa, Israel

³ Thomas Young Center, Department of Materials and Department of Physics, Imperial College, London SW7 2AZ, UK

⁴ Materials Science Division, Lawrence Livermore National Laboratory, Livermore, CA 94550, USA

⁵ Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, PA 19104, USA

⁶ Department of Materials Science and Engineering, City University of Hong Kong, Kowloon, Hong Kong SAR

Metal/ceramic interfaces are amongst the most commonly encountered interfaces in several technological applications such as Li-anode/electrolyte in all solid-state batteries, metal/gate-oxides in semiconductors and metal/YSZ in coatings for high-temperature applications in superalloys. While several high-diffusivity paths such as grain-boundaries, dislocations and surfaces have been extensively studied in the past, very little information is available on the diffusion along metal/ceramic interfaces. Using a combined experimental-theoretical study we show that certain metal/ceramic interfaces can show ultra-fast diffusion for which the diffusivity can be similar in magnitude or even larger than grain boundary diffusion in metals. For a prototypical system of Ni/ α -Al₂O₃, we experimentally observe this fast diffusion after annealing thin-films of Ni on the α -Al₂O₃ (sapphire) substrate. Our first-principles calculations indicate that this diffusion is due to Ni vacancies along the interface, which have lower formation and migration energies than their values for bulk Ni. Using a simple bond-breaking model, we generalize this result to several metal/ceramic interfaces and introduce a novel empirical descriptor which can predict which of these interfaces should be high-diffusivity paths. We then validate these predictions by carrying out explicit first-principles calculations on Cu/ α -Al₂O₃ and Ti/ α -Al₂O₃ interfaces. We further carry out classical molecular dynamics simulations using a ReaxFF potential developed to demonstrate this fast interface diffusion for a semi-coherent interface of Ni/ α -Al₂O₃, which shows even faster diffusion due to the presence of misfit dislocation networks, further short-circuiting the diffusion paths.

Acknowledgments Work partly performed under the auspices of US DOE by LLNL under contract DE- AC52-07NA27344.

Some mechanisms controlled by diffusion at interphases: lateral growth and dewetting of silicides thin films

D. Mangelinck^{1*}, T. Luo¹, M. El Kousseifi¹, F. Panciera¹, K. Hoummada¹, C. Girardeaux¹

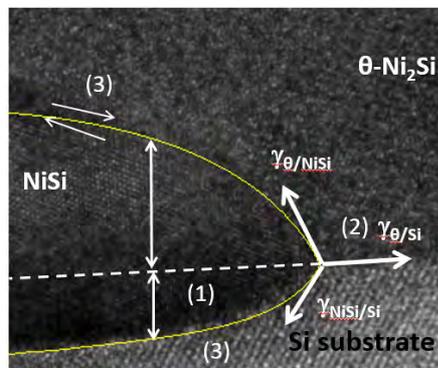
*dominique.mangelinck@im2np.fr

¹ CNRS, Aix Marseille University, IM2NP, Faculté de saint Jérôme, 13397 Marseille cedex 20, France

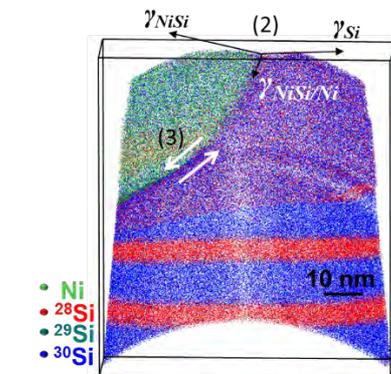
Abstract

The formation and the stability of phases in thin films involve phenomena at the interphases. Due to their applications in microelectronics and in other fields, the mechanisms of silicide thin film formation and thermal stability have been largely studied. Among the established mechanisms, two involve directly diffusion along the interphases: the lateral growth during the formation at low temperature and the dewetting (or agglomeration) at higher temperature. In this presentation, recent results obtained by in situ XRD, transmission electron microscopy TEM and atom probe tomography (APT) on the lateral growth and dewetting of Ni silicide will be presented and confronted to different models. The similitudes and differences between the two phenomena will be discussed.

Lateral growth: In thin film reactions, the formation of a phase usually occurs by the following steps: (i) nucleation (ii) lateral growth (ii) growth perpendicular to interface. Several models were developed for lateral growth but experimental observations are scarce. In this work, the lateral growth of NiSi at the epitaxial θ -Ni₂Si/Si interface has been evidenced by in situ-XRD annealing coupled with APT and TEM. The experimental shape of isolated NiSi precipitates resulting from the lateral growth are confronted to several models in order to obtain a better understanding of lateral growth and on the associated kinetics and thermodynamics parameters .



TEM images of lateral growth of NiSi at the θ -Ni₂Si/Si interface and 3 mechanisms: (1) volume conservation (2) interface energy equilibrium (3) diffusion at interface



APT volume showing the dewetting of NiSi on Si isotope enriched multilayer

Dewetting: Polycrystalline thin films are generally metastable and will dewet to form islands when heated. With decreasing film thickness, the driving force for dewetting increases, the rate of dewetting is accelerated, and the temperature at which dewetting occurs decreases. Dewetting of thin films is of concerns for integrated circuits and nanomaterials. In this work, the dewetting of a 30 nm NiSi film on a Si isotope enriched multilayer is characterized by APT. By looking at the Si isotopes inside NiSi and Si substrate, (i.e. remaining multilayer structure or isotopes mixing), a mechanism of the NiSi agglomeration is proposed based on diffusion of Si at the NiSi/Si interphase and confronted to models for grain boundary grooving and dewetting.

Coherent topotactic interfaces

S.Y. Liang, X. Zheng, J. Zhu, R. Yu*

*ryu@tsinghua.edu.cn

National Center for Electron Microscopy in Beijing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China.

Abstract

Most of epitaxial thin films and interfaces are formed between materials of the same type of crystal structure. Typical examples are semiconductor thin films of the Zinc-Blende structure (e.g. GaAs/AlAs) and transition metal oxide interfaces between perovskites (e.g. $\text{LaAlO}_3/\text{SrTiO}_3$). Compared to the isostructural epitaxy, the thin films and interfaces formed between different crystal structures are more flexible in tuning atomic and electronic properties. In this work, we first show that coherent heterostructural interfaces can be formed between corundum and rutile structures ($\text{Ti}_2\text{O}_3/\text{TiO}_2$) employing topotactic transitions. The two oxides share the same oxygen sublattice. Only the arrangement of cations changes across the interface. In this way, fully coherent interfaces are formed. Then, the scheme is used to generate coherent heterostructural interfaces in other combinations, including spinel/corundum ($\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$) and spinel/rock-salt ($\text{Fe}_3\text{O}_4/\text{FeO}$). Employing the topotaxy between oxides of different crystal structures offers rich choices to construct coherent interfaces.

Coherent Interface $\text{Ti}_2\text{O}_3/\text{TiO}_2$

Figure 1 shows the experimental aberration-corrected TEM image and the atomic model of the interface between the corundum-type Ti_2O_3 and rutile TiO_2 . DFT calculations show that two-dimensional electron gas is generated at the interface through charge transfer from Ti_2O_3 to rutile TiO_2 at the interface. In addition, the existence of Ti interstitials close to the interface indicates that the topotactic transition occurs via the migration of cations, instead of oxygen as suggested previously.

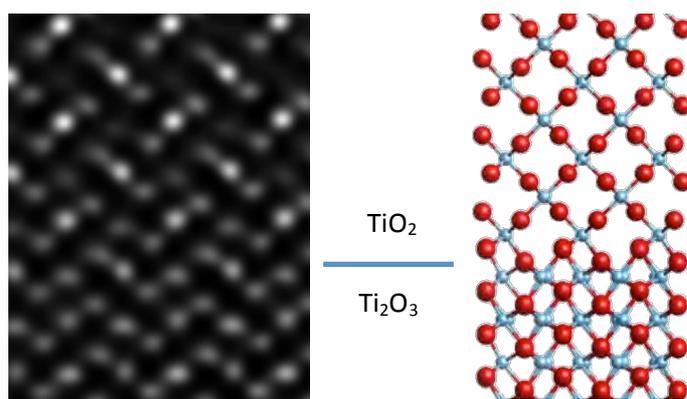


Fig. 1. Aberration-corrected TEM image and the corresponding atomic model, showing a topotactic interface between rutile TiO_2 and corundum-type Ti_2O_3 .

Interface effects in the protective hard coatings. Insight into the structure-property relationship at the atomic scale

Zaoli Zhang¹

*Zaoli.zhang@oeaw.ac.at

¹Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria

Transition metal nitrides have found wide-spread applications in the cutting- and machining-tool industry due to their extreme hardness, thermal stability and resistance to corrosion. The increasing demand of these nitrides requires an in-depth understanding of their structures at the atomic level. This has led to numerous experimental and theoretical researches [1-2].

In this paper, we will firstly present the recent results on the atomic and electronic structures of the interface between various metal nitride mono-layer films (CrN, VN and TiN) on MgO and Al₂O₃ substrate using C_s-corrected high resolution transmission electron microscopy (HRTEM), scanning TEM, electron energy loss spectroscopy (EELS), quantitative measurements, and theoretical calculations. Interfacial detailed atomic and electronic structures are revealed. Interface induced phenomena between nitride films and substrates are unveiled [1-2]. The emphasis will also be placed on the nitrogen vacancy effect at the interface.

The second example will be on CrN/AlN nanolayers which exhibit a peak in hardness of ~ 40 GPa under certain bilayer period (Λ). These improvements in mechanical properties in comparison with their monolithic counterparts have a close relationship with the existence of a metastable face-centered cubic (*fcc*) AlN phase which can be epitaxially stabilized in thin films. Here, interplanar spacing oscillations in cubic CrN/AlN multilayers were experimentally observed by using spherical aberration-corrected HRTEM, and were corroborated by first principles calculations. Electron spectroscopy and microscopy were employed to analyse the strain distribution in the multilayers and obtain generalized relationships between the electronic structure on the one hand, and (non-)stoichiometry or strains in the multilayers on the other hand. The present study provides atomic-scale insights in the mechanisms of extraordinary strength pertaining to the CrN/AlN multilayers [2-3].

[1] Zaoli Zhang, *et al*, *Physical Review B* 87, 014104-9(2013).

[2] Zaoli Zhang, *et al*. *Physical Review B* 95, 155305 (2017).

Acknowledgments The author would like to thank David Holec, Rostislav Daniel and Christian Mitterer (Montanuniversität Leoben), Matthias Bartosik and Paul H. Mayrhofer (TU Wien) for helpful discussions and preparing the film materials. Thanks are also given to Gerhard Dehm (Max-Planck-Institut für Eisenforschung, Düsseldorf) for inspiring discussion.

Posters

On some features of interfacial intermetallics in Al/Mg/Al laminated composite fabricated by accumulative roll bonding

K. Abib¹, W. Habila¹, H. Azzeddine^{1,2}, A-L. Helbert³, F. Brisset³, T. Baudin³, D. Bradai¹

* abib_khadidja@yahoo.com

¹ Faculty of Physics, University of Sciences and Technology Houari, Boumediene, BP 32 El-Alia, 16111, Algiers, Algeria.

² Departments of Physics, University Mohamed Boudiaf, BP 166, 28000, M'Sila Algeria

³ ICMMO, SP2M, Univ. Paris-Sud, Université Paris-Saclay, UMR CNRS 8182, 91405 Orsay Cedex, France

In the last decades, light-metallic laminate composites have received a considerable interest owing to their famous mechanical, electrical and magnetic properties. Different physical and/or mechanical processing techniques to elaborate these composites were build-up such as magnetic sputtering, vapor deposition, explosive welding, friction-stir welding and accumulative roll bonding (ARB). Among these techniques, the latter is more advantageous since it is low cost, large scale production and results in higher strength and grain refinement. Moreover, obtaining a continuous intermetallic layer in-between light metals is highly desirable. Therefore, the above-cited techniques are often combined with subsequent heat treatment in order to achieve a good quality of the interfaces with hard intermetallics in-between.

In this work, some features of interfacial intermetallics in an AA1050/AZ31/AA1050 laminated composite fabricated by ARB at 400 °C up to 5 cycles were highlighted through SEM-EDS and XRD analysis. The study focused mainly on the intermetallic Mg_2Al_3 and $Mg_{17}Al_{12}$ phases formation at the interface, their morphology and the elemental distribution within them and the laminates. These phases were found to form (only after the second ARB cycle) near the AA1050 and AZ31 sides respectively with global thickness ranging from 10 to 20 μm and length exceeding 100 μm . They were strongly broken and discontinuous. The diffusion zone of Mg_2Al_3 phase is thicker than that of $Mg_{17}Al_{12}$ owing to the fact that the diffusion ability of Al atoms is lower than that of Mg atoms.

Keywords: AA1050/AZ31/AA1050, Laminated Composite, Intermetallic Compounds, SEM/EDS, XRD.

On realization of superplastic flow in V-alloyed high-nitrogen steel

S.V. Astafurov*, E.G. Astafurova, G.G. Maier, E.V. Melnikov, V.A. Moskvina,
M. Yu. Panchenko, N.K. Galchenko

*svastafurov@gmail.com

Institute of Strength Physics and Materials Science, Siberian Branch of Russian Academy of Sciences, Akademichesky pr.
2/4, Tomsk, 634055, Russia

Abstract

The possibility of realization of superplastic flow (SPF) in V-alloyed high-nitrogen steel (HNS) was experimentally investigated. Using of multi-stage thermal-mechanical treatments included multipass cold rolling and intermediate annealing, a heterophase highly defective structure based on austenite with a small amount of ferrite and different volume fraction and dispersion of vanadium-based and chromium-based carbonitrides was produced. This structure demonstrates attributes of SPF in the temperature range of 900-1000 °C and wide range of strain rates.

Results

V-alloyed high-nitrogen austenitic Fe-19Cr-22Mn-1.5V-0.3C-0.6N (wt. %) steel was chosen as an object of investigation. Steel bars were cut out of the initial cast billet. These bars were subjected to a solid solution treatment (SS-treatment) for one hour at a temperature of 1200°C followed by water-quenching. After SS-treatment, the initial bars were subjected to thermal-mechanical treatments consisting of multiple cold rolling at room temperature to a total strain of 80% with intermediate 1-hour anneals in the temperature range of 900-1050 °C. After thermal-mechanical treatment flat dumb-belled shape specimens were cut from the billets for mechanical testing. Dimensions of the working part of the specimens were 12×2.7×1.5 mm. Uniaxial tension of the specimens was carried out in the temperature range from 25 to 1000 °C with an initial strain rates in the interval of 4.2×10^{-5} to $2.1 \times 10^{-3} \text{ s}^{-1}$.

Thermal-mechanical treatment regimes were revealed, which allowed the occurrence of superplastic flow for vanadium-containing HNS with elongation to failure up to 900%. Based on the analysis of the structural and phase states of steel after various heat treatments, it was found that vanadium-containing HNS is promising for use as materials capable of superplastic flow. Experimentally evaluated multistage thermomechanical processing allowed the formation of heterophase highly defective states, which are based on austenite with a small amount of ferrite and different volume fraction and dispersion of vanadium and chromium carbonitrides. In the range of strain rates of $4.2 \times 10^{-4} - 2.1 \times 10^{-3} \text{ s}^{-1}$ and test temperatures from 900 to 1000°C, the samples show attributes of superplastic flow (the sample elongation to failure exceeds 400%, the coefficient of strain-rate sensitivity of the stress exceeds 0.3, flow stresses are low – less than 40 MPa). The maximum elongation of 900% is achieved at a deformation rate of $4.2 \times 10^{-4} \text{ s}^{-1}$ and at temperature of 950°C.

Acknowledgements

The research was supported by the Russian Science Foundation (project No. 17-19-01197).

On the anisotropy of the mechanical properties in additively-manufactured stainless steel

S.V. Astafurov*, E.G. Astafurova, G.G. Maier, E.V. Melnikov, V.A. Moskvina, M. Yu. Panchenko, A.S. Fortuna, S.V. Fortuna, N.L. Savchenko, V.E. Rubtsov, E.A. Kolubaev

*svastafurov@gmail.com

Institute of Strength Physics and Materials Science, Siberian Branch of Russian Academy of Sciences, Akademichesky pr. 2/4, Tomsk, 634055, Russia

Abstract

The billet of AISI 304-type austenitic stainless steel was built by wire feed electron beam additive manufacturing. Mechanical properties of the specimens cut from the billet were investigated depending on orientation of tensile loading direction respective to growth direction and distance from the substrate. Ductility and strength properties of additively manufactured steel show substantial anisotropy, which is strongly correlated with macro- and microstructural peculiarities of the as-built billet.

Results

Mechanical properties of AISI 304-type austenitic stainless steel, produced by wire feed electron beam additive manufacturing, were investigated in room temperature tensile tests at initial strain rate of $5 \times 10^{-4} \text{ s}^{-1}$. Steel billets in the form of plates were grown on the substrate of the of AISI 304 type steel using electron-beam melting of 1mm-wire in vacuum chamber. A layer-by-layer strategy of the growth was used, and a final size of the billet was $5 \times 30 \times 100 \text{ mm}$ (30 layers). A set of specimens, which were differently oriented to the growth direction, were cut from different parts of the walls for investigation of dependence of mechanical properties on the peculiarities of production process.

Tensile mechanical properties (yield strength, ultimate tensile stress and elongation) of the additively-manufactured steel are strongly dependent on the distance from the substrate and on orientation of tensile axis respective to layers in the as-built billets. Specimens, which were cut along the wall growth direction (perpendicular to layers), are characterize by higher elongation (up to 40%) and lower ultimate tensile stress (about 15-20%) and yield stress (about 20-30%) in comparison with specimens which were cut perpendicular to growth direction (along layers). Ductility and strength properties of the latter samples (cut along layers) decreases with increase in distance from the substrate (up to 20%).

Such anisotropy of mechanical properties of the additively-manufactured austenitic stainless steel is associated with peculiarities of production of build process and depends on as-built microstructure. The layers near the substrate (bottom layers) possess higher density of the defects of the crystal lattice in austenite grains and microstresses as compared to top layers.

Microstructure and grain growth inhomogeneity in austenitic steel produced by wire-feed electron beam melting

E.G. Astafurova*, S.V. Astafurov, G.G. Maier, E.V. Melnikov, V.A. Moskvina, M. Yu. Panchenko, A.S. Fortuna, S.V. Fortuna, N.L. Savchenko, V.E. Rubtsov, E.A. Kolubaev

*elena.g.astafurova@gmail.com

Institute of Strength Physics and Materials Science, Siberian Branch of Russian Academy of Sciences, Akademicheskyy pr. 2/4, Tomsk, 634055, Russia

The microstructure, grain boundary assemblage and phase composition of AISI 304-type austenitic stainless steel produced by wire feed electron beam additive manufacturing (EBAM), were investigated in as-built specimens using methods of transmission electron microscopy (TEM), electron back scattered diffraction (EBSD) analysis and energy dispersive analysis (EDS). Steel billets in the form of plates were grown using 1-mm wire of AISI 304-type steel using electron-beam wire melting in vacuum chamber. A layer-by-layer strategy of the growth was used, and final billet consisted of 30 layers (30mm in height, 100mm × 5 mm in cross-section parallel to the layers). According to EBSD data, a macroscopical columnar grain growth occurs during EBAM-processing. Coarse austenitic grains, bounded by general high-angle grain boundaries, grow up to several millimeters long in direction of billet growth (perpendicular to the layers). In spite of rather long heating of the billet during building process, coarse grains form, but structure is not completely recrystallized. Large fraction of low-angle boundaries with misorientations less than 15° (up to 60% relative to the total fraction of boundaries) are characteristic for grain bodies of as-built coarse microstructure. Analysis of TEM-images show that coarse-grained austenitic structure also contains ferrite of dendritic morphology in as-built specimens. Ferrite areas are enriched with Cr and depleted with Fe and Ni, and the concentration of these elements varies abruptly when passing via interphase boundary. The volume fraction of ferrite in as-built specimens varies in the interval of 30-40% depending on distance from the substrate. The planar dislocation arrangement peculiar for both lower and upper layers of the material. The main difference between upper and lower layers in as-built billets consists of different dislocation density and microstresses in austenitic phase. Due to the multiple cooling and heating of the billet during building, the lower layers of the billets accumulate high density of the defects of crystal lattice in austenitic grains and microstresses as compared to the top layers. Therefore, as-built specimens of austenitic stainless steel produced by EBAM are highly anisotropic heterophase material with high fraction of interphase boundaries (austenite/ferrite) and grain boundaries with low and high angle misorientations. This provides inhomogeneity in strength properties of the billets built in feed electron beam additive manufacturing.

Acknowledgments This work was performed within the frame of the Fundamental Research Program of the State Academies of Sciences for 2013-2020, line of research III.23.

This work was performed within the frame of the Fundamental Research Program of the State Academies of Sciences for 2013-2020, line of research III.23.

Ion irradiation-induced grain boundary segregation in a Fe12Cr model alloy: a coupled TKD/APT study

Q. Barrès^{1,2,3}, O. Tissot¹, E. Meslin², C. Pareige³ and M. Loyer-Prost⁴

quentin.barres@cea.fr

¹ CEA, DEN, Service de Recherches Métallurgiques Appliquées, Laboratoire d'Analyse Microstructurale des Matériaux, F-91191 Gif-sur-Yvette, France

² CEA, DEN, Service de Recherches de Métallurgie Physique, F-91191 Gif-sur-Yvette, France

³ Groupe de Physique des Matériaux, Université et INSA de Rouen - UMR CNRS 6634, 76801, B.P.12, Saint-Etienne du Rouvray Cedex, France

⁴ CEA, DEN, Laboratoire Jannus, Service de Recherches de Métallurgie Physique, F-91191 Gif-sur-Yvette, France

For the next generation of reactor (GEN IV and Fusion) materials will be submitted to high flux of neutrons and high temperature. Ferritic Martensitic (F/M) steels and ODS alloys are potential candidates for structural and cladding applications. Irradiation create defects (interstitials-vacancies, dislocation loops, voids) which change the microstructure of these FeCr based alloys. The diffusion of point defects will lead to Cr rich phase precipitation and intergranular segregation [1]. These microstructural changes are among the main cause of hardening and embrittlement. Radiation Induced Segregation (RIS) at grain boundary (GB) is very dependent on the grain boundary structure [2]. The main goal of this study is to characterize Cr segregation at grain boundaries in FeCr alloys as a function of the GB structure.

Ion irradiation are frequently used to simulate neutron irradiation, which are long expensive and with a restricted access. We report here quantification of intergranular segregation in Fe-12% Cr high purity alloy irradiated with 2 MeV Fe³⁺ ions at 450°C up to 2 dpa using the JANNUS-Saclay facility. Atom Probe Tomographic (APT) characterization has been done to obtain chemical and spatial distribution along GBs at the atomic scale. To provide information on the misorientation of the GB Electron BackScatter Diffraction (EBSD) mapping were made. APT tips were milled using Transmission Kikuchi Diffraction (TKD) crystallographic contrast. Using both TKD and APT volumes, the five degrees of freedom are collected. Here we focus on $\Sigma 3$ GB structure, a disorientation of 60° along $\langle 111 \rangle$ axe in cubic centered (CC) crystallographic structure. This kind of GBs are symmetric and present in each of our samples. APT analysis have been done on several tips with GB fully characterized. Effect of grain boundary structure on Cr segregation before and after ion irradiation will be discussed.

[1] Wharry and Was, Acta Materialia 65 (2014) 42-55

[2] Hu & al. Acta Materialia 61 (2013) 3490-3498

Atomic structure of (111) twist grain boundaries in diamond

C. Baruffi^{1,*}, C. Brandl²

*carolina.baruffi@kit.edu

¹Karlsruhe Institute for Technology, 76344 Eggenstein-Leopoldshafen, Germany

²The University of Melbourne, Parkville, Victoria 3010, Australia

Diamond has several outstanding properties: thermal conductivity, light transmission from the infrared to the ultra-violet, good electrical and semiconductor properties combined with radiation hardness, excellent mechanical properties, corrosion resistance, bio-compatibility [1]. Even the combinations of these properties makes diamond attractive for several applications such as coatings, electronic devices and, generally speaking, micro/nano-mechanical devices working in harsh environments [2].

For these applications, diamond is typically used in the form of poly-crystalline thin films obtained by chemical vapor deposition. The typical grain size in these thin films range from 1-5 micrometers (Micro-Crystalline Diamond) to 3-5 nm (Ultra-Nano-Crystalline Diamond) [3]. The resulting interface density may even dominate the material properties even to the limit that the interface structure, chemistry and energetic influence the overall materials behavior. Most of the numerical and experimental studies on diamond interfaces concern tilt grain boundaries, which are most frequently found in poly-crystals. Less work has been done on twist grain boundaries, which are usually characterized by a higher energy with respect to the tilt boundaries [4]. Nevertheless, the twist grain boundary structure is important for nanocrystalline materials, where internal stresses and random orientations of grains geometrically requires high energy interface beyond pure-tilt grain boundaries.

In the present work, we investigate systematically (111) twist boundaries in diamond to relate grain boundary energy to grain boundary structure with atomistic simulations based on bond-order potentials. Our results clearly show highly ordered low energy twist grain boundaries, whose structure is characterized by the presence of a sub-lattice of low energy sites corresponding to coincidence sites positions. The sub-lattices of low and high energy sites are discussed in term of local atomic environment (i.e., coordination and bond-angle) in relation to the so-called dichromatic pattern.

[1] Pierson, H. O., Handbook of carbon, graphite, diamonds and fullerenes: processing, properties and applications, William Andrew (2012)

[2] Luo, J. et al., Journal of Micromechanics and Microengineering, 17 (2007) S147

[3] Gruen, D. M., Annual Review of Materials Science, 29 (1999), 211

[4] Thibault, J. et al., Grain boundaries in semiconductors, Material Science and technology, Wiley Online Library (2006)

Acknowledgments This work was supported by Vector Foundation in the program “MINT Innovation”.

In silico (CD) study of hexagonal diamond (HD) silicon nanowire surfaces

Romuald Béjaud^{1*} and Olivier Hardouin Duparc¹

*romuald.bejaud@polytechnique.edu

¹ LSI, CEA-CNRS, École polytechnique, UP-Saclay & NewUni, 91128 Palaiseau

Silicon nanowires in hexagonal diamond (HD) structure are an excellent material for solar energy production. As nanostructures of a very rare crystallographic phase of a material nowadays very common, they also constitute an object of interesting fundamental studies.

Such nanowires have recently been obtained using vapour-liquid-solid (VLS) method in a plasma-enhanced chemical vapour deposition (PECVD) reactor at the École Polytechnique of Palaiseau [1]. The goal now is to understand how the HD phase is stabilized during growth to establish a protocol to reproduce it reliably. One step in this project is to study at atomic scale the structures and energies of different types of HD silicon surfaces using *ab initio* calculations and the density functional theory (these studies are done thanks to the silicon, in a cubic diamond structure, hence the title).

We have studied the possibilities of reconstructions of the various types of surfaces involved in nanowires. Our model consists of an entire section of a Si HD nanowire which allows us to observe the evolution of these surfaces reconstructions in this particular configuration. This simulation model also makes it possible to study edges, resulting from the intersection between the nanowire surfaces, whose structures and energies (linear) have been studied for different sizes and cross sectional shapes. We also considered the influence of hydrogen on the nanowire surfaces, given that the latter is bound to Si in the form of silane (SiH₄) or disilane (Si₂H₃) vapor under experimental conditions. Calculation of hydrogen-saturated surface energies and edge energies have therefore been carried out to approach the experimental setup conditions. This approach allowed us to identify the most stable nanowire structures for different sets of pressure temperature experimental conditions.

[1] J. Tang, J.-L. Maurice, F. Fossard, I. Florea, W. Chen, E. V. Johnson, M. Foldyna, L. Yu and P. Roca i Cabarrocas. *Nanoscale* 9 (2017) 8113-8118.

Acknowledgments This study is part of the generic project 'ANR-17-CE09-0011-03'.

Modeling the effect of chemical doping on the strength of a Ag/ZnO interface

Tianwei Wang and Paul D. Bristowe*

**pdb1000@cam.ac.uk*

Department of Materials Science and Metallurgy
University of Cambridge CB3 0FS
United Kingdom

Using first principles modelling we predict how substitutional doping can influence the mechanical strength of a Ag/ZnO interface commonly found in various multilayer thin-film systems. Replacing Zn with a monovalent dopant strengthens the interface while dopants with a valence greater than two weaken it. Isovalent dopants have little effect. The results are explained in terms of charge transfer and hybridization effects at the interface. Although monovalent dopants are mechanically preferred, they do not inhibit Ag inter-diffusion in ZnO and could possibly cause chemical degradation of the interface. It is suggested that other dopants, such as Bi, avoid this issue by creating larger diffusion barriers while maintaining a relatively strong interface. The results indicate that complete control over the mechanics, kinetics and chemistry of the interface requires a careful choice of dopant types and concentrations.

Properties of interfaces between cementite and a dilute α -Fe lattice from electronic structures

Océane Buggenhoudt^{1*}, Chu-Chun Fu¹, Elric Barbé¹ and Jean-Luc Béchade¹

**oceane.buggenhoudt@cea.fr*

¹DEN-Service de Recherches de Métallurgie Physique, CEA,
Université Paris-Saclay, F-91191 Gif-sur-Yvette, France

Abstract

This study aims at investigating the correlation between the atomic structure, energetics and mechanical stability of various interfaces between the cementite and a dilute α -Fe-Mo-C lattice. The calculated results are analyzed in terms of electronic and magnetic properties and the chemical ordering tendency. A particular attention is paid on the impact of chemical composition in the carbide and around the interfaces.

Introduction

Ferritic steels are widely used as structural materials for numerous technological applications. The presence of carbides is known to impact on mechanical properties of these materials. Such effects depend not only on the structure and chemical composition of the carbides, but also on the location (intra- or inter-granular) of the carbides, that is, the metal-carbide interface also plays a significant role. In the present study, we investigate structural, energetic and segregation properties of various carbide-metal interfaces, by considering the cementite (M_3C) in a dilute Fe-Mo-C alloy.

Main features studied

We employ density functional theory (DFT) calculations to explore low-energy interfacial structures for the cementite located at some tilt grain boundaries (*e.g.* $\Sigma 3$ and $\Sigma 5$) and inside the grains. The Fe_3C is firstly taken as a representation of M_3C . It is interesting to note that a linear relationship between the interfacial energies and the number and strength of atomic bonds at the interfaces can be established. This very simple model enables a reasonable estimation of the interfacial energies. Concerning mechanical properties, it is experimentally observed that a fracture often propagates from inside the cementite, located at a grain boundary, towards the metal lattice. Consistently, our DFT results predict indeed the intra-carbide Griffith energy to be smaller than the interfacial one. Finally, the impact of chemical composition (Mo versus Fe content) inside the carbide and around the interfaces (segregation) on the formation enthalpy and the mechanical stability of cementite is investigated. The obtained results are rationalized in the light of chemical ordering tendencies and electronic and magnetic properties.

Electronic transport in cubic-HfO₂ grain boundaries: a first principles study

Elena Degoli^{1,2}, Eleonora Luppi^{3,4} and Nathalie Capron^{5,6}

nathalie.capron@upmc.fr

¹Dipartimento di Scienze e Metodi dell'Ingegneria, Università di Modena e Reggio Emilia, Via Amendola 2
Padiglione Morselli, 42122 Reggio Emilia, Italy

²CNR-Istituto di Nanoscienze-S3, Via Campi 213/A, 41125 Modena, Italy

³Laboratoire de Chimie Théorique, Sorbonne Université, UPMC Univ Paris 06, UMR 7616, 75005 Paris, France

⁴CNRS, UMR 7616, Laboratoire de Chimie Théorique, 75005 Paris, France

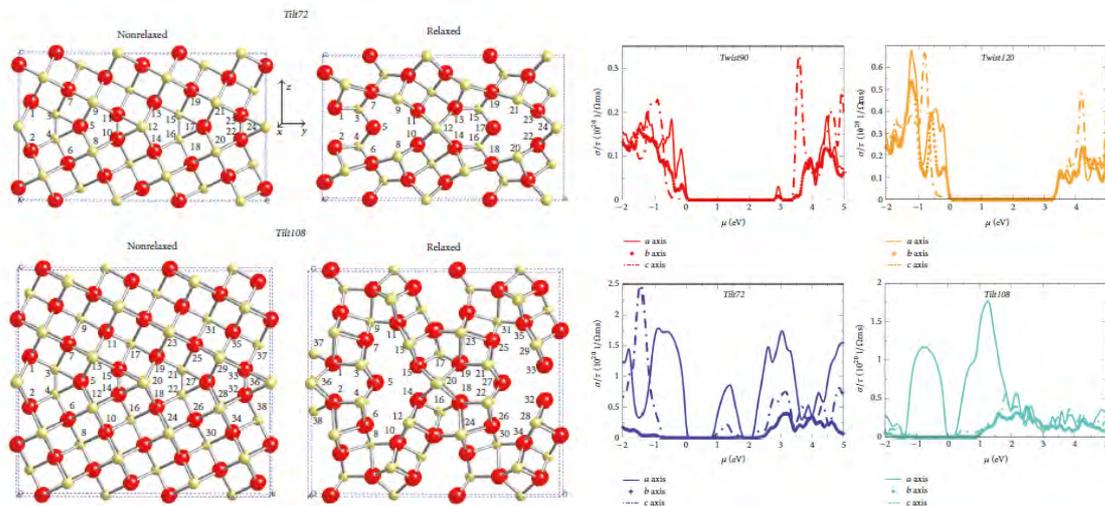
⁵Laboratoire de Chimie Physique-Matière et Rayonnement, Sorbonne Université, UPMC Univ Paris 06, UMR 7614,
75005 Paris, France

⁶CNRS, UMR 7614, Laboratoire de Chimie Physique-Matière et Rayonnement, 75005 Paris, France

Characterising the structure and properties of GBs is critical for understanding and controlling material property.

Here, we investigated how GBs can modify the structural, electronic, and transport properties of the polycrystalline material HfO₂. In general, grain boundaries are considered to be detrimental to the physical stability and electronic transport in HfO₂. Anyway, studying by first principles the two most stable and common types of GBs, the tilt and the twist, we found substantial differences on the impact they have on the material properties. In fact, while tilt defects create channels of different sizes and shapes in hafnia, along which the electronic transport is stronger in relation to leakage current through GBs, twist defects create a sort of amorphous structure that tends to resemble the bulk and which is independent of the number of rotated planes/atoms.

We used the Boltzmann transport theory within the constant scattering time approximation as implemented in the BoltzTraP code.



We will discuss these results ; for example in the case of Tilt72 and Tilt108 the anisotropy is much higher than in Twist90 and Twist120.

These structural differences and the strong anisotropy of tilt GBs reflect a major stability of twist with respect to tilt GBs.

A model for grain boundary thermodynamics based on a relative density parameter

Reza Darvishi Kamachali

kamachali@mpie.de

Max-Planck-Institut für Eisenforschung, Max-Planck-Str. 1, 40237 Düsseldorf, Germany

A model for grain boundary thermodynamics is proposed that allows an approximation of the grain boundary properties from the bulk thermodynamics data. A relative density field parameter –with respect to the corresponding bulk material– and its gradient are introduced to describe the grain boundary and its relevant thermodynamics properties and behavior. Based on this model, the equilibrium phase diagram and segregation behavior of a grain boundary were studied in a binary alloy. Different regimes of segregation are identified and the coexistence of the bulk and grain boundary phases are discussed and exemplified for the simple Pt-Au alloy system (see Figure 1). Finally, the relationships between the grain boundary density, energy and misorientation angle are established that enable studying the grain boundary tendency for segregation as a function of initial grain boundary energy and misorientation angle. The current model can be applied for studying and design of polycrystalline materials.

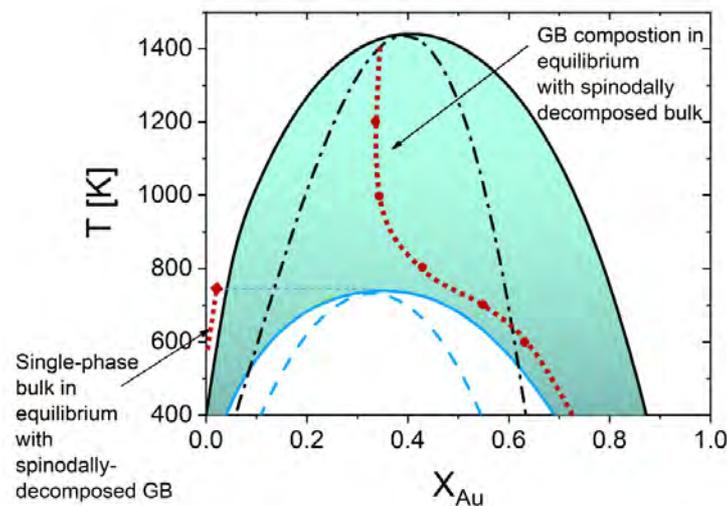


Figure 1: Using the current density-based model, the coexistence of the bulk and grain boundary phases can be discussed. The phase diagrams of the bulk and a grain boundary in Pt-Au binary system are shown as an example.

Modeling of ion-transport processes in space charge region on ideally polarized heterojunction

A.L. Despotuli*, A.V. Andreeva

*despot@ipmt-hpm.ac.ru

Institute of microelectronics technology and high purity materials RAS, Chernogolovka, Russia

The beginning era of nanoionic devices (operate in non-stationary impulse modes) demands the creation of a dynamic non-linear response theory. Impulse ionic devices should have an important role in nanoelectronics and microsystem technique. Another direction, "more-than-Moore", would be to increase the number of different device types on a chip, e.g., sensors, embedded power sources, etc. Efforts to sustain Moore's law is one of the grand current scientific and engineering challenges. For devices of new types, nanoionics tries to describe, for example, diffusion and reactions, in terms, which have sense only on a nanoscale, i.e., in terms of a non-uniform potential landscape. Therefore, search for fundamental properties (which can be included in a future theory of ionic transport on a nanoscale) is very important. The theoretical system – structure-dynamic approach (SDA) of nanoionics, propose by authors [1-4] is a step in this way. SDA includes: (1) layered 1D-hopping atomic model of ionic nanostructures, which unites a system of parallel crystallographic planes $\{X^j\}$, between which mobile ions overcome potential barriers; (2) method of "hidden" variables, i.e., excess non-equilibrium concentrations of mobile ions induced by an external influence on the $\{X^j\}$; (3) physicomathematical formalism (a system of differential equations) which operates by "hidden" variables and is based on the principle of detailed balance and the kinetic equations written in the form of the particle conservation law; (4) method of a uniform effective electrostatic field of a crystallographic plane. The SDA includes also (5) - a new notion - the Maxwell displacement current on a potential barrier, that enables a description of coupled non-stationary ionic hopping transport and dielectric-polarization processes in nanostructures.

The report gives results of works in which SDA has applied to an analysis of ion-transport phenomena and capacitive properties of model heterojunctions, such as blocking electrode (EC_b) – solid state superionic conductor. The behavior of capacitance $C(t)$, Maxwell displacement currents $I_{Dj,j+1}(t)$ and ionic currents $I_{j,j+1}(t)$ are presented for the charging of the model ideally polarizable heterojunction. The current generator operated in a galvanostatic mode, i.e., $G(t) = \text{const}$ at $t > 0$ and $G(t) = 0$ at $t \leq 0$. The calculated data show that Maxwell displacement currents dominate over the ionic conductivity currents at small t . Capacitance $C(t)$, determined by the ratio of the accumulated charge to the voltage on the $EC_b/\{X^j\}$ heterojunction, reaches its maximum due to an appearance of the steric effect at large t . The value of $C(t)$ grows with t because the width of the ionic charge becomes more narrow due to complementary processes of space charge relaxation. *Obvious*, in impulse supercapacitors, function $C(t)$ must reach its maximum at small t . It is possible if the heights of potential barriers $\eta_{j,j+1}$ are small in the interface region of a device. Therefore, nanoionic devices must be fabricated by interface engineering methods under the conception of structure-ordered (coherent) EC_b /advanced superionic conductor heterojunction [5,6].

[1] A.L. Despotuli, A.V. Andreeva // Ionics. 2015. V.21. P. 459–469.

[2] A.L. Despotuli, A.V. Andreeva // Ionics. 2016. V.22. P. 1293–1298.

[3] A.L. Despotuli, A.V. Andreeva // Ionics. 2018. V.24. P. 237–241.

[4] A.L. Despotuli, A.V. Andreeva // J. Electroanal. Chem. 2018. V. 829. P. 1–6.

[5] A.V. Andreeva, A.L. Despotuli// Ionics. 2005. V.11. P. 152–160.

[6] A.L. Despotuli, A.V. Andreeva and B. Rambabu // Ionics. 2005. V.11. P. 306–313.

Acknowledgments This work was financially supported by the State Task # 075-00475-19-00.

Intergranular corrosion of austenitic industrial stainless steels in oxidizing nitric media

A. Emery^{1,2*}, C. Duhamel¹, V.A. Esin¹, P. Laghoutaris², J. Crépin¹

**adrien.emery@cea.fr*

¹ MINES ParisTech, PSL Research University, MAT - Centre des matériaux, CNRS UMR 7633, BP 87 91003 Evry, France

² Den-Service de la Corrosion et du Comportement des Matériaux dans leur Environnement (SCCME), CEA, Université Paris-Saclay, F-91191, Gif-sur-Yvette, France

Intergranular corrosion (IC) of low carbon austenitic stainless steels in oxidizing nitric media is a long-known industrial matter. However, a special stainless steel Uranus S1N, with 4 wt.% of Si, can resist to this localized corrosion. Therefore, this work aims to better understand the origins of IC in industrial austenitic steels and to explain the resistance of Uranus S1N to find a way to improve the composition and, thus, properties of future steels.

The corrosion behavior of industrial steels of different chemical compositions sensitive to IC corrosion in oxidizing nitric media (304L, 316L, Uranus 65) was investigated in this work and compared to that of Uranus S1N and some model steels based on Uranus S1N. The microstructure of all steels before corrosion was systematically compared in terms of grain size, crystallographic texture and grain boundary misorientation distribution. Then all the steels were submitted to the same corrosion tests, and the results were compared with the microstructural study results.

It appears that the resistance to IC of Uranus S1N should be related to the differences in chemical composition. Previous works showed the negative influence of chemical impurities (N, S, P or B) on IC and the ambivalent role of Si, which can either enhance IC or protect the steel against corrosion. Those elements are known to segregate at grain boundaries. Using the analysis of grain boundary composition, this study aims to confirm or infirm this possible explanation of the origin of IC.

Application of the complex of methods to assess the level of grain-boundary segregation in nuclear reactor pressure vessel steels

S.V.Fedotova^{1*}, E.A.Kuleshova^{1,2}, Z.V.Bukina¹, D.A.Maltsev¹

*s_v_fedotova@mail.ru

¹ National Research Center "Kurchatov institute"

² National Research Nuclear University MPhI

Abstract

In this paper the level of grain boundary segregation in nuclear reactor pressure vessel steels was determined by a combination of methods of Auger-electron spectroscopy, atom probe tomography and fractographic analysis. The results obtained are in a good agreement and complementary to each other.

Studies of grain boundary segregation

Water-moderated reactor pressure vessel steels under operation are subjected to the long-term thermal and neutron exposure (for 30÷60 years at ~ 300 ° C up to a dose of ~ $(5\div 10) \cdot 10^{22} \text{ m}^{-2}$). This leads to the properties degradation of reactor pressure vessel materials manifested in the ductile-to-brittle transition temperature shift to the higher temperature range. This, in turn, may hinder the safe operation of the nuclear power plant as a whole. Formation of grain boundary segregation under operation is one of the degradation mechanisms of reactor pressure vessel steel structure and properties, which becomes most relevant at prolonged operation. It leads to appearance of the brittle intergranular fracture and to the crack resistance decrease. Herewith brittle intergranular fracture starts after a certain level of grain boundary segregation.

In this paper the level of grain boundary segregation in water-moderated nuclear reactor pressure vessel steels was assessed by the combination of methods:

- **Auger electron spectroscopy** (using the certified PHI–Ulvac PHI 700 Auger spectrometer) – by the phosphorus content in grain boundaries in the percentage of monolayer coverage, and by the grain boundary concentration of elements in atomic percent (phosphorus, carbon, chromium, nickel, molybdenum) determined by the method developed in “Kurchatov institute”.
- **atom probe tomography** (using Cameca LEAP 4000-HR atom probe) – by the Gibbsian interfacial excess that can be converted to the monolayer coverage percentage. Besides, atom probe tomography also provides additional information about the content of some elements, the concentration of which is difficult to measure by Auger electron spectroscopy due to line overlap (manganese for example).
- **fractographic analysis** (using Zeiss Merlin scanning electron microscope) – by the maximum fraction of brittle intergranular fracture in the fracture surfaces of Charpy specimens that correlate with the level of grain boundary segregation.

It is shown that the results obtained by the Atom probe tomography, Auger electron spectroscopy and fractographic analysis are in good agreement and complement the picture of grain boundary embrittlement.

Prediction of grain boundary micro-crack initiation during cyclic deformation

J. Hazan^{1,2}, M. Sauzay¹

jerome.hazan@cea.fr

¹ DEN-Service de Recherches Métallurgiques Appliquées, CEA, Université Paris-Saclay, F-91191, Gif-sur-Yvette, France

² Universités Paris-Sorbonne - UPMC, 75005, Paris, France

Abstract

Prediction of grain boundary (GB) micro-crack initiation is a major issue to understand lifetime of ductile metals and alloys subjected to cyclic deformation. Finite element simulations of the cyclic deformation of small aggregates of various fcc metals and alloys are performed. Calculations account for (i) cubic elasticity and crystal plasticity, (ii) slip localization in PSBs and (iii) production, annihilation of vacancies within PSBs and their diffusion toward the surrounding matrix, inducing a free dilatation increasing cycle by cycle. Grain boundary micro-crack initiation is predicted using both finite fracture mechanics and cohesive zone modeling.

Main results

The classical approach for predicting GB micro-crack initiation is based on dislocation pile-ups impingement on grain boundaries [1], [2]. It often conducts to wide overestimation of stress fields and underestimation of cycles to initiate micro-cracks. Indeed, contrary to pile-ups, the PSBs thickness is finite, varying from one hundred nanometer to a few micrometers depending principally on the considered material. Numerical predictions were performed for nickel, copper and 316L SS using finite element calculations, accounting for:

- i. Cubic elasticity and crystal cyclic plasticity constitutive laws, which parameters are adjusted using single crystal data provided by experimental cyclic tests ;
- ii. Production, annihilation of vacancies within PSBs and their diffusion toward the surrounding matrix, inducing PSB dilatation and extrusion [3]. The parameters were previously evaluated through resistivity measurements of copper single and polycrystals cyclically deformed at very low temperature.

The continuously increasing PSB leading to GB fracture is predicted using both finite fracture mechanics and cohesive zone modeling. The effects of many microstructural parameters on GB normal and tangential stress fields are estimated, such as grain size, cubic elasticity anisotropy, crystallographic orientation and GB parameters (critical stress and energy, based on atomistic simulations). Plasticity in grains impinged by PSB is discussed in contrast to GB fracture. Finally, a statistical evaluation of microcrack density produced during lifetime is provided.

[1] K. Tanaka and T. Mura, "A Dislocation Model for Fatigue Crack Initiation," *J. Appl. Mech.*, vol. 48, no. 1, pp. 97–103, Mar. 1981.

[2] M. D. Sangid, H. J. Maier, and H. Sehitoglu, "A physically based fatigue model for prediction of crack initiation from persistent slip bands in polycrystals," *Acta Mater.*, vol. 59, no. 1, pp. 328–341, Jan. 2011.

[3] J. Polák and M. Sauzay, "Growth of extrusions in localized cyclic plastic straining," *Mater. Sci. Eng. A*, vol. 500, no. 1–2, pp. 122–129, Jan. 2009.

Geometrical analysis for misorientation angle dependence of grain boundary - dislocation interaction

Seiichiro Ii*, Toru Hara and Takahito Ohmura

*Ii.Seiichiro@nims.go.jp

Research Center for Structural Materials, National Institute for Materials Science

Abstract

We have geometrically analyzed the grain boundary – dislocation interaction such as an angle between the dislocations and a character of the dislocation remained at the boundary as the result of the interaction in modelled bicrystal by means of the rotation matrix calculation. Based on those results, we also discussed those misorientation angle dependence of the interaction in fcc crystal.

Results

Mechanical properties of polycrystalline materials are often governed by their grain boundaries, which acts as the barrier for the dislocation motion. So far, many researchers have been reported the analysis of an interaction between grain boundaries and dislocations. Particularly, Shen et al. reported that those interactions can be categorized as four processes, (1) Nucleation at the grain boundary, (2) Pass-through, (3) Boundary Absorption and (4) Absorption and Emission [1]. Several experimental evidences have been supported those models, however, those experimental studies are conducted to the specific grain boundaries. In this study, we analyzed the interaction between grain boundary and dislocation in fcc bicrystal related by rotation matrix and discussed the misorientation angle dependence of the grain boundary - dislocation interaction.

Bicrystal consisting of grain 1 (g_1) and the adjoining grain 2 (g_2) is modelled for the analyses. We assumed fcc crystal with a rotation axis of [110] and a burgers vector of the dislocation activated in the g_1 of $[10\bar{1}]$ (\vec{b}_1) with one of the highest Schmidt factors deformed along the [110] in fcc. The burgers vector of \vec{b}_1 is transformed by the rotation matrix and resulting as \vec{b}_1' , which is explained in the orthogonal coordinate system of g_2 . Based on this transformation, we calculated an inner product of the \vec{b}_1' and $\langle 110 \rangle$ presumed as the burgers vector of the dislocations in g_2 (\vec{b}_2) corresponding to the angle between \vec{b}_1' and \vec{b}_2 . We also evaluated a magnitude of the dislocation remained at the grain boundary expressed as $\vec{b}_2 - \vec{b}_1'$.

When \vec{b}_1 and \vec{b}_2 are same and the misorientation angle is 0 corresponding to dislocation motion in single crystal, the inner product is 1 and the magnitude of the burgers vector of remained dislocation is 0. And the former decreases and the latter increases with increasing of the misorientation angle. Moreover, the misorientation angle is beyond about 30 degrees, the different dislocation has the maximum inner product and the minimum magnitude. These results suggest that the dislocations would easily transfer to the adjoining grain with the small misorientation angle. On the other hand, when the misorientation angle is beyond a certain angle, the other process, such as a nucleation at the grain boundary, may be activated.

[1] Z. Shen et al., Acta metall., 36 (1988), 3231-3242.

Mathematical analysis of grain-boundary atomic arrangements and atomic-scale observations

Kazutoshi Inoue^{1,2*}, Mitsuhiro Saito³, Motoko Kotani² and Yuichi Ikuhara^{2,3,4}

*kinoue@wpi-aimr.tohoku.ac.jp

¹ JST-PRESTO, Kawaguchi, Saitama 332-0012, Japan

² WPI Research Center, Advanced Institute for Materials Research, Tohoku University, Sendai, 980-8577, Japan

³ Institute of Engineering Innovation, The University of Tokyo, Tokyo 113-8656, Japan

⁴ Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya 456-8587, Japan

Abstract

The mathematical structure behind atomic arrangement of grain boundaries are analyzed in conjunction with atom-resolved scanning transmission electron microscopy (STEM). The grain-boundary structural units are defined according to their three-dimensional atomic structures. Then, the arrangement of structural units can be well predicted by an algorithm utilizing the Farey sequence. The estimated arrangements had a nice agreement with those observed by aberration-corrected STEM in atomic scale.

Results

It has been recognized that most of materials are used by polycrystalline form, and crystalline defects such as dislocations and grain boundaries (GBs) affect significantly on materials properties. It is important to unveil the mathematical structure behind the atomic arrangement of crystalline defects in order to elucidate the origin of the structure-property relationships in polycrystalline materials. Low-angle GBs have been described by an arrangement of dislocations while high-angle GBs by structural units that have often been defined two dimensionally. However, it is essential to consider three dimensionally since atomic arrangement of materials is considered to be a dense packing of atomic polyhedra regardless of the existence of defects. It has been observed that symmetrical tilt GBs are composed of two kinds of two-dimensional reference structural units which can be resulted from an array of atomic polyhedra projected onto the two-dimensional plane. Consequently, the maximal separation of GB dislocations in high-angle GBs can be achieved due to their locally interacting nature and the continuity of GB structures as a function of misorientations in order to minimize the GB energy.

Therefore, it can be concluded from those properties that the periodicity and the arrangement of structural units are closely related to the distribution of rational numbers that has been well described by the Farey diagram (FIG.) [1]. We predicted the arrangement of structural units in tilt GBs based on a geometrical approach, and it has been verified by atomic-scale observations with aberration-corrected STEM in various kinds of materials [1,2]. Twist GBs, though they have not been often observed by STEM, can also have a similar mathematical structure behind them. We investigate the structure of tilt and twist GBs to establish a unified theory so as to analyze the structure of random GBs.

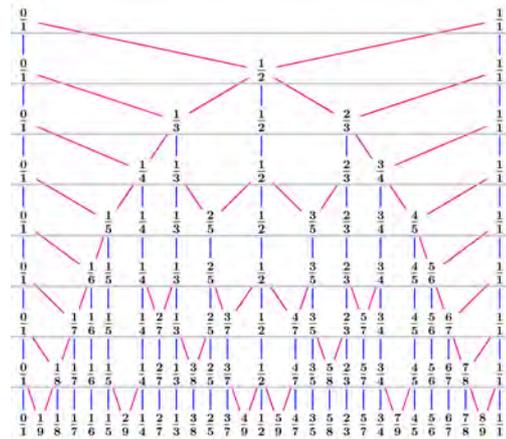


FIG. The Farey diagram that is closely related to the arrangement of structural units [1].

[1] K. Inoue, M. Saito, C. L. Chen, M. Kotani, Y. Ikuhara, *Microscopy*, **65**, 479-487 (2016).

[2] K. Inoue, B. Feng, N. Shibata, M. Kotani, Y. Ikuhara, *J. Mater. Sci.*, **52**, 4278-4287 (2017).

Dopant effects on the surface morphology of α -alumina

Saki Ishihara^{1*}, Eita Tochigi¹, Naoya Shibata^{1,2}, Yuichi Ikuhara^{1,2}

*s.ishihara@sigma.t.u-tokyo.ac.jp

¹Institute of Engineering Innovation, The University of Tokyo, Tokyo, 113-8656 Japan

²Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, Japan

α -alumina is widely used in polycrystalline forms which are fabricated by sintering processes. During sintering processes, their grain growth behavior is strongly affected by dopants or impurities. Abnormal grain growth (AGG), formation of a small number of huge grains in a fine-grained matrix, is one of the representative phenomena induced by dopants. Since AGG inhibits the densification of sintered alumina, the mechanism of AGG suppression has been an important research subject for many years. It is known that CaO and SiO₂ addition promote AGG in alumina, while MgO addition suppresses it [1]. However, detailed mechanisms for these dopant effects on the grain growth behavior have not been fully understood. Previously, a relationship between AGG and grain boundary faceting was considered [1]. Grain boundary faceting is a phenomenon where initial grain boundary plane is decomposed into several flat segments. The experimental studies revealed that such faceted grain boundaries are frequently observed in polycrystalline alumina with CaO and SiO₂ addition but rarely observed in one with MgO addition. Moreover, the faceted grain boundaries tend to consist of low-index planes such as (0001) or {11 $\bar{2}$ 0} [2]. These results suggest that CaO/SiO₂ and MgO addition may show different effects in terms of stabilizing the low-index planes. Therefore, it is of interest to understand the stability of low-index grain boundary planes depending on additives. However, this problem is rather complicated, because a grain boundary consists of two different planes. In this study, as the simplest case, we investigated the dopant effects on faceting phenomena for free surface in α -alumina.

We prepared an α -alumina substrate with an off-cut surface inclined about 2° from (0001) plane along [11 $\bar{2}$ 0] direction by mechanical and chemical polishing. Several small chips were cut from the single substrate to minimize the surface orientation difference between the chips. Three kinds of samples, as-polished, CaSiO_x-deposited, and MgO-deposited, were prepared. The deposition layers were formed on the polished surface with a thickness of about 5nm by Ar ion sputtering. These three samples were annealed for 24 h at 1400°C in air separately. The surface morphology of the samples were observed by atomic force microscopy (AFM: JSPM-5200, JEOL) and transmission electron microscopy (TEM: JEM-2010HC, 200kV, JEOL).

Our observations revealed that the as-polished sample had a faceted surface with a step-terrace structure. The terrace and step planes were identified to be (0001) and (1 $\bar{2}$ 16), respectively. This morphology is considered to be formed by surface reconstruction to reduce the total energy of the surface, since the off-cut surface should have a relatively high energy. The surface of CaSiO_x-deposited sample also consisted of (0001) terraces and (1 $\bar{2}$ 16) steps, but their dimensions were larger than those of the as-polished sample. This suggests that CaSiO_x accelerates the surface faceting. The MgO-deposited sample had a more complicated surface structure consisting of (0001) terrace, (1 $\bar{2}$ 16) step and another step presumed to be (1 $\bar{1}$ 00). These results indicate that MgO causes a change of the surface energy anisotropy (i.e. Wulff shape). In the presentation, the surface morphology of these samples will be shown, and the surface reconstruction mechanisms will be discussed in detail.

[1] C. Park et al., J. Am. Ceram. Soc. **11**, (2003)

[2] A. Mehmet et al., J. Am. Ceram. Soc. **56**, (1999)

Role of grain boundaries on the martensitic phase transformation in NiTi shape-memory alloys: an atomistic simulation

Won-Seok Ko^{*}

**wonsko@ulsan.ac.kr*

School of Materials Science and Engineering, University of Ulsan
93 Daehak-ro, Nam-gu, 44610 Ulsan, Republic of Korea

Molecular dynamics simulations are performed to investigate temperature- and stress-induced phase transformations in nanocrystalline nickel-titanium shape-memory alloys. Our results provide detailed insights into the origins of the experimentally reported characteristics of phase transformations at the nanoscale, such as the decrease of the transformation temperature with grain size and the disappearance of the plateau in the stress-strain response. The relevant atomic scale processes, such as nucleation, growth, and twinning are analysed and explained. We suggest that a single, unified mechanism--dominated by the contribution of a local transformation strain--explains the characteristics of both temperature- and stress-induced phase transformations in nanocrystalline nickel-titanium.

Control of low-angle boundary network for improving high-cycle fatigue in 430 ferritic stainless steel

Shigeaki Kobayashi^{1*}, Weitao Yang², Yuuki Tomobe¹, Rei Okada¹, Sadahiro Tsurekawa³

*skoba@ashitech.ac.jp

¹ Division of Mechanical Engineering, Department of Innovative Engineering, Faculty of Engineering, Ashikaga University, Omae 268-1, Ashikaga, Tochigi 326-8558, Japan

² Department of Information Science and Manufacturing Engineering, Graduate School of Engineering, Ashikaga University, Omae 268-1, Ashikaga, Tochigi 326-8558, Japan

Present address: Shanghai Research Institute of Materials, No.99 Handan Road, Hongkou District, Shanghai, China

³ Structural Materials, Division of Materials Science and Chemistry, Faculty of Advanced Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan

The fatigue fracture in 430 ferritic stainless steel is strongly affected by grain boundaries (GBs) with different character. Recently, we have revealed that the fatigue cracks preferentially nucleate at the random GBs, while cracks never nucleated at the low-angle GBs [1]. The propagation rate of fatigue cracks decreased when the crack crossed GBs irrespective of the GB character, but the crack propagation rate accelerated when the crack propagated along the random GBs [2]. These results suggested that the introduction of fine-grained structure and high fraction of low-angle GBs is effective for improving high cycle fatigue property in the 430 stainless steel. In this work, the development of sub-boundaries (low-angle GBs) during annealing from the highly cold-rolled structure was quantitatively evaluated, to obtain a clue to GB microstructure control consisting of fine-grained structure and high fraction of low-angle GBs in the 430 stainless steel. The fatigue property in the 430 stainless steel specimens with different magnitude of low-angle GB network was investigated.

Fully annealed 430 stainless steel was subjected to cold rolling to 95 % and subsequent annealing at 973 K - 1123 K for 600 s to 172.8 ks. The evaluation of the obtained GB microstructure was carried out by FEG-SEM/EBSD/OIM analysis. The high-cycle fatigue tests of 430 stainless steel specimens with different fraction of low-angle GBs were carried out using a servo-hydraulic machine in air at room temperature. Sinusoidal stress of different levels were applied at a stress ratio of 0.1 and at a frequency of 10 Hz.

The 430 stainless steel specimens produced by annealing at 973 K for less than 1.8 ks mainly composed of subgrain structure where quite high fraction of low-angle GBs ($F_L > 60$ %) interconnected and formed network. The Kernel average misorientation (KAM) maps suggested that the strain (dislocation density) in the subgrains was slightly higher than that in the recrystallized grains. Although the specimen annealed at 1023 K for 600 s contained the high low-angle GBs ($F_L > 50$ %), the strain in the subgrains decreased to same degree as recrystallized grains. The fatigue property in the specimens with the different magnitude of low-angle GB network was compared with that in the specimen produced by annealing from commercially available 430 stainless steel sheet. As a result, it has been demonstrated that the grain refinement and the introduction of the larger network of low-angle GBs can achieve higher fatigue strength and longer fatigue life of 430 stainless steel.

[1] W. Yang, S. Kobayashi, S. Saito, Trans. JSME, 83(2017), DOI:10.1299/transjsme.16-00460.

[2] W. Yang, S. Kobayashi, S. Saito, Trans. JSME, 83(2018), DOI:10.1299/transjsme.17-00353.

Surface and interface effect on mechanical properties of wrinkled film coating with nanosized thickness

Sergey Kostyrko¹, Mikhail Grekov¹, Holm Altenbach²

s.kostyrko@spbu.ru

¹ Department of Computational Methods in Continuum Mechanics,
St. Petersburg State University, St. Petersburg, Russia

² Institute of Mechanics, Otto von Guericke University, Magdeburg, Germany

The mechanical aspects of materials for thin electronic films and coatings have been studied in the recent years in connection with different fields of nanoengineering. Properties of these materials were found to be highly dependent on fabrication and post processing techniques. Under the thermomechanical and chemical impacts, the interaction between surface and bulk energies of film-substrate system gives a rise to varieties of ordered surface patterns. The elastic properties and geometrical characteristics of a film and substrate primarily control the wavelength and amplitude of the film wrinkling on nanometer scale. In most cases, the instability phenomenon is considered as an undesired failure mode which lead to the debonding and microcrack formation. However, many promising applications of wrinkled surfaces have been demonstrated recently in micro- and nanoelectronics. To maintain the stable patterns and have a better control over the size, shape and spacing during the fabrication process, it is important to understand the mechanical properties of wrinkled films on the nanoscale.

In this paper, the continuum model for an analysis of the size-dependent mechanical properties of the wrinkled thin film coating with the nanosized thickness is developed. We formulate the two-dimensional boundary value problem for the film-substrate system under plane strain conditions in terms of the complex variable. Within the framework of the Gurtin-Murdoch theory, the surface and interphase domains are modeled as negligibly thin layers adhering to the bulk phases without slipping. The mixed boundary conditions are formulated in terms of generalized Young-Laplace equations and relations describing the continuous of displacements across the surface and interphase regions. According to Muskhelishvili's technique, the components of stress and strain tensors are related to the unknown Goursat-Kolosov's complex potentials. Taking into account these relations, we rewrite the boundary equations. Unfortunately, it is impossible to find analytically complex potentials in terms of the right-hand sides of the boundary equations in the case of curvilinear boundaries. To solve this problem, we obtain approximate expressions using the boundary perturbation method whereby the unknown functions are sought in the form of a power series in the small parameter that is the ratio of the amplitude to the wavelength of the film wrinkling. Based on the solution of Riemann-Hilbert problem, the integral dependencies of complex potentials on the surface and interface stresses for the first-order approximation are derived. In this way, the original boundary value problem is reduced to the integral equations system which is solved in terms of trigonometric polynomials, employing the properties of Cauchy type integrals. Using the developed mathematical model, the effect of the relevant parameters of thin film materials on the stress concentration factor is analyzed as it is widely used in engineering applications to predict the failure.

Acknowledgements The work is supported by Russian Foundation for Basic Research under grant 18-01-00468.

Interface of Al/Ni connections manufactured by explosive welding

Izabella Kwiecien^{1*}, Piotr Bobrowski¹, Marta Janusz-Skuza¹, Anna Wierzbicka-Miernik¹,
Zygmunt Szulc², Joanna Wojewoda-Budka¹

*i.kwiecien@imim.pl

¹ Institute of Metallurgy and Materials Science, Polish Academy of Sciences, 25 Reymonta Street, 30-059 Krakow, Poland

² High Energy Technologies Works 'Explomet', 100H Oswiecimska Street, 45-641 Opole, Poland.

Combination of aluminum and nickel has large practical application, in particular regarding multilayers, oxidation resistant coatings, aircraft industry or electronics industry. Moreover, the intermetallic phases such as AlNi and AlNi₃ due to their good corrosion resistance and high strength are of high importance. Explosive welding (EXW) is the welding process that attracts growing attention as it allows joining materials difficult or impossible to connect using traditional techniques. During EXW the stable joint is obtained by dynamic clamping of the joined surfaces as a result of collision of the flyer plate with the base plate. Flyer plate contacted with the base plate with the extremely high velocities, being in the range of 2000-3000 m/s. Although such collision excludes the presence of impurities or oxides located on the surfaces of joined materials, it also causes strong plastic deformation of joined sheets close to their interface. Therefore, in this work authors focused on the microstructure examination in the neighbourhood of the interfaces of Al/Ni welds after explosive welding as well as on their transformation after annealing.

Experimental samples were prepared from A1050 aluminum alloy and 201 nickel alloy sheets of 150 x 300 mm dimensions and thickness of 1 mm for both metals. Microscopy examination showed typical wave character of the interface after EXW. Melted zones, formed as a result of very high pressure and locally temperature during the explosion act, were composed of mixture of Al and Ni and their intermetallics of different chemical composition. To fully examine the microstructure of the obtained connections it was necessary to apply the complex testing procedure consisting of the following techniques: Optical Microscopy to reveal the size and shape of the grains, Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS) to verify the connection's quality and to determine the chemical composition within the melted zones and in the regions between the waves. Moreover, application of Electron Backscattered Diffraction technique revealed any possible crystallographic relation, and the character of grain boundaries of the joined materials. Due to the ultrafine microstructure of grains, the key examination technique for this type of materials was Transmission Electron Microscopy supported with Focused Ion Beam used for lamella preparation. Electron diffractions unambiguously determined the phases' composition within the melted zones and at the Al/Ni interface between them, where the SEM/ EDS analytical resolution was not sufficient.

Acknowledgments The research was co-financed by the European Union from resources of the European Social Fund (Project No.WND-POWR.03.02.00-00-I043/16).

Elementary mechanisms of shear coupled grain boundary migration

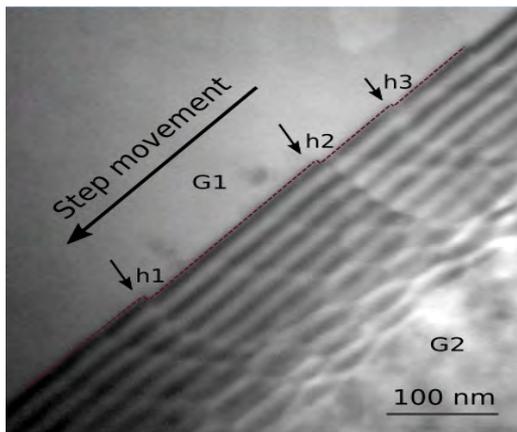
M. Larranaga¹, F. Momprou¹, N. Combe¹ and M. Legros¹

melvyn.larranaga@cemes.fr

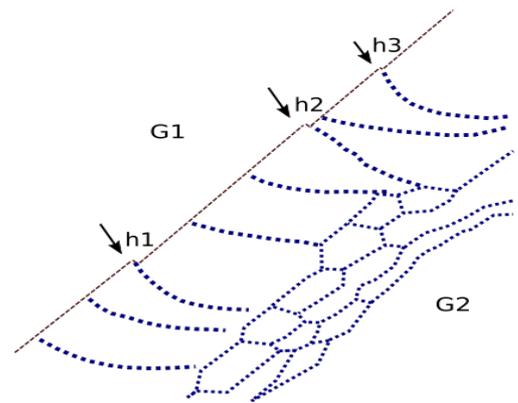
¹CEMES-CNRS and Université Toulouse, Toulouse, France

The grain size reduction in metals (Al, Cu) under less than a few hundreds of nanometers tends to suppress usual intra-granular plasticity, leading to the activation of grain boundary (GB) mechanisms. Among them the shear coupled GB migration has been extensively studied because of its ability to relax strain. It has been shown that this mechanism is the result of the nucleation and propagation of GB defects called disconnections. In order to investigate the role of these disconnections we combine both molecular dynamics (MD) simulations and in-situ transmission electron microscopy (TEM) straining experiments of aluminum bicrystals.

Experimentally, aluminum bicrystal thin foils with $\Sigma 3[110](1-1-1)$ and $\Sigma 41[001](540)$ tilt GB were strained in-situ in the TEM at 400°C in order to favor shear migration coupling. The observations show the propagation of dislocations with a step character along the GB, i.e. disconnections (fig. A and B). Moreover lattice dislocations interacting with the GB were frequently



A - TEM image of GB steps and dislocations



B - Sketch of A displaying the dislocations line

Theoretically, the $\Sigma 41[001](540)$ aluminum bicrystal has been studied using MD simulations. We have first investigated the migration of a perfect GB by calculating the minimum energy path (MEP) using the nudged elastic band method. The configurations along the MEP shows the nucleation and propagation of a pair of opposite disconnections. Because homogeneous nucleation is unlikely to occur in real crystals, we have also investigated the shear coupled migration of the same GB where a simple defect, a row of vacancies, is introduced. We show that the presence of this defect decreases both yield stress at 0K and energy barriers for the GB migration. We reveal the migration mechanism at the atomic scale of an imperfect GB containing a row of vacancies.

Interfaces structure and defects in directionally solidified oxide-oxide eutectics

S. Lartigue-Korinek*, L. Londaitzbéhère, L. Mazerolles

*Sylvie.lartigue@icmpe.cnrs.fr

Institut de Chimie et des Matériaux Paris-Est, UMR 7182 CNRS-Université Paris Est, 2-8 rue Henri Dunant, 94320 Thiais, France

Oxide-oxide eutectics are envisaged as potential candidates for thermo-mechanical applications at high temperatures such as for gas turbine parts. They associate Al_2O_3 and a perovskite phase (SmAlO_3), or Al_2O_3 and a garnet $\text{RE}_3\text{Al}_5\text{O}_{12}$ phase (RE= Er, Y). The microstructures consist of two eutectic phases continuously entangled in a three-dimensional interpenetrating network. Stabilized zirconia was added inside the interconnected microstructure, as a third eutectic phase, leading to a significant increase of toughness.

Preferred orientation relationships occur between the constituent phases. Interfaces Alumina-Zirconia and Alumina-Perovskite have been analysed at the atomic scale. They are semi coherent and most often present facets parallel to dense planes of both phases, in favour of a strong interfacial cohesion.

Alumina-Zirconia interfaces are always curved and are strongly faceted at the atomic level along dense planes of alumina. Disconnections at the facet junctions induce local rotations of the crystals. For Al_2O_3 - Sm_2O_3 interfaces the mean plane of the interface goes through the nodes of the near coincidence lattice, and misfits are accommodated by steps [1]. All most dense interfaces expected from the dichromatic pattern analysis are found. The results reveal that the alumina phase controls the interface formation.

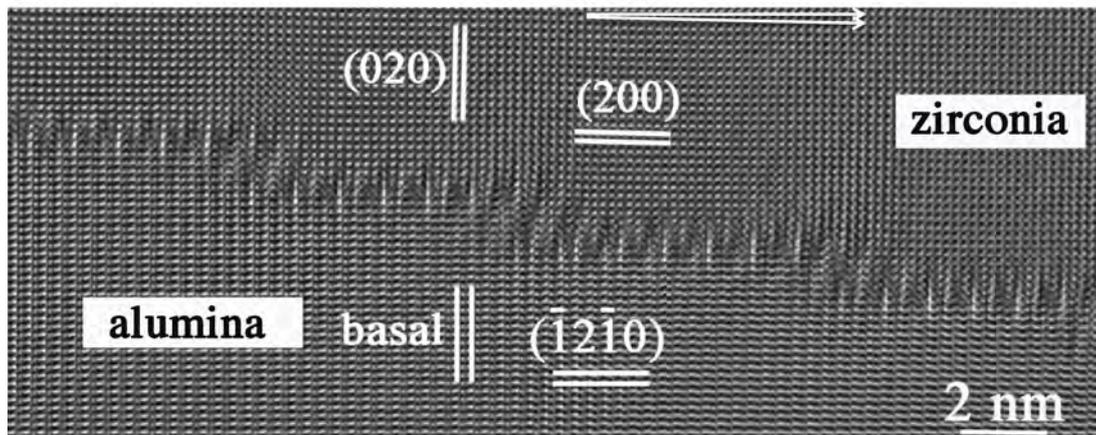


Figure: Interface Alumina-Zirconia parallel to a prismatic alumina plane.

[1] L. Londaitzbéhère, S. Lartigue-Korinek, L. Mazerolles, *J. Materials Science*, 52 (2017) 5489–5502

Acknowledgments Agence Nationale pour la Recherche through the CINATRA project ANR-12-RNMP-0008, the METSA network and the European 7th framework program “ESTEEM2”

Experimental study of twist grain boundaries in WC-Co alloys

Maxime Pellan¹, Sabine Lay*, Jean-Michel Missiaen

*sabine.lay@grenoble-inp.fr

Univ. Grenoble Alpes, CNRS, Grenoble INP, SIMAP, 38000 Grenoble, France

¹Present address, Sandvik Hyperion SAS, Grenoble, France

The combination of high resolution transmission electron microscopy (HRTEM) studies and atomistic modelling of grain boundaries has provided a better understanding on the atomic arrangement at grain boundaries. In the particular case of tilt boundaries, the structural unit (SU) model for the description of the atomic structure was validated, at least in cubic materials. It seems also a powerful approach to study tilt boundaries in non-cubic materials, taking into account effects of additional parametric misfit, although experimental data are still seldom. Developing a similar approach to model twist boundaries is tricky as experimental data at the atom scale are severely lacking, due to the difficulty in HRTEM analysis to simultaneously image the atomic structure of crystals at each side of a twist boundary. More generally, collecting experimental data on the occurrence and orientation characteristics of twist boundaries would help in a better knowledge on the structure and stability of these boundaries.

This work is devoted to twist boundaries in a hexagonal material. WC-Co cemented carbides can be considered as a model material for this kind of study. They are prepared by powder metallurgy at a temperature where cobalt is liquid and WC solid. During the powder compaction stage and then during sintering, contacts form between WC grains and further rearrangement of the grains and mutual re-orientation are expected to optimize the boundary structure and decrease the boundary energy, especially in alloys with high Co content. After sintering, WC grains form a more or less continuous skeleton depending on the amount of cobalt in the alloy. The occurrence and orientation relationship of $\langle 10\text{-}10 \rangle$ twist boundaries was investigated by EBSD in a range of alloys with increasing Co content (Fig. 1), and further characterisation on the boundary plane and dislocations was obtained by TEM and HRTEM. The results are interpreted in terms of CSLs and accommodation from coherency strains.

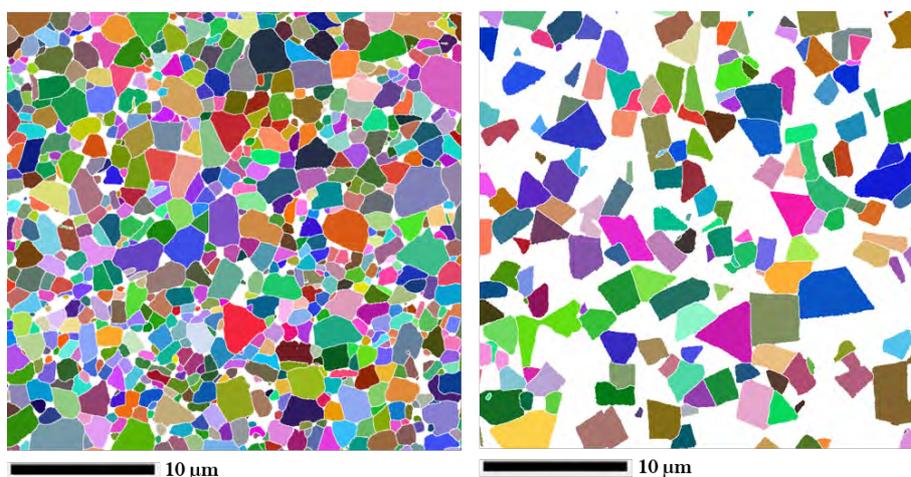


Fig. 1. Grain orientation maps of WC-10Co (left) and WC-50Co (right) (vol%) (Co binder in white).

Study of dislocations in AlN films deposited on sapphire: a geometrical approach

S. Lay, F. Mercier, R. Boichot, M. Pons, E. Blanquet

sabine.lay@grenoble-inp.fr

Univ. Grenoble Alpes, CNRS, Grenoble INP, SIMAP, 38000 Grenoble, France

The performance of electronic or optoelectronic AlN based devices prepared by thin film technology is affected by the presence of dislocations in the films (Fig. 1). Complex mechanical or thermal stress distributions occur during the elaboration of the films and strategies are developed to decrease the amount of dislocations in the devices as several step elaboration or substrate engineering. AlN films are mainly deposited on sapphire substrate leading to a high parametric mismatch at the interface. When the thickness of the AlN film exceeds a critical value, misfit dislocations are necessary to accommodate the deformation at the interface, the nucleation of which being not yet completely understood. In addition to interfacial dislocations, dislocations lying in the film called threading dislocations are observed. A part of them may form arrays between slightly misoriented regions of AlN, as also observed for GaN. This microstructure is inherited from the characteristics of AlN growth on sapphire, which takes place by nucleation, growth and coalescence of three dimensional islands. The islands in GaN were shown to slightly rotate from the perfect epitaxy relationship with the substrate leading to twist deviations between the islands after coalescence. It was observed that a part of the dislocations in the arrays are connected to misfit dislocations lying in the interface.

In this work, the effect of the island rotation on the characteristics of misfit dislocations at AlN/sapphire interface is studied using a geometrical approach based on Bollmann formalism. Two starting misfit dislocation configurations are assumed to determine their spacing and line direction. Their energy is also evaluated as a function of the twist angle. The connection with threading dislocations in arrays is studied, in particular if dislocation emerging from the interface fully accommodate the rotation between twisted AlN regions.

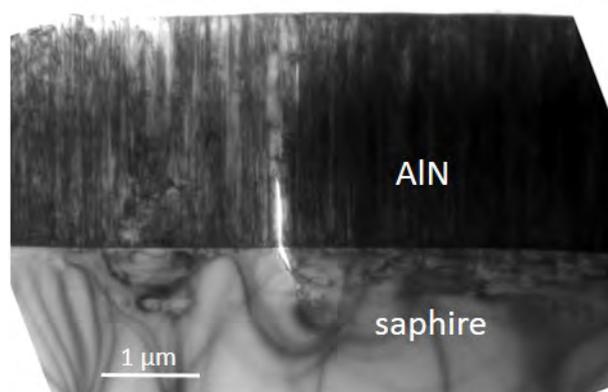


Figure 1. Bright field TEM image of threading dislocations in an AlN film deposited on (0001) sapphire.

Topology evolution during coarsening of nanoporous gold via kinetic Monte Carlo simulation

Yong Li^{1,2}, Bao-Nam Dinh Ngô², Jürgen Markmann^{2,1}, and Jörg Weissmüller^{1,2}

1- Institut für Werkstoffphysik und -technologie, Technische Universität Hamburg, Hamburg

2- Institut für Werkstoffforschung, Werkstoffmechanik, Helmholtz-Zentrum Geesthacht, Geesthacht

Nanoscale metal network structures, such as nanoporous gold, can be made by dealloying with characteristic structure size is as small as 5 nm. Many experiments explore the fact that annealing-induced coarsening affords adjusting the structure size precisely and reproducibly, up to 1 μm . The present study is motivated by controversial reports, from experiment, on the time exponent for the size evolution and on the change of network connectivity. We also explore the impact of surface faceting or roughness on the microstructure evolution and specifically on its topology-changing events, the Plateau-Rayleigh like pinch-off of struts (“ligaments”) of the network. We use atomistic kinetic Monte Carlo simulations of large FCC lattices with spinodal-like initial microstructures, allowing for curvature-driven surface diffusion. The results confirm the $t^{1/4}$ coarsening law predicted by theory, provided that “size” is adequately defined and measured. Remarkably, and contrary to what has been proposed for prismatic rods based on a continuum analysis, the degree of faceting appears to have no effect on the coarsening kinetics of the network. We describe the network connectivity by a scaled density of topological genus. Genus is a topological invariant which represents, in essence, the number of struts in the network. We find that, dependent on its solid fraction, the network can retain its connectivity during coarsening, as in a self-in similar evolution, or it can lose connectivity and undergo a percolation-to-cluster transition.

Interfacial structure in AZ91 alloy composites reinforced by graphene nanosheets

Yong Liu^{1*}, Weicheng Wang¹

*liuyong@ncu.edu.cn

¹ Key Laboratory of Lightweight and High Strength Structural Materials of Jiangxi Province, Nanchang University, Nanchang 330031, PR China

Graphene nanosheets (GNS) are the promising nano-reinforcements to fabricate bulk graphene-metal composites due to their excellent mechanical properties and large yield. However, the effective synthesis of such bulk graphene reinforced magnesium (Mg) composites remains challenging because of the poor interfacial bonding and the aggregation of GNS. Here, GNS possessing about 12 at. % residual oxygen (~7:1 C/O ratio) was synthesized by a thermal reduction method. These residual oxygen in GNS is beneficial to increase the interfacial bonding between GNS and the matrix of α -Mg by MgO nanoparticles, which synthesized through the occurrence of a reaction between the residual oxygen and α -Mg in the composites. TEM analysis reveals that the in-situ synthesized MgO nanoparticles can significantly improve the interfacial bonding between GNS and α -Mg owing to the formation of semi-coherent interface of MgO/ α -Mg and the distortion area bonding interface of GNS/MgO. By filling 0.5 wt. % of GNS, the yield strength and elongation of the composite increased by 76.2% and 24.3%, respectively as compared to the matrix alloy. The significant improvement in mechanical properties of the composites is mainly due to the grain refinement, strong interfacial bonding and dislocation strengthening.

Acknowledgments: This work was supported by the National Key Research and Development Plan (Nos. 2016YFB0701201, 2016YFB0701203), the Natural Science Foundation of China (Nos.51671101, 51761037),

Boron segregation at austenite grain boundaries: an equilibrium phenomenon

G. Da Rosa¹, P. Maugis¹, A. Portavoce¹, S. Lartigue-Korinek²,
J. Drillet³, N. Valle⁴ and K. Hoummada¹

* *philippe.maugis@univ-amu.fr*

¹ Aix Marseille Univ, CNRS, Université de Toulon, IM2NP, 13397 Marseille, France

² MCMC, ICMPE, CNRS, Université Paris-Est, 94320 Thiais, France

³ ArcelorMittal, 57280 Maizières-lès-Metz, France

⁴ LIST, Luxembourg

The addition of very small quantities of boron as an alloying element in high-strength steels increases remarkably their mechanical resistance without impairing their formability. This effect is related to the state of boron at the austenite grain boundaries, which shifts the transformation kinetics of austenite. It is admitted that segregation of boron is controlled by the non-equilibrium segregation phenomenon.

The objective of this work is to understand the mechanisms of boron segregation at austenite grain boundaries and their effect on the austenite subsequent transformation.

We have coupled various characterization techniques (NanoSIMS, SEM and atom probe tomography) to reach the best quantification of the state and localization of boron atoms in the microstructure (solid solution, grain boundaries and precipitates). Specific heat treatments were designed to reveal the mechanisms at stake during heating, soaking and cooling stages.

Our results lead us to rule out the contribution of non-equilibrium segregation and confirm the existence of local equilibrium between the grain boundaries and the neighbouring solid solution.

Atom probe tomography investigation of solute atom segregation during thermal ageing in the carbon-depleted heat-affected zone of dissimilar metal welds

Ilyès Médouni^{1,2}, Jonathan Emo¹, Philippe Maugis¹, Miguel Yescas², François Roch², Pierre Joly², Alain Portavoce¹, Khalid Hoummada¹

ilyes.medouni@gmail.co

¹ Aix Marseille Univ, CNRS, Université de Toulon, IM2NP, 13397, Marseille, France

² Framatome, Développement (DTID) et Ingénierie Mécanique (DTIM), 92084 Paris La Défense CEDEX

Solute segregation at grain boundaries (GBs) is considered as an important phenomenon since it affects the properties of polycrystalline materials. For example, impurity GB segregation can induce intergranular fracture. Furthermore, the level of atomic segregation is known to depend on material thermal ageing conditions. Indeed, this phenomenon is usually used to explain the shift to higher temperatures of the brittle-to-ductile transition curve of the carbon-depleted heat-affected zone of dissimilar metal welds (DMW).

New narrow gap design of DMW was developed for GEN III/III+ French nuclear plants aiming to join the main components of the nuclear reactor vessel made of low alloy steel (LAS) with the pipes of the cooling circuit made of austenitic stainless steel 304L type. The carbon-depleted heat-affected zone of DMW is located next to the interface LAS/Nickel base alloy weld metal, and it is precisely in this zone where the prefatigue crack of fracture toughness specimens is machined, and also where the rupture takes place.

In this work, the carbon-depleted zone of the bainitic low alloy steel part of the DMW has been investigated by atom probe tomography (APT). The main goal of this study was to investigate the segregation of phosphorous and other residual elements such as Sb, Sn, As often considered as responsible for thermal aging GB embrittlement. Our results show that phosphorous segregation is accompanied by a significant segregation of other solute elements, namely C, Mn, Si, Ni, Mo, Cr, Cu, and S. This is the case in all analysed samples, before and after long-term thermal ageing treatments between 350 °C and 450 °C. The results also show Cu-rich clusters in GBs, dislocations, and inside the ferritic grains in the case of thermal aged samples.

BCC-FCC interface leading to Ni precipitation under irradiation in a FeNi alloy

L.T. Belkacemi¹, E. Meslin^{1,*}, M. Nastar¹, and M. Loyer-Prost²

*estelle.meslin@cea.fr

¹ DEN-Service de Recherches de Métallurgie Physique, CEA, Université Paris-Saclay, F-91191, Gif-sur-Yvette, France

² Laboratoire Jannus, DEN-Service de Recherches de Métallurgie Physique, CEA, Université Paris-Saclay, F-91191, Gif-sur-Yvette, France

Reactor pressure vessel (RPV) steel embrittlement under neutron irradiation is the main lifetime limiting factor of nuclear reactors. To predict this change in mechanical properties, particle-accelerator based experiments are conducted in model alloys of RPV steels. Within this study, a bcc Fe-3%at. Ni ferritic alloy has been irradiated with 27 MeV Fe⁹⁺ ions at 673 K to a damage rate of 10⁶ dpa.s⁻¹ within the Jannus Saclay facility, up to a displacement damage of 1.2 dpa. We recently report the formation of a fcc phase in this purely bcc matrix. Since the alloy was initially undersaturated, the out-of-equilibrium fcc phase formation was radiation induced [1]. The characterisation of the Ni-enriched phase has been performed by complementary experimental techniques (HR-TEM, STEM/EDX, EELS and APT). In this presentation, we will focus on the atomic scale description of the fcc/bcc interface. First, there is a Kurdjumov-Sachs (KS) relationships: $\{111\}_{\gamma(\text{fcc})} // \{110\}_{\alpha(\text{bcc})}$ between the bcc matrix and the fcc precipitates. Second, the fcc precipitates are grouped by blocks of 2 variants exhibiting a twin relationships between the 2 variants (Figure below). Explanations about the formation mechanism of these precipitates, involving the defects created under irradiation, will be given.

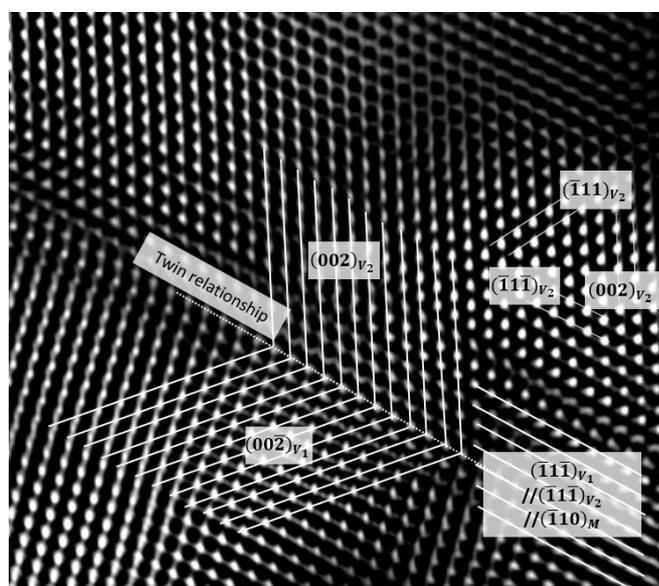


Figure 1: Twin relationship between 2 fcc variants (v_1 and v_2) formed in a bcc Fe-3%at. Ni matrix (M). The 2 variants are along a $\{110\}$ zone axis.

[1] L.T. Belkacemi, E. Meslin, B. Décamps, B. Radiguet, J. Henry, Acta Materialia Vol. 161 (2018)) page 61-72.

Acknowledgments The authors wish to thank Brigitte Décamps, Bertrand Radiguet and Jean Henry for fruitful and stimulating discussions. The authors also acknowledge A. Fraczkiewicz from EMSE for providing the material.

3D-Laue micro diffraction to characterize fatigue damage in bi-crystalline micro cantilevers

Jean-Baptiste Molin^{1,*}, Loïc Renversade^{2,3}, Olivier Ulrich^{2,3}, Odile Robach^{2,3}
Jean-Sébastien Micha^{2,3} and Christoph Kirchlechner¹

* *molin@mpie.de*

¹Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Straße 1, 40237 Düsseldorf, Germany

²Univ. Grenoble Alpes, INAC, 38000 Grenoble, France

³CRG-IF BM32, ESRF, BP 220, 38043 Grenoble Cedex 9, France

Laue microdiffraction (μ Laue) – a synchrotron based technique applying sub-micron sized ($0.5 \times 0.5 \mu\text{m}^2$), polychromatic x-ray beams – has proven to shed unprecedented light onto the deformation behaviour of small volumes. So far, μ Laue was used *in situ* as well as for 2D mapping to understand the tensile, compression and fatigue behaviour of metals.

3D- μ Laue – also called “Differential Aperture X-ray microscopy” [1] – extend the capabilities of μ Laue to achieve submicron 3D spatial characterization. An absorbing wire is placed between the sample surface and the detector. It is used to partially shadow the Laue pattern in order to reconstruct depth-resolved Laue patterns. The achieved depth-resolution is in the order of $0.5 \mu\text{m}^3$.

In this work we present an *in situ* characterization of low cycle fatigue damage in focussed ion beam (FIB) milled, micron sized copper single and bi-crystalline cantilevers ($5 \times 5 \times 25 \mu\text{m}^3$). Each sample contains one single grain boundary located at the neutral plane. The experiments were performed at BM32 of the European Synchrotron (ESRF), using a combination of a micro straining rig and 3D- μ Laue (see Fig.1). From the measurements the lattice orientation, deviatoric strain tensor and the density of unpaired dislocations are extracted with sub-micron resolution. This is done at several different deformation stages, i.e. after $1/4$, $1/2$, $3/4$ and full cycle.

In the talk we will discuss the cyclic dislocation accumulation in the vicinity of and at single grain boundaries with superior spatial resolution, which is a pre-requisite to thoroughly understand fatigue damage initiation at grain boundaries.

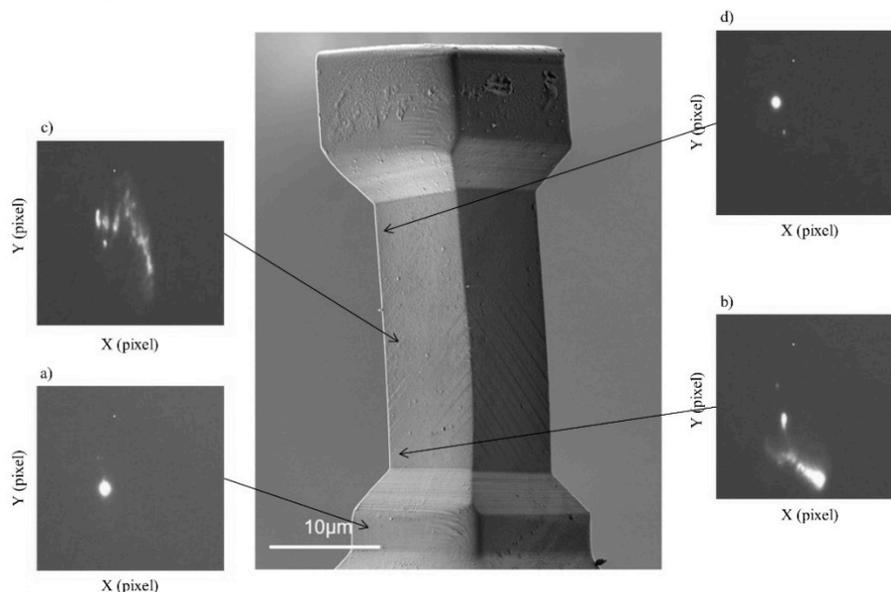


Figure 1: SEM image of a copper single crystal cantilever after $1/4$ cycle. One selected Laue peak is presented for each region of the cantilever.

[1] B.C. Larson et al, Three-dimensional X-ray structural microscopy with submicrometre resolution, *Nature*, 415(6874) (2002) 887-890.

The effect of VN-based precipitates on tensile properties and fracture micromechanism of high-nitrogen steel

V.A. Moskvina*, E.G. Astafurova, G.G. Maier, S.V. Astafurov, E.V. Melnikov, M. Yu. Panchenko,

A.I. Gordienko, N.K. Galchenko

* *valya_moskvina@mail.ru*

Institute of Strength Physics and Materials Science SB RAS, Akademichesky pr. 2/4, Tomsk, 634055, Russia

The experimental study on the effect of phase composition, distribution and size of VN-based precipitates on tensile properties and microstructure of high nitrogen steel was done. Based on microstructural analysis, a new structural scheme was proposed for description of the effect of non-coherent V-based precipitates and emission of dislocations from the interfaces “particle-matrix” on microstructure and fracture micromechanism of high-nitrogen steel.

V-alloyed high-nitrogen austenitic Fe-19Cr-21Mn-1.5V-0.3C-0.9N (wt. %) steel was chosen as an object of investigation. Steel bars were hot-rolled, a solid solution treated (SS-treatment) for one hour at temperatures of 1100°C (HNS-1100) and 1200°C (HNS-1200) followed by water-quenching. The specimens were tensile tested in a wide temperature range of 77 K to 673 K at a strain rate of $1 \times 10^{-4} \text{ s}^{-1}$. Scanning and transmission electron microscopies (SEM, TEM), X-ray structural and phase analyses were used to study microstructural peculiarities of the specimens.

As revealed by TEM and XRD methods, the SS-treatment of CrMnVCN steel leads to precipitation of non-coherent (V,Cr)(N,C) particles in austenitic matrix. Such precipitates act as non-deformable hard inclusions in austenite during plastic deformation of the steel specimens. As a result, the stress-field associated with elastic deformation of hard precipitates in plastically deformed matrix promotes to emission of dislocations from the interface “particle-matrix” [1]. Such dislocation sources suppress planar dislocation arrangement in austenite during tensile testing, enhance multiple slip and promote an accumulation of dislocations. Precipitates also contribute a redistribution of stresses in the bulk of material and terminate crack propagation during low-temperature testing (suppress cleavage-like fracture).

Both solution-treated HNS-1100 and HNS-1200 specimens possessed fine-grained austenitic structure with non-coherent (V,Cr)(N,C) particles, which were randomly distributed in grain bodies and along grain boundaries. With increasing in the SS-temperature, the grain size does not change, but the volume fraction of precipitates decreases significantly due to the partial dissolution of particles. The decrease in fraction of interphase boundaries “particle-matrix” causes a change in low-temperature fracture mode of HNS-1100 and HNS-1200 specimens. With an increase in the SS-temperature (decrease in fraction of precipitates) the fraction of brittle components on the fracture surfaces grows for specimens tensile tested at 77 K.

[1] Astafurova E.G. et al., *Materials Science and Engineering: A*, Vol. 745 (2019) 265–278.

Acknowledgements

The research was supported by the Russian Science Foundation (project No. 17-19-01197).

The effect of post-built annealing on mechanical characteristics of additively-manufactured AISI 304 stainless steel

V.A Moskvin^{*}, Astafurova E.G., Astafurov S.V., Maier G.G., Melnikov E.V., Panchenko M.Yu.
Fortuna A.S., Fortuna S.V., Savchenko N.L., Rubtsov V.E., Kolubaev E.A.

^{*}valya_moskvina@mail.ru

Institute of Strength Physics and Materials Science, Siberian Branch of Russian Academy of Sciences, Akademicheskyy pr.
2/4, Tomsk, 634055, Russia

Abstract

Effect of solid-solution treatment on the mechanical properties of the AISI 304-type austenitic stainless-steel billets, produced by wire feed electron beam additive manufacturing, was investigated. Post-built annealing allows to align the density of the defects of the crystal lattice in austenite grains and internal stresses among the billet volume and, hence, decrease the inhomogeneity of tensile mechanical properties in additively-manufactured stainless steel.

Results

Influence of post-built annealing on mechanical properties of AISI 304-type austenitic stainless steel, which was produced by wire feed electron beam additive manufacturing, was investigated. Flat steel billets (walls) with dimensions of 5×30×100 mm were grown by layer-by-layer strategy using electron-beam melting of 1 mm-wire in vacuum chamber. The substrate of the of AISI 304-type steel was used. Tensile specimens were cut in different orientation relative to the growth direction. Part of them was subjected to a solid solution treatment (SS-treatment) for one hour at temperature of 1050°C followed by water-quenching. Tensile tests of as-built and SS-treated specimens were performed at room temperature and at initial strain rate of $5 \times 10^{-4} \text{ s}^{-1}$.

Mechanical characteristics of the as-built samples (cut along layers) are substantially dependent on distance from the substrate (ductility and strength properties decrease with increase in distance from the substrate). SS-treatment weakly influences tensile mechanical properties of stainless steel as compared to the as-built specimens (which were cut in the same orientation relative to growth direction), but post-producing annealing allows to decrease the inhomogeneity of the tensile properties in as-built specimens. This inhomogeneity is associated with peculiarities of production process. In as-built material, the layers near the substrate (bottom layers) undergo more cycles of heating and cooling in comparison with top layers. This provides accumulation of higher density of the defects of the crystal lattice in austenite grains and high internal stresses in bottom layers of the billets. Post-producing annealing allows to eliminate these microstructural differences and to align mechanical properties in the volume of the billet.

Acknowledgements This work was performed within the frame of the Fundamental Research Program of the State Academies of Sciences for 2013-2020, line of research III.23.

Effect of grain size and boundaries on mechanical behaviour and fracture of Re-rich nickel-based superalloy

Shamil Mukhtarov^{1,*}, Ruslan Shakhov¹, Artem Ganeev¹, Alexander Logunov²,
Valery Imayev¹ and Renat Imayev¹

*shamil@anrb.ru

¹Institute for Metals Superplasticity Problems, Russian Academy of Sciences, 39 Stepan Khalturin st, Ufa 450001, Russia
²PJSC "UEC-Saturn", 163 Lenin Ave, Rybinsk 152903, Russia

Experimental Ni-based superalloy Ni-28(Cr,Co)-12.5(Al,Ti,Nb,Ta)-9(Mo,W,Re)-0.17(C,La,Y,Ce,B) have been designed for gas turbine engine disc application. The chemical composition of novel superalloy is close to a third generation single crystal superalloy [1-3]. Cast superalloy was annealed and cannot be forged at recrystallization temperature.

The homo- and heterogenization annealing intended before forging was included treatment at around the γ' solvus temperature. That was improved the hot workability of the superalloy in contrast to the as-cast condition. Microstructure investigation showed that slow cooling rate during annealing led to coarsening of the γ' phase due to its coagulation and appearance non-coherent boundaries between the matrix γ phase and the γ' precipitates.

It was shown that the deformation at the optimal temperature-strain rate conditions led to development of recrystallization processes. The increase in the deformation temperature as compared to the optimal one led to formation of coarse-grained structure. Study performed by SEM and TEM showed that the base mechanism responsible for the microstructure formation during hot deformation under the optimal temperature-strain rate conditions was continuous dynamic recrystallization. The absence of low-angle grain boundaries in fine recrystallized grains, the formation of predominantly high-angle grain boundaries confirm the development of dynamic recrystallization. The fraction of high-angle grain boundaries after hot deformation under optimal temperature-strain rate conditions was more than 80%.

The effect of heat treatment that involves solution treatment followed by thermal ageing and without solution treatment on mechanical properties of a superalloy have been carried out. It is shown that heat treatment without treatment on a solid solution of the superalloy, like in work [4], led to the preservation of fine grains in the structure and to obtain high strength properties. Grain growth at solution treatment was result in formation of coarse-grained structure and it does not ensure the attainment of high strength properties. The fractures of the tested samples were investigated. The superalloy subjected to solution treatment was broken down mainly along grain boundaries. Samples out of superalloys subjected to deformation followed by thermal ageing were ruptured transgranular.

[1] Li J.R. et al., *Superalloys 2000*, (2000) 777-783.

[2] Walston W.S. et al., *Superalloys 1996*, (1996) 27-34.

[3] Bhadeshia H.K.D.H. <http://www.msm.cam.ac.uk/phase-trans/2003/nickel.html>

[4] Cao W.-D., et al., *Superalloys 718, 625, 706 Deriv.*, (2005) 213-222.

Acknowledgments The present work was supported by the Russian Science Foundation (Grant No. № 18-19-00594). The work was performed using the facilities of the shared services center «Structural and Physical-Mechanical Studies of Materials» at the Institute for Metals Superplasticity Problems of Russian Academy of Sciences.

Effect of severe plastic deformation and annealing on the microstructure and microhardness of Inconel 718 produced by selective laser melting

Kamilla Mukhtarova^{1,*}, Ruslan Shakhov², Shamil Mukhtarov² and Valery Imayev²

*kamilla551@gmail.com

¹Ufa State Aviation Technical University, 12 Karl Marx, Ufa, 450008, Russia

²Institute for Metals Superplasticity Problems RAS, 39 Stepan Khalturin, Ufa, 450001, Russia

Comparative investigation of nickel base superalloy Inconel 718 produced by conventional technology and selective laser melting (SLM) was carried out. The microstructure of the Inconel 718 produced by SLM is different from the material produced by conventional methods due to the rapid solidification process and numerous cycles of heating and fast cooling during production [1]. This process leads to formation of complex microheterogeneous structure of alloy [2]. The microstructure of alloy consists of γ grains with a size of about 10 μm , banded with δ phase particles and small carbides. The γ grains consist of columnar and equiaxed subgrains. SEM and TEM examination showed that the columnar subgrains in their turn consisted of equiaxed subgrains with a size of about 0.5 μm . The δ -phase plates were mainly located along grain boundaries as it takes place in the commercial alloy Inconel 718. Dispersed γ'' particles with a size less than 50 nm were homogeneously precipitated during cooling. Interestingly, carbides with a size of 2-10 μm typically observed in this commercial alloy were not detected. Thus, the use of SLM resulted in a very untypical microstructure in Inconel 718. The microstructure features of the SLM material include a developed substructure in γ grains and the presence of dispersed precipitates, oxides along subgrain boundaries. EBSD analysis showed distribution of low- and high-angle grain boundaries corresponding with the data of SEM micrographs.

Microstructure of superalloys produced by SLM and traditional method subjected to severe plastic deformation by high pressure torsion (HPT) was compared. Refinement of microstructure down to nanocrystalline size and partial dissolution of Nb contains phases [3] as γ'' and δ were observed during HPT at room temperature. Grain boundaries were nonequilibrium that corresponds to very high strain of the sample. δ phase particles were revealed after subsequent annealing at a temperature close to the aging temperature as for commercial superalloy [4]. Nanostructure of SLM Inconel 718 that formed by HPT with duplex ($\gamma+\delta$) structure was thermally stable at 600°C during 2 hours. Such annealing led to achieve the maximum microhardness (9 GPa) of SLM Inconel 718. Microhardness of the SLM Inconel 718 depends on γ grain size, presence of δ , γ'' particles, oxides in microstructure and slightly higher than for commercial superalloy.

[1] Tucho W.M., Materials Science & Engineering A, Vol. 689 (2017) 220.

[2] Trosch T., Materials Letters, Vol. 164 (2016) 428.

[3] Burke M.G., et al., Superalloys 718, 625 and Various Derivatives, (1991) 337.

[4] Mukhtarov Sh., et al., Materials Science Forum, Vol. 683 (2011) 127.

Acknowledgments. The reported study was accomplished according to the state assignment of IMSP RAS (AAAA-A17-117041310215-4). The work was performed using the facilities of the shared services center «Structural and Physical-Mechanical Studies of Materials» at the Institute for Metals Superplasticity Problems of Russian Academy of Sciences.

Characterization of recovery by boundary migration and dynamic recrystallization in experimentally deformed polycrystalline olivine

Alexandre Mussi^{1*}, Billy Clifton Nzogang¹, Caroline Bollinger²,
Patrick Cordier¹, Jérémie Bouquerel¹

*alexandre.mussi@univ-lille.fr

¹ Univ. Lille, CNRS, INRA, ENSCL, UMR 8207 - UMET - Unité Matériaux et Transformations
F-59000 Lille, France

² Bayerisches GeoInstitut, Universität Bayreuth, D-95445 Bayreuth, Germany*

* Now at Washington University in Saint Louis, Saint Louis, 63117 MO, USA

Plastic deformation mechanisms of olivine (main constituent of the upper mantle) are the key features to understand the dynamics of the upper mantle dynamics. Despite more than five decades of study (starting with Raleigh, 1968), those mechanisms are not yet completely understood.

Polycrystalline specimens of olivine have been deformed at the upper mantle temperature and pressure conditions. The overlapping of dislocation contrasts of high dislocation density specimens makes it difficult to use conventional transmission electron microscopy. The Automated Crystal Orientation Mapping technique in Transmission Electron Microscopy mode (ACOM-TEM) has been employed to decipher these microstructures.

Orientation mapping associated with tools like grain orientation spread, grain reference orientation deviation and kernel average misorientation (Wright et al., 2011) allows getting this information.

Specimens contain wavy grain boundaries and sub-grain boundaries ((S)GBs), feature of boundary migrations and so of recovery mechanisms.

The ACOM-TEM technique associated with EBSD tools leads to note that the effect of the tension/curvature driving force of (S)GBs is far more important than the driving force due to the stored dislocation produced by plastic strain. Indeed, small radii of curvature of GB (40-50 nm) have been measured using the high spatial resolution available with TEM.

We characterized bulging mechanisms and identified an alternative mechanism: we noted that the SGB migration is a very active mechanism; these migrations accumulate SGB at GB which generate misoriented domains. This conducts in turn, as in the case of bulging, to the creation of new small grains around the parent grains.

[1] C.B. Raleigh *J. Geophys. Res.* 73, 5391–5406 (1968).

[2] S.I. Wright, M.M. Nowell, D.P. Field *Microsc. Microanal.* 17(3), 316–329 (2011).

Structures and electrical conduction properties of boundary dislocations at low-angle grain boundaries in SrTiO₃

Atsutomo Nakamura^{1*}, Yuho Furushima, Eita Tochigi², Kento Noji¹, Tatsuya Yokoi¹,
Yuichi Ikuhara² and Katsuyuki Matsunaga¹

*E-mail: anaka@nagoya-u.jp

¹ Department of Materials Physics, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan

² Institute of Engineering Innovation, University of Tokyo, 2-11-16, Yayoi, Bunkyo-ku, Tokyo, 113-8656, Japan

Dislocations in crystalline materials play an important role not only in mechanical properties but also in functional properties. A dislocation has a dangling bond array at its core, and a localized strain field is induced in the vicinity of the core. As a result, core structure of dislocations can affect various physical properties of crystals such as electrical properties, optical properties, magnetic properties, and so on. Therefore, it is essential to clarify the relationship between dislocation structures and the effects on physical properties. In this study, we fabricated SrTiO₃ bicrystals with low angle grain boundaries, and investigated the relationship between the atomic structure of the boundary dislocations and their electrical conduction properties. Observations by using transmission electron microscopy revealed that dislocation structures formed at the low angle grain boundaries depend on the boundary plane direction and the tilt and twist angles of the boundaries. It was found that (001)/[100] and (011)/[100] low angle boundaries of SrTiO₃ can exhibit distinct electrical conductivities if reduction treatment is conducted. The conductivities tend to be enhanced along dislocation lines at low angle tilt grain boundaries, and therefore electrical conduction should originate from dislocations themselves. In addition, the conductivity was more enhanced by adding a slight twist angle with the tilt angle of boundaries. It is suggested that the unique electrical conductivity should be due to the characteristic dislocation structures with a large Burgers vector formed by a slight twist angle.

STEM analysis of interfacial structure in Mn₃GaN/Mn₃Ga superlattice film

Gahee Noh^{1*}, Gi-Yeop Kim¹, Chang Beom Eom² and Si-Young Choi¹

*gahui@postech.ac.kr

¹Department of Materials Science and Engineering, POSTECH, Pohang, South Korea

²Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin, USA

Current-induced spin-orbit torques enable the control of magnetization and perpendicular-magnetization is used for spintronic application. Heusler alloys Mn₃Ga (MG) is a ferrimagnetic material with strong perpendicular anisotropy and high spin polarization and can be used as a spintronic application [1]. In ferrimagnetic MG, the control of perpendicular-magnetization with spin polarization is possible, and it is also possible through non-collinear antiferromagnetic material. A typical example of material with antiferromagnetic property is Mn₃GaN (MGN) thin film, which exhibit anti-perovskite structure and generates spin-hall torques corresponding to spin polarization at room temperature [2]. In particular, MGN/MG superlattice thin films consisting of alternating antiferromagnetic MGN with a spin-hall effect and ferrimagnetic MG with strong perpendicular magnetic anisotropy layers have recently shown the potential of controlling spin-orbit torque, wherein magnetic property appears at the interface.

In this study, we investigated correlation between interfacial structure of MGN/MG superlattices and magnetic properties using image analysis tool and scanning transmission electron microscopy (STEM), including the high-angle annular dark field (HAADF) image. We analyzed atomically interfacial roughness, strain effect in MGN/MG superlattice interface, and atomic disordering in each material by HAADF-STEM images. In addition, we found correlation between these properties and magnetic properties. In the interface, the lattice-parameter and the spin polarization are changed, and then the effect of MG spin polarization on MGN changes and the magnetic properties that appear in the interface vary.

[1] H. Kurt, K. Rode, M. Venkatesan, P. Stamenov, and J.M.D. Coey, Phys. Rev. B 83, 020405 (2011)

[2] H. Lee, H. Sukegawa, J. Liu, T. Ohkubo, S. Kasai, S. Mitani and K. Hono, Appl. Phys. Lett. 107, 032403 (2015)

Impact of polymorphic nanostructures at grain boundaries on segregation ability; for asymmetric $\Sigma\{111\}/\{115\}$ tilt boundaries in silicon

Y. Ohno¹, Y. Shimizu¹, N. Ebisawa¹, K. Inoue¹, Y. Nagai¹, H. Yoshida², S. Takeda², T. Yokoi³, A. Nakamura³, K. Matsunaga³

yutakaohno@imr.tohoku.ac.jp

¹Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

²Institute of Scientific & Industrial Research, Osaka University, Osaka 567-0047, Japan

³Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan

Polymorphism in crystallography means the ability of a solid material to exist in more than one crystalline form, and the forms differ in physical and chemical properties even though their chemical components are identical. In this study, we have found two-dimensional (2D) polymorphic nanostructures self-organized inside silicon ingots grown by Czochralski method; they are composed of different 2D periodic units just along $\Sigma\{111\}/\{115\}$ grain boundaries (GBs). The atomistic structure of the 2D polymorphic GBs, as well as their segregation ability, are determined by a 3D chemical nanoanalysis technique using atom probe tomography (APT) combined with scanning transmission electron microscopy (STEM) and ab-initio calculations [1].

STEM revealed that, $\Sigma\{111\}/\{115\}$ GBs have a periodic interface structure with a period of 2 nm along the GBs, and the GB unit is composed of $\Sigma\{221\}$ -like and $\Sigma\{114\}$ -like nanofacets involving 2 $\langle 110 \rangle$ reconstructed bonds (type-I GBs) [2]. Ab initio calculations reveal the GB energy of 0.6 J/m², that is higher than the GB energy of $\Sigma\{221\}$ (0.18 J/m²) and $\Sigma\{114\}$ (0.36 J/m²) GBs. Also, the $\langle 110 \rangle$ bonds are rather longer in comparison with the $\langle 111 \rangle$ bonds in bulk Si. Thus, those long bonds would induce an energy in addition to the energy of $\Sigma\{221\}$ -like and $\Sigma\{114\}$ -like nanofacets.

The GB unit in type-I GBs is changed by annealing at 1100°C. The GB unit in the annealed GBs, that was observed in a cast-grown Si ingot [3], is composed of $\Sigma\{111\}$ -like nanofacets involving 4 $\langle 110 \rangle$ bonds, with the period of 2 nm (type-II GBs). Type-II GBs can be introduced by forming stacking faults of low GB energy (~ 0 J/m²) on the $\Sigma\{221\}$ -like and $\Sigma\{114\}$ -like nanofacets in type-I GBs. The GB energy of type-II GBs is estimated to be 0.45 J/m². Therefore, type-I GBs change into type-II GBs so as to remove $\Sigma\{221\}$ -like and $\Sigma\{114\}$ -like nanofacets of high GB energy, via the formation of $\Sigma\{111\}$ -like nanofacets of low GB energy, even though 2 $\langle 110 \rangle$ bonds of high-energy are added in each GB unit.

APT reveals the oxygen segregation ability of type-I GBs (0.04-0.06 atoms/nm²) and that of type-II GBs (0.03 atoms/nm²). The ratio of the abilities is the same as the ratio of the GB energy of type-I and type-II GBs; i.e., the ability is proportional to the GB energy, as previously proposed [1, 2]. We will discuss potential controls of the 2D polymorphic nanostructures, as well as of their segregation ability, by changing growth conditions.

[1] Y. Ohno, *et al.*, J. Microsc. **268** (2017) 230.

[2] Y. Ohno, *et al.*, Appl. Phys. Lett. **110** (2017) 062105.

[3] A. Stoffers, *et al.*, Phys. Rev. Lett. **115**, 235502 (2015).

Acknowledgments This work is supported by JST/CREST (Grant No.: JPMJCR17J1, 2017-2023).

Grain boundary location and misorientation measurement from particle coordinates

Nicholas H. P. Orr^{1*}, Taiki Yanagashima¹, Eric Maire², Dirk G. A. L. Aarts¹ and Roel P. A. Dullens¹

**nicholas.orr@chem.ox.ac.uk*

¹ Department of Chemistry, Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, UK

² Univ Lyon, CNRS, INSA-Lyon, MATEIS UMR5510, F-69621, Villeurbanne, France

Grain boundary networks are central to macroscopic properties of polycrystalline materials. In particular, the misorientation has profound effects microscopically, governing grain boundary properties such as the mobility and stiffness. Therefore, it is essential to measure both the grain boundary locations and misorientations to understand the behaviour of polycrystalline materials. Here, we introduce a method to characterise locations and misorientations of grain boundaries from particle coordinates only, i.e. without scattering experiments or a priori knowledge of the boundary. The misorientation assignment is achieved with a spatial resolution corresponding to the lattice constant and is robust against imperfections associated with real systems, namely vacancies and particles displaced from their lattice sites. The method may be applied to any polycrystalline system as long as the coordinates of the constituent particles are available from simulations or imaging experiments. We demonstrate our method by applying it to coordinates obtained from confocal microscopy experiments on a colloidal bicrystal and a polycrystalline colloidal material.

Slip deformation behavior of zinc sulfide crystals under controlled light conditions

Yu Oshima^{1*}, Atsutomo Nakamura¹, Tatsuya Yokoi¹, Katsuyuki Matsunaga^{1,2}

*ooshima.yuu@f.mbox.nagoya-u.ac.jp

¹ Department of Materials Physics, Nagoya University, Nagoya, Aichi, Japan.

² Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, Aichi, Japan.

Deformation stresses and hardness in compound semiconductors are often influenced by light exposure, which is known as photoplastic effect [1]. Recently, it has been reported that cubic zinc sulfide (ZnS) crystals, a representative II-VI semiconductor, exhibit extraordinarily large plasticity even at room temperature in the case of deformation in darkness (see figure 1) [2]. This is surprising because inorganic semiconductors are expected to be brittle at room temperature. The plastic deformation in darkness is brought about by glide and multiplication of dislocations. In the case under light exposure, in contrast, glide and multiplication of dislocations are partly suppressed, resulting in twinning deformation. That is, dislocation behavior in ZnS crystals is strongly influenced by light exposure.

It is most likely that cores of dislocations introduced by plastic deformation have a characteristic band structure. As a result, electrons and/or holes excited by light exposure can be trapped at the cores of dislocations, affecting the dislocation behavior. However, it is still unclear how and why the introduced dislocations interact with electrons and/or holes. It is desirable to quantitatively evaluate effects of light exposure on mobility of the dislocations and to understand electronic states at cores of the dislocations in more detail.

In this study, we conducted the room-temperature compressive deformation tests of ZnS single crystals under controlled light conditions to investigate how light exposure influences mobility of dislocations. It was found that plastic strain-rate of ZnS crystals at a constant stress is drastically reduced under light exposure. This means that average mobility of glide dislocations for slip deformation is decreased by light exposure. It was also found that plastic strain-rates during stationary deformation in darkness reached to over 10^{-3} /s. It can be said that ZnS crystals can bring about slip deformation up to a high strain-rate if they deformed in darkness.

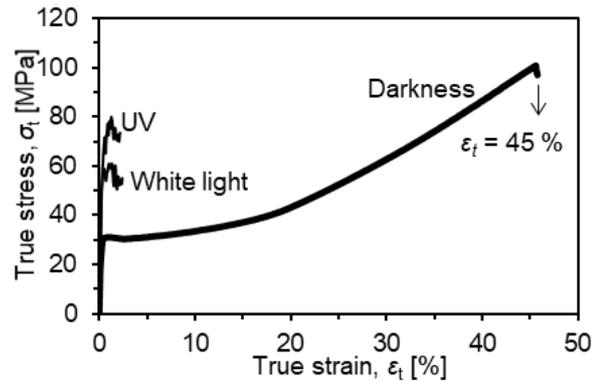


Fig. 1. Stress-strain curves of ZnS specimens deformed at a constant strain rate of 1.0×10^{-5} /s at room temperature under white light or UV light (365 nm), or in darkness [2].

[1] Y. A. Osip'yan, V. F. Petrenko, A. V. Zaretskiĭ, R. W. Whitworth, *Adv. Phys.* **35**, pp. 115–188 (1986).

[2] Y. Oshima, A. Nakamura, K. Matsunaga, *Science* **360**, pp. 772-774 (2018).

The effect of age-hardening on hydrogen embrittlement in high-nitrogen austenitic steel

Marina Yu. Panchenko*, Elena G. Astafurova, Galina G. Maier, Sergey V. Astafurov, Irina A. Tumbusova, Valentina A. Moskvina, Eugene V. Melnikov, Nina K. Galchenko

*panchenko.marina4@gmail.com

Institute of Strength Physics and Materials Science, Siberian Branch of Russian Academy of Sciences, Tomsk, Russia

Abstract

The effect of the age-hardening treatment on hydrogen embrittlement in high-nitrogen austenitic Fe-19Cr-22Mn-1.5V-0.3C-0.9N steel (HNS) was investigated. According to the aging regimes, different hydrogen-assisted tensile properties and fracture peculiarities were found for the specimens with discontinuous precipitation of Cr₂N-particles and with continuous precipitation of (V,Cr)(N,C) and Cr₂N particles. After aging, grain boundaries in austenite and interphase boundaries act as effective trap sites for hydrogen atoms.

Results

For austenitic Fe-19Cr-22Mn-1.5V-0.3C-0.9N HNS, different thermal treatments (solid-solution hardening at the temperature 1200°C, 0.5 h and aging at 700 and 800°C for 0.5 h and 10 h) were conducted. After thermal treatments, an electrochemical hydrogen-charging (H-charging) was performed at a current density of 10 mA cm⁻² for 100 h. H-charging was carried out at room temperature in a 3% NaCl water solution containing 3 g l⁻¹ of NH₄SCN as recombination poison.

The solution-treated HNS possesses austenitic structure with coarse (V,Cr)(N,C) particles (300-400 nm), which homogeneously distribute in material. Hydrogen saturation does not affect the mechanical properties and ductility of solution-treated HNS, but significantly influences its fracture micromechanism. H-charging leads to the appearance of hydrogen-saturated surface layers (20-25 μm in depth), which undergo brittle intergranular fracture, while the central part of solution-treated specimens possesses ductile transgranular fracture micromechanism.

In addition to presence of incoherent (V,Cr)(N,C) particles in solution-treated HNS, aging 700°C, 30 min leads to the appearance of Cr₂(N,C) precipitates predominantly along the boundaries of austenitic grains (discontinuous cellular precipitation). With increased duration and temperature of aging (700°C, 10 h; 800°C, 0.5 h and 10 h), the homogeneous growth of (V,Cr)(N,C) particles in austenite and the coarsening of Cr₂(N,C) particles take place. Thus, different aging regimes ensure the formation of various structural-phase states including chromium and vanadium-based particles, which nucleate and grow in different age-hardening mechanisms (discontinuous and continuous decomposition). Independently on age-hardening mechanism, H-charging of aged specimens causes a decrease in their ductility. The formation of Cr₂N particles both predominantly along the grain boundaries and in the grain bodies contribute to the additional embrittlement of the HNS after H-charging. It was revealed that cells of discontinuous decomposition (Cr₂(N,C) particles and austenite) at the boundaries of austenitic grains give an additional trap sites for hydrogen atoms additionally to grain boundaries (austenite/austenite) and interphase boundaries (austenite/(V,Cr)(N,C) particle). The cells of discontinuous decomposition prevent a bulk diffusion of hydrogen into the specimen. Thus, the depth of surface hydrogen-assisted brittle layer of H-charged specimens after aging using regimes for discontinuous decomposition is 2-2.5 times thinner than that for H-charged solution-treated specimens.

Acknowledgments The research was supported by Russian Science Foundation (Project No. 17-19-01197).

Pores pinning and Bi diffusion induced grain boundary migration in ultrafine grain Cu processed by high pressure torsion

Yuanshen Qi¹, Anna Kosinova¹, Askar R. Kilmametov², Boris B. Straumal^{2,3,4}, Eugen Rabkin¹

yuanshen.qi@campus.technion.ac.il erabkin@technion.ac.il

¹ Department of Materials Science and Engineering, Technion – Israel Institute of Technology, 32000 Haifa, Israel

² Karlsruhe Institute of Technology, Institute of Nanotechnology, Eggenstein-Leopoldshafen, Germany

³National University of Science and Technology MISIS, Moscow, Russia

⁴Institute of Solid State Physics, Scientific Center in Chernogolovka, Russian Academy of Sciences, Chernogolovka, Russia

Cu disks of 99.9995 wt% purity were processed by high pressure torsion (HPT) and percolating porosities were induced in the upper/bottom surface layers contacting anvils. Using electron energy loss spectroscopy and scanning transmission electron microscopy we demonstrated that these nano-sized pores were filled with nitrogen. A combination of severe plastic deformation and heterogeneous strain distribution was believed to cause the capture of N₂ molecules into Cu from the ambient. During storage at ambient temperature and annealing at elevated temperatures the N₂ filled nano-pores formed and grew in the near-surface layers. These gas-filled nano-sized pores pinned the grain boundaries and contributed to very high thermal stability of ultrafine Cu grains up to the temperature of 600 °C.

Using these HPT-processed Cu disks as model material, we studied diffusion induced grain boundary migration. Bi was used as the foreign atoms to penetrate into Cu disks at elevated temperatures. Due to the Bi atoms diffusion along the Cu grain boundaries, the drag effect from the N₂-filled nano-pores was reduced. The resulting grain boundary migration caused significant grain growth. More importantly, we found that ~80% of the newly generated grain boundaries were twin boundaries. These boundaries prevented further penetration of Bi into Cu. This may indicate that the diffusion induced grain boundary migration is accompanied by a very high level of stresses generated by the shear-coupling.

Acknowledgments The work was supported by the Ministry of Science & Technology, Israel (grant 3-12418), and by Russian Foundation for Basic Research (grant 15-53-06008).

Z-module defects in a NiZr alloy

A. Sirindil¹, R. Kobold², F. Momprou³, S. Lartigue-Korinek⁴, L. Perrière⁴,
G. Patriarche⁵, M. Quiquandon^{1,*} and D. Gratias¹

**marianne.quiquandon@chimie-paristech.fr*

¹Laboratoire de Métallurgie de l'UMR 8247, IRCP Chimie-ParisTech,
11 rue Pierre et Marie Curie, 75005 Paris, France

²Institute of Material Physics in Space, German Aerospace Center (DLR) Linder Höhe, 51170 Cologne, Germany

³CEMES-CNRS and Université de Toulouse, 29 rue Jeanne Marvig, 31055 Toulouse, France

⁴ICMPE UMR 7182 CNRS-UPEC, 2-8 rue Henri Dunant, 94320 Thiais, France

⁵C2N-CNRS – Marcoussis UMR 9001, Route de Nozay, 91460 Marcoussis, France

The orthorhombic structure of NiZr has the specific property of all the atoms being distributed on the nodes of a pentagonal Z-Module, that results from the irrational projection of a 5D hypercubic lattice. New kinds of defects thus appear that correspond to 5D symmetry operations that vanish during the projection. These are quinary twins, translation defects and associated Z-module dislocations and have been identified on images taken at the atomic resolution.

An example of HAADF images is presented on the figure and shows a translation defect with fault vector $\vec{T} = (0, 0, \bar{1}, 2, \bar{1})_{5D}$, $\vec{t} = (2 - \tau)/2[\bar{1}, 1, 0]_{3D}$ bounded by a module dislocation with Burgers vector $\vec{B} = \vec{T}$.

A perfect agreement is found at the atomic level between theoretical models and experiments [1]. This justifies the physical pertinence of introducing Z-modules in the crystallography of those kinds of alloys that have local hidden non crystallographic symmetries.

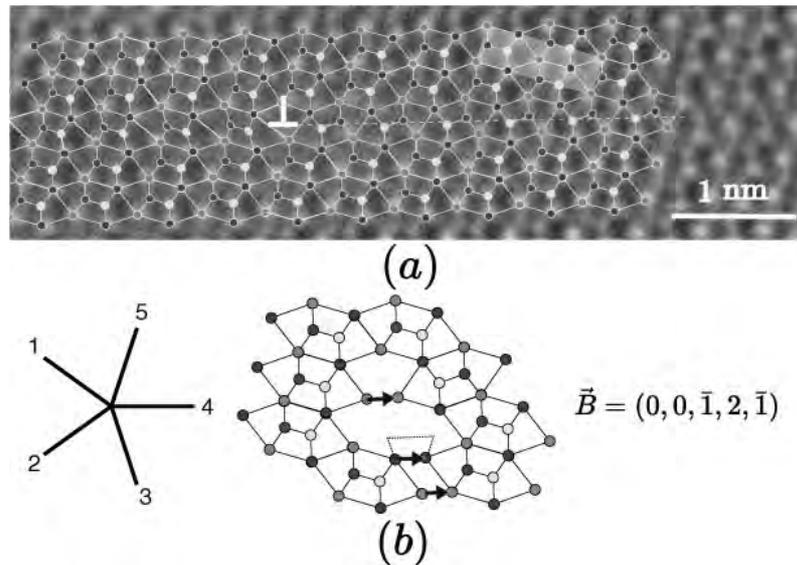


Figure: (a) HAADF image of the elementary module dislocation defect in NiZr : the translation defect (in white) with fault vector $\vec{T} = (0, 0, \bar{1}, 2, \bar{1})_{5D}$, $\vec{t} = (2 - \tau)/2[\bar{1}, 1, 0]_{3D}$ in the Cmc₂m unit cell, is bounded by the module dislocation with Burgers vector $\vec{B} = \vec{T}$. (b) Example of a circuit constructed on the Z-module determining the Burgers vector $\vec{B} = (0, 0, \bar{1}, 2, \bar{1})$ (black arrows) consistent with the translation vector \vec{T} of the corresponding planar fault.

[1] A. Sirindil, R. Kobold, F. Momprou, S. Lartigue-Korinek, L. Perrière, G. Patriarche, M. Quiquandon and D. Gratias, Acta Crystallographica. A74 (2018) page 647-658.

Thermal stability of thin Ni-Fe films on sapphire

Amit Sharma^{1*} Aakash Kumar² David J. Srolovitz² Eugen Rabkin¹

**amitsharma@campus.technion.ac.il*

¹ Materials Engineering, Technion-Israel Institute of Technology, Haifa, Israel

² Department of Materials Science and Engineering, Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, PA, USA

We deposited thin Ni-Fe bilayers on *c*-plane (0001) sapphire (α -Al₂O₃) substrates at room temperature employing the electron beam deposition method. Annealing the films at elevated temperatures led to full intermixing of the layers. The Ni-rich films (Ni-20 at.% Fe) exhibited a strong fiber [111] texture, and their prolonged annealing at a temperature of 1050 °C resulted in full dewetting and formation of [111]-oriented single crystalline faceted particles. The dewetting of the Fe-richer films (Ni-27 at.% Fe and Ni-50 at.% Fe) proceeded differently. At the temperature of 350 °C we observed the onset of abnormal grain growth in the films: sparsely spaced [100]-oriented grains nucleated in the [111]-textured polycrystalline matrix. These abnormal grains grew rapidly and consumed the surrounding matrix. The dewetting of these films proceeded in two stages: the agglomeration began in [111]-textured polycrystalline patches of the film, and then a slower agglomeration process of the [100]-oriented abnormal grains followed. As a result, two distinct populations of small [111]-oriented particles, and larger [100]-oriented particles were formed at the late stages of dewetting. We demonstrated that the nucleation of abnormal grains and their growth are associated with the ordering reaction in Ni-Fe films. Both the existing literature data and our DFT calculations demonstrate that ordering in Ni-Fe alloys is associated with a decrease of the energy of the Ni-Fe (001)-sapphire (0001) interface, as compared to the Ni-Fe (111)-sapphire (0001) interface. We demonstrate that it is this energy decrease which allows the nucleation and growth of ordered abnormal grains.

Mesoscopic modeling and computer simulation of intercrystallite boundaries in graphene

A.E. Romanov^{1,*}, M.A. Rozhkov¹ and A.L. Kolesnikova^{1,2}

*alexey.romanov@niuitmo.ru

¹ ITMO University, 49 Kronversky Pr., St. Peetrsburg, 197101 Russia

² Affiliation, Address, Country

To model intercrystallite boundaries (IBs) in graphene polycrystals we explore the properties of wedge disclinations that are viewed as the main structural defects in 2D graphene crystal hexagonal lattice. Disclinations are associated with improper carbon atom rings, i.e. rings having 4, 5, 7 or 8 members to the contrary of proper 6-member carbon atom rings constituting an ideal 2D graphene crystal lattice [1].

Intercrystallite boundaries in graphene include grain boundaries (GBs) associated with lattice misorientation of neighbouring domains (grains) and interfaces that produce no misorientation. In the proposed approach IBs are considered as disclination chains. The geometry and energy of straight-linear disclination chains are analyzed with the help of molecular dynamics (MD) simulation technique and in the framework of the theory of defects in elastic continuum. We demonstrate that the energy of the modeled graphene IBs reaches the value of 2 eV/Å. For symmetric tilt GBs in graphene the energy stays below 0.5 eV/Å when the boundaries are in so-called equilibrium state. In the case of transition of a grain boundary to non-equilibrium state, the energy of the boundary can be up to three times higher [2].

In addition, we study pseudo-graphene periodic structures with extremely high density of IBs. We demonstrate substantial energy excess for pseudo-graphene in comparison to conventional graphene; the found energy excess can be of the order of 1eV per carbon atom [3].

[1] A.E. Romanov, M.A. Rozhkov, A.L. Kolesnikova, Letters on Materials, 8 (2018) 384.

[2] A.E. Romanov et al. Carbon, 81 (2015) 223.

[3] M.A. Rozhkov et al., Low Temperature Physics, 44 (2018).

Acknowledgments The support from RSF under the project 19-19-00617 is kindly acknowledged.

Comparison between the cohesive curves of various metal–carbide interfaces predicted by DFT & the universal bounding energy relationship (UBER) theory

Elric Barbé^{1,2}, Chu Chun Fu¹ and Maxime Sauzay^{2,*}

**maxime.sauzay@yahoo.fr*

¹CEA, UP-Say, DEN-DMN-SRMP, 91191 Gif-sur-Yvette, cedex, France

²CEA, UP-Say, DEN-DMN-SRMA, 91191 Gif-sur-Yvette, cedex, France

The fracture of interfaces between carbides and metallic lattices is often reported as an essential mechanism of cavity or nano-crack initiation, observed in ductile, brittle and intergranular creep damage of alloys containing carbides. Understanding fracture mechanisms allows further prediction of cavity density evolution with respect to applied strain, affecting damage evolution (Huang, 2018). This first focus of this work concerns interfaces between a metallic FCC matrix (Fe, Ni) and a representative carbide: Cr₂₃C₆ (Barbe et al., 2018). A special attention is paid on the correlation between electronic, magnetic, energetic, elastic and fracture properties. Surface, interface and fracture energies are calculated via density functional theory (DFT) based on a chemical potential analysis. Then, critical stresses for interfacial fracture are estimated by the UBER (Universal Binding Energy Relation) model, which uses input parameters such as interface thickness, Young's modulus and Griffith energy, provided by DFT calculations. The dependence of the obtained interfacial mechanical behavior on the chemical composition and magnetic state of the considered metallic lattice is investigated. A careful definition of the interfacial fracture process zone allows a precise evaluation of the interface thickness of interest, based on the first order bounds to be fractured. Analyses of chemical bonding are performed in order to provide better scientific founding to that definition and to explain the various fracture tendencies.

The predictions of the UBER model is validated against results obtained with DFT simulations of tensile loadings applied to coherent metal-carbide interfaces. It is carefully taken care of the way boundary conditions are applied and how local fracture properties can be extracted from the simulations of the deformation of the whole bi-crystal. The resulting fracture stresses of all the coherent interfaces are rather high, ranging between 14 and 20GPa. In addition, incoherent interfaces associated some metal grain boundaries are also studied. The obtained critical stresses are about two times lower. This is fully consistent with observations of micro-cracks and cavities along carbide in austenitic stainless steels and Ni-based alloys, showing fracture at incoherent interfaces only.

The deformation and fracture of coherent and incoherent interfaces between the same Cr₂₃C₆ carbides and BCC iron is then investigated based on the same approaches: the UBER model using inputs provided by quick DFT simulations and DFT simulation of the bi-crystal deformation up to fracture. Once more, fracture is predicted to occur at incoherent interfaces but neither at coherent interfaces or in the bulk crystals. This agrees once more with numerous observations of interface fracture or cavitation at incoherent interfaces in ferritic steels and tempered ferrite-martensitic steels. Finally, for the sake of comparison, the fracture properties of other carbides known as exhibiting an intra-precipitate cleavage fracture (Ti_xC in FM Ni, x=1-2 and Fe₃C in BCC Fe) are also investigated. In agreement with observations, fracture is predicted to occur first inside the carbides.

Surprisingly, even if the UBER theory was derived specifically for jellium metals subjected to uniaxial straining without relaxation, it provides estimations of the critical fracture stress generally close to the ones computed by DFT simulations run up to fracture. This holds for the investigated bulk metals and carbides investigated here, the considered tensile crystallographic orientations and both uniaxial stress or strain loadings. It still holds for singular grain boundaries and both coherent and incoherent carbide – metal interfaces, considering nine different carbide/metal bicrystal systems. One of the main reason of the partial validity of the UBER theory is the generally observed decay of the electronic density with the increasing distance between the planes under separation.

Local stress analyses of grain boundaries in iron based on artificial neural network potential

Yoshinori Shiihara^{1,*}, Ivan Lobzenko¹, Daisuke Matsunaka², and Hideki Mori³

*shiihara@toyota-ti.ac.jp

¹Toyota Technological Institute, 2-12-1 Hisakata, Tempaku-ku, Nagoya, Japan

²Shinshu University, 4-17-1 Wakasato, Nagano, Japan

³College of Industrial Technonology, 1-27-1 Nishi-Konyo, Amagasaki, Japan

Lattice defects have different atomic and electronic structures from the bulk, then inhomogeneous stress distribution can appear in the vicinity of the defects. Some experimental studies have recently discussed how the stress distribution is useful to reveal material behaviors: seeing stress intensity induced by the interaction between dislocation pile-up and a grain boundary can be useful finding preferential sites for damage nucleation under loading [1]. Despite such interests from an experimental side, theoretical approaches to calculate stress distribution near grain boundaries have not been well developed yet. Approaches with traditional molecular dynamics are less accurate and less transferable. While *ab initio* approaches [2] are essential if one wants to reveal the relationship between stress distribution and an electronic state [3], it is difficult to treat large atomic systems with huge number of atoms in those framework. An approach with good accuracy and less computation cost is desirable, especially for treating complicated problem like interaction between a dislocation and a grain boundary. In this study, we have proposed a method to calculate local stress distribution using a machine-learning approach, where atomic interaction potential is constructed using an artificial neural network. The method has comparable accuracy to the *ab initio* method and allows us to easily treat a system with thousands atoms as shown in Fig. The local stress calculation is formulated based on pair forces acting between atoms and implemented to the software called $\text{\ae}net$ [4]. In the presentation, the details of the formulation and some computational results on the stress distribution near Fe grain boundaries will be shown and discussed.

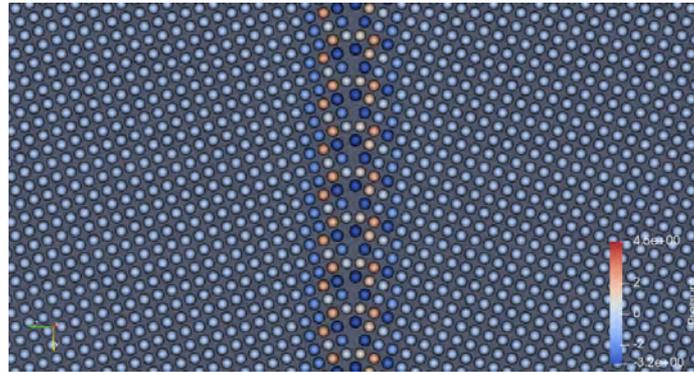


Fig. Pressure distribution near grain boundary in bcc Fe. The atomic pressure is calculated from the atomic stress tensor. This system involves 3720 Fe atoms.

[1] Y. Guo, D. M. Collins, *et al.*, *Acta Materialia*, 96 (2015) 229-236.

[2] For example, Y. Shiihara, M. Kohyama, *et al.*, *Physical Review B*, 81(2010) 075441; Y. Shiihara, M. Kohyama, *et al.*, *Physical Review B* 87 (2013) 125430.

[3] S. Kr Bhattacharya, S. Tanaka, *et al.*, *Journal of Physics: Condensed Matter*, 25 (2013) 135004.

[4] <http://ann.atomistic.net>

Work hardening by grain boundary transformation in multilayer nanopillars

Tomotsugu Shimokawa¹, Tomoaki Niiyama¹, Kenji Higashida²

simokawa@se.kanazawa-u.ac.jp

¹ Faculty of Mechanical Engineering, Kanazawa University, Kakuma-machi, Kanazawa, Ishikawa 920-1192, Japan

² Kyushu University, now at National Institute of Technology, Sasebo College, 1-1 Okishinmachi, Sasebo, Nagasaki, 857-1193, Japan

Abstract

Conventional work hardening mechanisms established based on dislocation-dislocation interactions in coarse-grained materials hardly operate in nanostructured materials because of the limited space for dislocation structure formation. Here we propose a new concept of “grain boundary transformation induced plasticity (GB-TRIP)” to realize high strength and high ductility in nanostructured materials that strength should be controlled by the dislocation generation at grain boundaries. If an equilibrium grain boundary structure contains a portion of the Burgers vector component of a lattice dislocation, the first dislocation generation from a site of the grain boundary can change the grain boundary structure [1] from which the following dislocation is hardly generated; hence, the next dislocation should be generated at other sites of the grain boundary or other grain boundaries. Consequently, the grain boundary transformation results in the suppression of localized plastic deformation causes the necking. We demonstrate the new concept through atomic simulations. We first investigate the inherent properties of various Al and Cu tilt grain boundaries about dislocation source hardening at grain boundaries by grain boundary transformation using bicrystal models with different grain sizes and then consider the effect of the new concept of GB-TRIP on ductility of nanostructured materials by performing tensile loading tests of multilayered nanopillar specimens. Similar to the Lüders band propagation, plastic deformation clearly propagates along the specimen due to GB-TRIP; hence, the new concept of GB-TRIP impacts on the defect design by the grain boundary engineering [2] to nanostructured materials.

[1] T. Shimokawa, Asymmetric ability of grain boundaries to generate dislocations under tensile or compressive loadings, *Physical Review B*, 82, 174122 (2010)

[2] T. Watanabe, S. Tsurekawa, The control of brittleness and development of desirable mechanical properties in polycrystalline systems by grain boundary engineering, *Acta Materialia*, 47, 4171 (1999)

Modeling of the magnetoplastic effect in polycrystalline Cu-Be alloys

Dmitriy Sineglazov^{1*}, Alexander Pokoev¹

**sineglazov-dima@rambler.ru*

¹Department of Physics, Chair of Solid State Physics and Nonequilibrium Systems
Samara National Research University, 34, Moskovskoe Shosse, Samara, 443086, Russia

Experimental studies of the aging of hardened BrB-2 beryllium bronze in a constant magnetic field (PMF) show a noticeable “negative” magnetoplastic effect (MPE), which consists in reducing the ductility of the alloy and increasing the microhardness to 30% [1]. In some cases, the using is accompanied by the formation of structural formations — coherent scattering blocks — with a size of less than 100 nm [2], which we have identified as the nano-magnetoplastic effect (NMPE). It is of interest to search and to establish the physical mechanisms of these effects, including grain boundary properties also.

We solved a range of particular problems using density functional theory and phase field method aimed at modeling MPE and NMPE arising in model copper-beryllium alloys after aging of hardened alloy in a constant magnetic field [1]. In particular, calculations were made of the energy states of binary residual solid solutions of copper-beryllium with different concentrations of beryllium, and the phase energy of the γ -CuBe phase formed during decomposition with and without external CMF superimposed. It is shown that the energy state of the residual solid solution weakly depends on the inclusion of CMF, while the imposition of CMF gives a significant gain in the energy of the states of the γ -CuBe phase. The results obtained are consistent with experimental data on the X-ray phase analysis of copper-beryllium alloys aged in CMF and without it, which indicate a higher quantitative content of the γ -CuBe phase formed in CMF.

We also calculated potential barriers for discontinuous precipitation at grain boundaries and triple junctions with a nickel concentration of the corresponding experimental nickel concentration with applying CMF and without CMF, appropriate experimental data [3], where it was shown that the application of CMF leads to an increase nickel concentration in these structural defects.

[1] Osinskaya J.V., Pokoev A.V., Magneto-plastic Effect in Cu-Be Alloys with Ni Additives. Defect and Diffusion Forum, Vol. 363 (2015) pp 186-189.

[2] Pokoev A.V. and Osinskaya J.V., Russian Patent Specification № 2218423 (2001).

[3] Regina P., Osinskaya Y.V., Divinski S.V., Pokoev A.V., Gerhard W., Impact of a Constant Magnetic Field on Decomposition of Cu-Be-Ni-Based Solid Solution. Defect and Diffusion Forum, Vol. 383 (2018) pp 173-179.

Tuning the grain boundary magnetization by ab initio grain boundary segregation engineering

Mojmir Šob^{1,2,3*}, Monika Všíanská^{1,2}, Martin Friák², Fan-Shun Meng^{4,5}

**mojmir@ipm.cz*

¹ Masaryk University, Faculty of Science, Department of Chemistry, Brno, Czech Republic

² Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Brno, Czech Republic

³ Central European Institute of Technology, CEITEC MU, Masaryk University, Brno, Czech Republic

⁴ Department of Materials Physics and Chemistry, School of Materials Science and Engineering, Northeastern University, Shenyang, China

⁵ School of Science, Liaoning University of Technology, Jinzhou, China

We present an ab initio study of Sigma5(210) grain boundary and selected free surfaces (FS) in nickel-based intermetallic compounds with L1₂ structure. Usually, there are two different GB or FS stoichiometries, (Ni,X) with both Ni and X atoms at the GB and FS as well as (Ni,Ni) with Ni atoms only (X being the other component). We consider both clean GBs and FSs as well as those with segregated impurities.

It turns out that magnetic moments at GBs and FSs behave very differently in comparison with those in the bulk. In some cases, we even encounter ferromagnetic arrangement at the surface of non-magnetic bulk material. Further, we calculate and analyze (tensorial) anisotropic elastic properties of GBs. Focusing on the Sigma5(210) GBs, we assess the mechanical stability of the corresponding interface states by checking rigorous elasticity-based Born stability criteria. For example, in Ni₃Al the critical elastic constant is found three-/five-fold softer contributing thus to the reduction of the mechanical stability of Ni₃Al polycrystals (experiments show their GB-related failure). The tensorial elasto-chemical complexity of interface states associated with the studied GBs exemplifies itself in high sensitivity of elastic constants to the GB composition. As another example we study the impact caused by impurity atoms segregating into the atomic layers close to the GB and substituting Al atoms. If wisely exploited, our study paves the way towards solute-controlled design of GB-related interface states with controlled stability, magnetization and tensorial properties. Our results may motivate experimentalists to conduct new investigations in this field.

Self-assembled (Ti, V)O₂ superlattices by spinodal decomposition

Kyung Song^{1*}, Gi-Yeop Kim², Jaeseoung Park², Junwoo Son² and Si-Young Choi^{2*}

*ksong@kims.re.kr, youngchoi@postech.ac.kr

¹Department of Materials Analysis & Evaluation, Korea Institute of Materials Science (KIMS),
Changwon 642-831, Republic of Korea

²Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH),
Pohang 790-784, Republic of Korea

Since TiO₂/VO₂ superlattices are uniquely composed of 3d¹-correlated functional materials coupled with isostructural 3d⁰ insulators, they were predicted to have electrical and optical properties that can be tuned by external stimuli, and thus to provide a new platform for thin-film devices [1,2]. Layer-by-layer growth of TiO₂/VO₂ superlattices has been previously attempted, but the methods allowed excessive Ti diffusion into VO₂ layers, and formation of TiO₂ anatase polymorphs, and therefore did not guarantee tunable and steep metal-insulator (MI) transition behavior in the superlattice [3]. Recently, the TiO₂/VO₂ system has been demonstrated as an example of spinodal decomposition in the rutile family [4, 5]. The structure with compositional fluctuations formed by spinodal decomposition tend to form at nanometer scale.

Thus, spinodal decomposed (Ti, V)O₂ system offers a practical route to produce new class of microstructure in the form of self-assembled superlattices for the possible application using steep metal-insulator transition. However, the mechanism of spinodal decomposition in (Ti, V)O₂ systems has not been fully revealed. Here we report the atomic-scale structure of self-assembled high quality (Ti, V)O₂ superlattices by spinodal decomposition. Atomically ordered superlattices were confirmed by scanning transmission electron microscopy (STEM) combined with electron energy loss spectroscopy (EELS). V-rich layers alternate with Ti-rich layers on the (001) TiO₂ substrate. Unlike the phase-separated bulk (Ti, V)O₂, the in-plane lattice constant of both Ti-rich and V-rich layers were coherently constrained by interaction with the rigid TiO₂ substrates in our superlattices; as a result, tension was significant only in V-rich layers with negligible strain in Ti-rich layers along the in-plane direction. This structural modulation in our superlattices is inconsistent with previous reports on phase-separated bulk (Ti, V)O₂. By combining EELS and 2D strain analysis decomposition-structure-property relation will be discussed.

[1] Z. Chen et al., ACS Nano, 10 (2016), 10237-10244.

[2] V. Pardo et al., Phys. Rev. Lett., 102 (2009), 166803.

[3] Harish N. S. Krishnamoorthy et al., Appl. Phys. Lett., 104 (2014), 121101.

[4] Z. Hiroi Z et al., Chem. Mater., 25(11) (2013), 2202-2210.

[5] Z. Hiroi Z et al., APL Mater., 3 (2015), 062508.

Acknowledgments This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (NRF-2018R1A2B6008258) and the Global Frontier Hybrid Interface Materials of the National Research Foundation of Korea (NRF) funded by the the Korea government (MSIT) (2013M3A6B1078872).

An experimental set up to study the micro-mechanisms of stress corrosion cracking

Leonel Stermann^{*}, Loic Vanel and Dôme Tanguy

**leonel.stermann@univ-lyon1.fr*

Institut Lumière Matière - UMR CNRS 5306 - Université Claude Bernard Lyon 1

Stress Corrosion Cracking (SCC) has an important impact on the economy and causes safety issues. Despite many efforts, a fully physical model has not been proposed yet. One reason is the variety of phenomena involved (H production, diffusion and trapping, local anodic dissolution and plastic deformation) and their interactions with complex materials' microstructures, at a fine scale. The goal of our study is to set up an experiment where crack propagation can be followed in situ at a scale appropriate for extracting the essential physical information: grain boundary crystallography, active slip system orientation, threshold stress intensity factor and local crack propagation velocity.

For this purpose, a material and a sample design have been chosen to favor fast single intergranular cracking. The material is a rolled plate of aluminum alloy AA7108 (AlZnMg with low Cu content, sensitive to SCC) such as the grains exhibit a strong morphological texture with flat grains elongated in the rolling direction. The traction samples are oriented in the short transverse direction to take advantage of this texture. A thin U-notch is machined to initiate a single crack. A DEBEN micro-traction stage is used to apply the mechanical load. A millimeter size container, built from a 3D printer, is mounted on the sample. It brings saline water in contact with the notch, which is left at free electrochemical potential during the test. Finally, a crystallographic characterization must be done before the exposition to the corrosive solution, using Electron Backscatter Diffraction (EBSD) for revealing texture, grain size and grain boundary orientation.

During the tensile test, brittle crack propagation is obtained at the tip of the notch and it is followed on the surface at a magnification x100 by an optical microscope. It enables to determine the intergranular SCC crack propagation velocity as a function of the applied stress intensity factor. In addition, the displacement field on the side surface can be mapped using Digital Image Correlation (DIC), giving us the possibility to estimate the extent of the plastic zone. The role of plasticity and his relation with the texture are also considered overlapping the strain field with an EBSD mapping of the grains. Finally, the fracture surface is also examined as a post-mortem specimen using Scanning Electron Microscopy (SEM) confirming the intergranular nature of the crack.

Comparative analysis of the grain boundary spectra in Cu-Ag and Cu-In polycrystalline systems

A.B. Straumal^{1,2}, G.V. Aslanyan¹

a.str@issp.ac.ru

¹Laboratory for Interfaces in Metals (LIM), Institute for Solid State Physics (ISSP) RAS, Chernogolovka, Russia

²Laboratory for Hybrid Nanostructured Materials, National University for Science and Technology (NITU MISiS), Moscow, Russia

The study of the spectrum of encountered grain boundaries is a very important task in modern materials science and, in particular, in the study of surface effects such as diffusion, surface phase transitions and segregation. The different ratios of the special coincidence site lattice boundaries, random grain boundaries with different misorientation angles and small-angle grain boundaries can significantly affect the macroscopic properties of the material. The more high energy grain boundaries in the system, the easier grain boundary diffusion goes through them. The more boundaries are wetted during the wetting phase transition; the easier is the segregation of impurities and the more difficult it is for dislocations to cross the polycrystal during deformation. Low energy boundaries, on the contrary, do not contribute to diffusion, but at the same time, they preserve the structural integrity of the sample if a liquid phase has already separated many grains at high temperature along the high energy boundaries.

The study of the spectrum grain boundaries was carried out by us using the electron backscatter diffraction technique of (EBSD) together with the study of wetting of those grain boundaries. Based on the previous study of the grain boundary spectrum in the Cu-In system, we see that information on the wetting temperatures of the grain boundaries we found allows us to estimate their energy [1].

In addition to studying the actual spectrum of boundaries in the systems, the question of the influence of the second element on the formed structure and the grain boundary spectrum, in particular, is of great interest. To study the effect of the second element, we compared the wetting data and the spectrum of the grain boundaries of the two copper-based systems. In the Cu-Ag system, there are much fewer boundaries of coincident nodes, such as $\Sigma 3$, $\Sigma 5$ and $\Sigma 7$, and, therefore, more random boundaries with high energy. This is confirmed by the grain boundary wetting phase transition data. While in the Cu-In system only 95% of the grain boundaries reach full wetting, in the Cu-Ag system only a small fraction of the low-angle grain boundaries do not reach full wetting. Such a difference in the effects of silver and indium may be because silver with copper has a positive mixing enthalpy, and indium has a negative enthalpy.

[1] A.B. Straumal, V.A. Yardley, B.B. Straumal, A.O. Rodin. *J Mater Sci* **50** (2015) 4762–4771 DOI 10.1007/s10853-015-9025-x

Acknowledgments This work was partially supported by the Russian Foundation for Basic Research (Grant 18-33-00473)

Distribution of SiC particles in silicide eutectic alloys of the Mo-W-Si-C system

I.B. Gnesin¹, B.A. Gnesin¹, A.B. Straumal¹, G. Eggeler²

ibgnesin@issp.ac.ru

¹ Institute of Solid State Physics Russian Academy of Sciences, Chernogolovka, Russia

² Chair for Materials Science and Engineering, Ruhr-Universität Bochum, Bochum, Germany

Abstract

The phase composition and microstructure of the silicide eutectics alloy of the Mo-W-Si-C system were investigated. The structure composed of dispersed (~ 1-3 μm in diameter) SiC particles located within the grains of a tetragonal silicide (W,Mo)₅Si₃ was the main object of investigation. Using the EBSD technique, it was determined that the observed morphology features of this structure are not correlated to the formation of the Novotny phase (P6₃/mcm) in the alloy. It was also found that the observed boundaries of the regions in which the SiC particles were precipitated do not coincide with the grain boundaries of the (W,Mo)₅Si₃ phase.

Materials, Methods and Results

The alloy studied was obtained by melting and crystallizing in a graphite crucible of a powder of an eutectic mixture of silicides (W, Mo)Si₂ – (W, Mo)₅Si₃. The ratio of atomic concentrations of W / Mo in the alloy was 7/3. Melting was carried out in a resistance furnace in an argon atmosphere. After holding for about 3 minutes at the maximum temperature (~ 2200 ° C), the furnace was turned off and the alloy crystallized, the sample was cooled with the furnace. The specimen obtained was studied using Scanning electron microscopy (SEM), X-ray microanalysis (XRM) and Electron backscatter diffraction (EBSD). It was found that in addition to the main phases (W, Mo)Si₂ and (W, Mo)₅Si₃ the alloy contains a noticeable amount of SiC particles that precipitated within the (W, Mo)₅Si₃ phase grains. The regions of the (W, Mo)₅Si₃ phase without SiC particles had a well distinguished boundary with the (W, Mo)₅Si₃ regions containing SiC. Taken into account presence of carbon in the alloy, it was impossible to exclude the formation of a hexagonal phase, isomorphic to the molybdenum Nowotny phase Mo_{4.8}Si₃C_{0.6} P6₃/mcm, which is almost indistinguishable on SEM from the tetragonal phase (W, Mo)₅Si₃. These phases could interact with carbon in different ways during crystallization and that could explain the observed structure. To test such hypothesis, specimen was studied with help of Electron backscatter diffraction. This method allows to clearly distinguish the Nowotny phase from the tetragonal phase (W, Mo)₅Si₃ in case of its presence in alloy. As a result, the Nowotny phase was not detected in the investigated alloy in appreciable amounts. It was determined that dispersed SiC particles exist only within the tetragonal phase (W, Mo)₅Si₃. The crystalline lattice orientation data shows that the regions of SiC particles presence can be smaller than a single grain of the (W, Mo)₅Si₃ phase. To investigate the exact nature of formation of dispersed SiC precipitates within the (W, Mo)₅Si₃ phase additional studies are needed.

Acknowledgments This work has been supported by the Russian Science Foundation (project N 17-73-10401).

Observations of grain boundary phase transformations in copper-based alloys using differential scanning calorimetry

I.A. Mizilkin¹, O.A. Kogtenkova^{1*}, A.B. Straumal¹

*kogtenkova@issp.ac.ru

¹Laboratory for Interfaces in Metals (LIM), Institute for Solid State Physics (ISSP) RAS, Chernogolovka, Russia

The phase transformations can proceed not only between bulk phases but also in free surfaces, grain boundaries (GB) and interphase boundaries. The formation of thin layers of a second phase in grain boundaries and grain boundary triple junctions can lead to the drastic changes in the properties of alloys especially those of nanocrystalline and ultra-fine-grained materials. The properties of nanostructured materials depend critically on the behavior and parameters of interfaces because the volume fraction of grain boundaries and interphase boundaries in such alloys is much higher than that in coarse-grained polycrystals.

The goal of this work was to study the grain boundary phase transformations *in-situ*, in poorly quenchable metallic alloys, deep in the solid solutions area (i.e. far away from solidus or solvus lines), by comparing the samples with low and high specific area of grain boundaries, using the thermal effect of such transformations and abnormal grain growth. The choice of alloys (Cu–Co, Cu–Ag and Cu–Ni) are primarily related to the wide technological application of these materials.

Copper alloys (Cu–Co, Cu–Ag and Cu–Ni) before and after high pressure torsion have been studied. The samples were heated in the differential scanning calorimeters (TA Instruments 910 and 1600) from room temperature to the melting point at a rate of 10 K/min.

Small endothermic peaks were observed in ultra-fine-grained Cu–Ag and Cu–Co solid solutions during their heating in the differential scanning calorimeter. These peaks are far away from solidus and solvus lines of respective bulk phase diagrams. The endothermic effect is more pronounced in ultra-fine-grained samples with high specific area of grain boundaries than in their coarse-grained counterparts. In Cu–Ni ultra-fine-grained solid solution the amount of twin grain boundaries drastically increases with increasing temperature. We explain these observed phenomena by the phase transformations between GB complexions. The new lines of these grain boundary phase transformations have been constructed in Cu–Ag, Cu–Co and Cu–Ni bulk phase diagrams.

Acknowledgments This work was partially financed by the Russian Foundation for Basic Research (contract 18-33-00473).

Effective activation enthalpy of grain boundary motion

V.G . Sursaeva* , A.B. Straumal

**email@sursaeva@issp.ac.ru*

*Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Ac. Ossipyan str. 2,
Moscow district, 142432 Russia*

Our experimental data on the study of the movement of individual grain boundaries indicate that the enthalpy of activation lies in the range of 0 - 6 eV. Unreasonably high values of the enthalpy of activation suggest that the application of the Arrhenius equation in such cases is incorrect. The Arrhenius equation was originally applied to chemical reactions in gases and liquids in which there was one activated state. In a solid, many processes are not elementary reactions with a single activated state and a single activation enthalpy. as a rule, this is a multistage process with an effective apparent activation enthalpy and a pre-exponential term. In the process of studying the movement of individual boundaries, we found that there are phase transitions of faceting - defaceting, phase transitions of the appearance and disappearance of grain boundary edges, we obtain information about such transitions by monitoring the change in the shape of the grain boundary. With an increase in the temperature of isothermal annealing, phase transitions of coarsening of the grain boundary structure usually occur. An ordered grain boundary structure becomes disordered. We learn about such transitions from the analysis of temperature dependence of mobility. The temperature dependence of mobility is influenced by internal factors: the impurity composition and structure of the material. Separation from the impurity and adsorption of internal material defects at the boundaries, such as vacancies and dislocations, can lead to a sharp increase in mobility. What gives us the enthalpy of activation obtained in the experiment? It can not be used to determine the mechanism of movement. It simply describes the temperature dependence of a complex process under certain experimental conditions. The hysteresis of grain boundary mobility discovered by us once again confirms the impossibility to draw conclusions about the mechanism of boundary movement.

Acknowledgments The authors acknowledge the partial financial support from the Russian Foundation for Basic Research (contract 19-03-00168)

The effect of individual layer thickness on the Cu/W nano-multilayer to a nanocomposite transformation

A. V. Druzhinin^{1,2,3,*}, D. Ariosa⁴, S. Siol¹, N. Ott¹, B. B. Straumal^{2,3,5}, J. Janczak-Rusch¹, L. P.H. Jeurgens¹, C. Cancellieri¹

**druzhininsas@mail.ru*

¹Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Joining Technologies and Corrosion, Überlandstrasse 129, Dübendorf CH-8600, Switzerland

²National University of Science and Technology «MISIS», Leninsky prospect 4, Moscow 119049, Russian Federation

³Institute of Solid State Physics and Chernogolovka Scientific Center, Russian Academy of Sciences, Moscow district, Academician Ossipyan str., Chernogolovka 142432, Russian Federation

⁴Instituto de Física, Facultad de Ingeniería, Universidad de la República, Herrera y Reissig 565, C.C. 30, Montevideo 11000, Uruguay

⁵Karlsruhe Institute of Technology (KIT), Institute of Nanotechnology, Hermann-von-Helmholtz-Platz 1, Eggenstein-Leopoldshafen 76344, Germany

Nano-multilayers (NMLs) and nanocomposites (NCs) are functional nano-architectures, which mechanical, chemical and/or physical properties can be tailored by smart microstructural and interfacial design [1]. The phase constituents in a NML or NC have a dimension in the nanometer range, resulting in the unique functional properties governed by size-effects, as well as by the atomic and chemical structure of the internal phase boundaries [2]. NMLs, constituted of alternating nano-layers of immiscible metals, can evolve upon thermal treatment in a NC (multilayer structure degradation) with tailored mechanical, electrical and/or thermal properties. Particularly, NML-to-NC transformation was observed in Cu/W NMLs (successive bilayers: 5 nm Cu + 5 nm W) during high temperature annealing in vacuum [3]. It was shown that the driving force for the transformation is provided by the minimization of the total Gibbs energy, as achieved by a reduction of internal interfaces, like high energetic W/W grain and Cu/W interface boundaries.

In the present work, the role of the individual Cu and W nano-layer thicknesses (3, 5, 10 nm) in Cu/W NMLs produced by Physical Vapor Deposition (PVD) on the final microstructure of the NC is systematically investigated [4]. It is revealed that the NC microstructure depends on the initial design of the Cu/W NML: W grains recrystallize into a more spherical shape (with a smaller size), embedded in a matrix of Cu atoms, for NMLs with the combination of thick Cu and thin W layers. Variation of a Cu-to-W individual nano-layer thickness ratio also results in the change of annealing temperature sufficient for a NC formation. High internal stresses in as-deposited Cu and W nano-layers hinder the onset of the NML degradation process: the stress in W needs to fall below a critical stress level to accelerate W grain coarsening and subsequent NC formation. Different kinetics of stress release in NML with different Cu/W individual nano-layer thicknesses is the reason for the change in the degradation onset temperature: Cu outflow to the NML surface acts as a stress relaxation mechanism.

[1] J. Janczak-Rusch et al., *J. Mater. Eng. Perform.*, Vol. 23 (2014) page No. 1608–1613.

[2] T.W. Barbee, *MRS Proceedings*, Vol. 524 (1998) page No. 145–151.

[3] F. Moszner et al., *Acta Materialia*, Vol. 107 (2016) page No. 345–353.

[4] A. V. Druzhinin et al., *Acta Materialia*, submitted.

Energetics of intergranular and interphase boundaries in Ti-6Al-4V alloy

A.S. Gornakova, S.I. Prokofjev, B.B. Straumal*

*alenahas@issp.ac.ru

Institute of Solid State Physics of the Russian Academy of Sciences, Chernogolovka, Russia

The Ti-6Al-4V alloy is most used of titanium alloys. It is well-known that intergranular (GB) and interphase boundaries (IPB) influence the mechanical properties and kinetics of their evolution (formation, degradation) in multiphase alloys, especially at small grain sizes or/and high temperature. However, data on the surface tension of GB and IPB in the Ti-6Al-4V alloy are very scarce. In this work, the surface tension of the GB in (α Ti) and (β Ti) as well as of (α Ti)/(β Ti) IPB in the Ti-6Al-4V alloy is studied in the (α Ti) + (β Ti) region.

The study was conducted on (89.83 \pm 0.07) wt.% Ti, (6.21 \pm 0.05) wt.% Al, (3.92 \pm 0.06) wt.% V and (0.04 \pm 0.02) wt.% Fe alloy. The alloy samples were annealed in vacuum ($\sim 10^{-4}$ Pa). The annealing temperatures were in the range of 660–900°C, i.e. in the two-phase region (α Ti) + (β Ti) of the phase diagram. The duration of annealing was from 672 to 972 hours. Thereafter, the samples were quenched in water. Their microstructure images were obtained using a scanning electron microscope in BSE mode. The chemical composition of the alloy phases was determined using an X-ray energy dispersive spectrometer. The phase composition of the samples and the crystal structure of the alloy phases were determined at room temperature using X-ray diffractometry.

After quenching, the microstructure of the alloy consisted of heterophase dark and light “grains”, which exactly replaced (α Ti) and (β Ti) grains formed during the annealing process, respectively. This was confirmed by the fact that the average chemical composition of dark and light grains corresponded to the composition (α Ti) and (β Ti), respectively. The samples microstructure stabilized using long-term annealing, ensured the achievement of mechanical equilibrium in GB triple junctions. The exact replacement of the grains (α Ti) and (β Ti) by the dark and light “grains” made it possible to measure reliable equilibrium angles in the triple junctions formed at the annealing temperatures. The measurements of the angles in the triple junctions formed by a one (α Ti) or (β Ti) GB and two (α Ti)/(β Ti) IPBs allowed to determine the ratios of the average surface tension of the GBs in (α Ti), g_a , and (β Ti), g_b , to that of (α Ti)/(β Ti) IPBs, g_i . Then, the temperature dependences of the ratios g_a/g_i and g_b/g_i were obtained. Finally, the temperature dependences of the average surface tension of the GBs in (α Ti), (β Ti) and (β Ti)/(β Ti) IPBs were estimated using these dependences and available published data.

Acknowledgements The study was carried out with the financial support of the Russian Foundation for Basic Research in the framework of the research project No. 16-03-00285.

Dual-phase lamellar high entropy alloys produced via high-pressure torsion

Shabnam Taheriniya*, Farnaz Davani, Harald Rösner, Sergiy V. Divinskiy, Gerhard Wilde

**s_tah01@uni-muenster.de*

Institute of Materials Physics, University of Münster, Münster, Germany

This report summarizes recent efforts to investigate the propensity of dissimilar high entropy alloys (HEAs) to deformation-induced bonding and mixing. To this end, high pressure torsion has been applied to process stacked disks of single-phase equiatomic FCC CoCrFeMnNi and single-phase BCC equiatomic HfNbTaTiZr alloys at ambient temperature. SEM, EDX and XRD analyses suggest that the resulting metallic multilayers exhibit a heterogeneity in microstructure refinement and mixing along the radial direction as well as a clearly visible interface between BCC and FCC HEA fragments. After 10 revolutions of high pressure torsion the FCC phase is significantly more refined, whereas the BCC phase remains coarser. The intergranular and interphase boundaries in this hybrid material are characterized using high-resolution TEM.

Keywords: hybrid systems, high entropy alloys, severe plastic deformation

Critical stress required to propagate yield past the grain boundary

Sadahiro Tsurekawa^{1,*}, Dmitri A. Molodov^{2,4} and Pavel Lejček^{3,4}

*tsekawa@kumamoto-u.ac.jp

¹Division of Materials Science and Applied Chemistry, Faculty of Advanced Science and Technology, Kumamoto University, kumamoto 860-8555, Japan

²Institute of Physical Metallurgy and Metal Physics, RWTH Aachen University, D-52056 Aachen, Germany

³Institute of Physics, Czech Academy of Sciences, Na Slovance 2, Prague, Czech Republic

⁴International Research Organization for Advanced Science and Technology (IROAST), Kumamoto University, kumamoto 860-8555, Japan

Grain boundaries exert significant influence on the mechanical properties of polycrystalline materials. This is because the grain boundaries act not only as barriers to dislocation glide but also as sources / sinks for lattice dislocations. Hall [1] and Petch [2] reported in 1951 and 1953, respectively, that the lower yield stress of mild steel increased as a function of inverse square-root of grain size, and explained this relation on the basis of a model of dislocation pile-up at the grain boundary. Now, this is usually represented well by the so-called Hall-Petch relation ($\sigma_y = \sigma_0 + k_y d^{-1/2}$). According to the dislocation pile-up model to describe the Hall-Petch relation, the Hall-Petch coefficient k_y reflects a critical stress required to propagate yield past the grain boundary.

Kurzydowski *et al.*, who conducted *in-situ* TEM observations, showed that the shear stress necessary to emit dislocations was to be about $\mu/320$ from the triple junction and about $\mu/8$ from the $\Sigma 9$ boundary [3]. Later, Varin *et al.* [4] evaluated the shear stresses required to generate lattice dislocations from the grain boundaries to be about $\mu/1000 - \mu/400$, depending on the materials, from the experimental observations that clearly showed plastic deformation starting at grain boundaries. On the other hand, the critical stresses were estimated to be in the range between $\mu/7$ and $\mu/5$ from the Hall-Petch coefficient obtained by the tensile tests for Fe-3mass%Si alloy. As mentioned above, depending on the experimental technique, there are large variations of the evaluated critical stresses for yield past the grain boundary. In order to clarify this controversial issue, we performed nanoindentation tests on orientation-controlled Al, Mg and Fe-3mass%Si bicrystals to evaluate the critical stress from the pop-in event observed in the load – penetration curves. In addition, we did *in-situ* compression tests in a TEM equipped with a load-displacement recording system to observe the mechanical response accompanied with the dislocation emission from the grain boundary and/or dislocation transmission across the grain boundary.

In this presentation, we will compare the experimental results obtained from the nanoindentation tests and *in-situ* deformation in TEM to comprehensively understand the Hall-Petch relation. The values of the critical shear stress evaluated from the pop-in event in nanoindentation tests were in agreement with the values from the Hall-Petch coefficients obtained from the bulk samples, whereas those from *in-situ* deformation in TEM were approximately one order of magnitude lower than the values obtained from the nanoindentation tests.

[1] E. O. Hall, Proc. Phys. Soc. Lond., **B64** (1951), 747.

[2] N. J. Petch, J. Iron Steel Inst., **174** (1953), 25.

[4] K. J. Kurzydowski *et al.*, Acta Metall., **32** (1984), 71.

[5] R. A. Varin *et al.*, Mater. Sci. Eng., **85** (1987), 115.

Acknowledgments This work was financially supported by Grain-in-Aid for Basic Research (S) (Grant No. 16H06366) from the JSPS (Japan Society for the Promotion of Science). This support is greatly appreciated.

Reaction dynamics of tricresyl phosphate on Fe₃O₄ (111) surface: a hybrid quantum-classical simulation with coarse-grained particles

Naoki Uemura^{1,*}, Yosuke Harada^{2,3}, Shuji Ogata¹

*uemura.naoki@nitech.ac.jp

¹Department of Physical Science and Engineering, Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

²Advanced Technology Research Laboratories, Idemitsu Kosan Co., Ltd.,
1280 Kamiizumi, Sodegaura, Chiba 299-0293, Japan

³Research Association of High-Throughput Design and Development for Advanced Functional Materials,
Central 5-1, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

Organic-inorganic interfaces widely exist in materials and devices and often attract our attention because of their unique physicochemical reactions. It is not easy to analyze such reactions at the interface by experimental measurements. The DFT-level accuracy dynamics simulations are highly expected to unveil them.

We have been developing the hybrid quantum-classical simulation code. In the code, the divide-and-conquer-type real-space grid DFT (DC-RGDFT) with the norm-conserving pseudopotential and the PBE-GGA functional [1] is used to treat the quantum region. To mimic the reaction dynamics at the interface under normal and shear stresses, we implement a novel stress application method, called the coarse-grained particle (CGP) displacement method, to the hybrid code. The CGP displacement method can seamlessly control the locally averaged atomic displacement in both liquid and solid phases.

In this study, we treat tricresyl phosphate (TCP) molecules to test the capability of the CGP displacement method. The TCP molecule has been widely used for various industrial applications such as anti-wear additives. It is well known that the phosphate layer forms on metal and metal oxide surfaces under high pressure and high temperature by decomposition reaction of TCP. However detailed formation mechanisms of it have still been discussed [2, 3]. To investigate the mechanisms, we carry out two types of the DFT simulations. In the one type, the molecular dynamics simulations with DC-RGDFT are performed for a TCP on a Fe₃O₄ surface. It mimics the pressurized situation through gradual shift of the TCP center-of-mass to the Fe₃O₄ surface. In the other type, we use the hybrid quantum-classical method with the CGP displacement method to treat a large system of TCP molecules (bulk like) on a large Fe₃O₄ surface. The quantum region is set to the interfacial region. Details of the simulation results will be explained in the presentation.

[1] N. Ohba *et al.*, *Comp. Phys. Comm.* 183, 1664 (2012).

[2] E. Osei-Agyemang *et al.*, *Tribol. Lett.* 66, 48 (2018).

[3] B. Guan *et al.*, *Lubr. Sci.* 28, 257 (2016).

Acknowledgments This work was funded by New Energy and Industrial Technology Development Organization of Japan (NEDO) Grant (P16010).

Free energy calculation of the interface between liquid and polymer-grafted surface

Masayuki Uranagase* and Shuji Ogata

*uranagase.masayuki@nitech.ac.jp

Department of Physical Science and Engineering, Nagoya Institute of Technology, Aichi 466-8555, Japan

It is important to understand the physical properties of the interface between solid and liquid, because they are related to important phenomena such as wetting, lubrication, and adhesion in science and technology. In the problem of adhesion, the strength of adhesion between solid and liquid is quantitatively evaluated by the work of adhesion [1], which is defined by subtracting the solid-liquid interfacial free energy from the sum of surface free energies of the solid and liquid. Generally, the interfacial free energy is evaluated from contact angle of liquid droplet on the solid surface. However, if the solid surface has complex structure, the boundary between liquid and solid may become obscure. For such interfaces, it is difficult to determine the contact angle without ambiguity. Typical example of the solid surface with complex structure is polymer-grafted surface, which is often produced to change the properties of the surface from those of the original one.

Not only laboratory experiments but also molecular simulations are often conducted to elucidate solid-liquid interfacial properties. In particular, since there are sophisticated methods to calculate the free energy using molecular simulations, several methods for evaluation of solid-liquid interfacial free energy have already been proposed [2, 3]. In these methods, liquid molecules are separated from the solid surface by shifting artificial planar potential. Then, the free energy difference for the operation of shifting the potential is calculated using thermodynamic integration, in which the free energy gradient is evaluated via molecular simulations. In this case, the free energy gradient corresponds to the force acting on the potential. Although, previous methods are applied to various solid-liquid interfaces, applications of these methods are still limited to flat solid surfaces and there is no method which appropriately treats complex surface structure.

We developed the novel method for evaluation of the work of adhesion of solid-liquid interface [4]. In this method, we adopted two ideas to enable efficient application to the polymer-grafted surface. Firstly, a set of spherical potentials are introduced instead of a planar potential. This enables separation of liquid molecules from the solid surface according to the surface structure (see, Fig. 1). Secondly, parameters contained in the potential are updated so as to suppress the variation in the free energy gradient. This contributes to accurate numerical integration with small number of evaluation of free energy gradient.

We applied this novel method to the interface between water and gold substrate modified by poly(ethylene oxide). This interface gathers much attention of chemical and biological researchers because this interface is closely related to resistance of protein adhesion to the surface. We studied the dependence of the work of adhesion on coverage ratio of the poly(ethylene oxide). Then, we found that the work of adhesion becomes large at the intermediate coverage ratio. This is because water molecules cannot access to oxygen atoms in poly(ethylene oxide) if coverage ratio is too large.

[1] A. J. Kinloch, *J. Mater. Sci.*, **15** (1980) 2141.

[2] F. Leroy et al., *Macromol. Rapid Commun.*, **30** (2009) 864.

[3] R. Benjamin and J. Horbach, *J. Chem. Phys.*, **137** (2012) 044707.

[4] M. Uranagase et al., *J. Chem. Phys.*, **149** (2018) 064703.

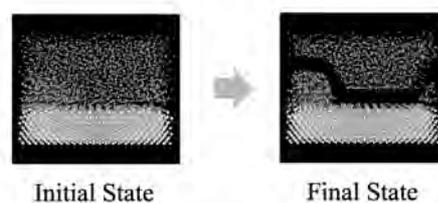


Fig. 1 Separation of liquid molecules according to the surface structure.

Microscopic mechanisms of weakening of adhesion strength at aluminum-epoxy resin interface under moist condition

Masayuki Uranagase* and Shuji Ogata

*uranagase.masayuki@nitech.ac.jp

Department of Physical Science and Engineering, Nagoya Institute of Technology, Aichi 466-8555, Japan

The adhesive bonding has become a key technique for automotive manufacturing. The bisphenol-A epoxy resin with curing agent has been used widely as the bonding glue. One of the fundamental open problems in the adhesion between metal and epoxy resin is that the adhesion strength reduces significantly in a moist environment. Although various possible mechanisms due to water have been suggested, such as the increased plasticity of resin, swelling of resin, corrosion of metal, and screened inter-atomic interaction between metal and resin, no detailed explanation exists. Microscopic understanding of the mechanisms is essential to propose an innovative method to solve the problem. The first-principles simulation of such a system is difficult because it requires a large system size due to the inhomogeneity of the interface and largeness of the epoxy molecule.

We perform the hybrid QM-CL simulation [1] of various aluminum and epoxy resin interface with water molecules inserted in the contact region (see, Fig. 1) [2,3]. In accordance with experimental conditions, the aluminum layer is surface oxidized to a depth of 10 Å while the bisphenol-A type epoxy molecule has both OH and ether groups. About 1,500 atoms at the contact region are treated as the QM region using our original real-space grid DFT code [4]. Shear deformations are applied dynamically to the system.

For the first time, calculated adhesion strengths compare well with the experimental values. Three types of chemical reactions that affect the adhesion strength occur depending on the terminal functional groups of the aluminum oxide surface and the water layer formation.

Separate calculations confirm small barrier energies for all the reaction processes.

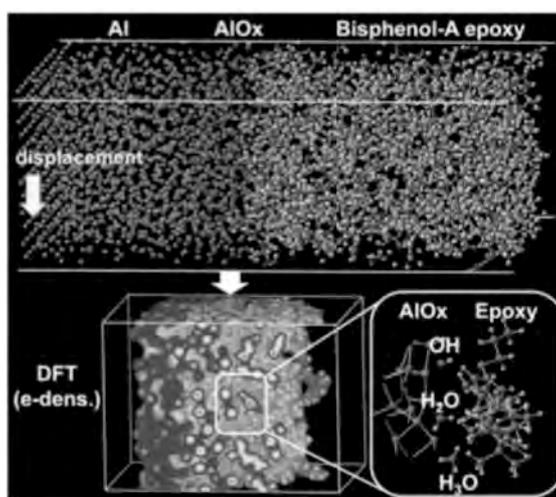


Fig. 1: Schematic of the present hybrid QM-CL simulation.

[1] S. Ogata, Phys. Rev. B, **72** (2005) 045348.

[2] S. Ogata and Y. Takahashi, J. Phys. Chem. C, **120** (2016) 13630.

[3] S. Ogata and M. Uranagase, J. Phys. Chem. C, **122** (2018) 17748.

[4] N. Ohba, S. Ogata et al., Comput. Phys. Commun., **183** (2012) 1664.

First-principles computational tensile tests of grain boundaries: effects of a bulk-region size and local-energy and local-stress analysis

Hao Wang^{1,2*}, Masanori Kohyama¹, Shingo Tanaka¹, JinKai Wang², and Ying Chen³

*haowang@shu.edu.cn

¹ Research Institute of Electrochemical Energy, Department of Energy and Environment, National Institute of Advanced Industrial Science and Technology, Ikeda, Osaka 563-8577, Japan

² School of Materials Science and Engineering, Shanghai University, Shanghai 200444, China

³ Department of Nanomechanics, School of Engineering, Tohoku University, Sendai 980-8579, Japan

First-principles computational tensile tests (FPCTTs) are powerful tools to investigate intrinsic strength and processes of failure of grain boundaries (GBs) or interfaces. For successive straining of a supercell, atomic relaxation is iterated according to atomic forces via density-functional theory calculations, leading to the energy-strain and stress-strain curves. FPCTTs of GBs were first applied to tilt GBs in SiC [1] and Al [2], followed by FPCTTs of impurity-segregated GBs [3-5], making great contributions in clarifying the effects of bonding nature or electronic behaviors on the strength and mechanical processes. However, we have to be careful in making comparisons with experiments, because FPCTTs inevitably adopt ideal conditions. On the other hand, it is desirable to deduce local energy-strain or energy-separation relations from FPCTTs of GBs so as to be combined with continuum simulations, while it is not so easy to extract such relations, because accumulated strain energies in a GB supercell depend on the bulk-region size. In the present study [6], first, we examine the effects of the bulk-region size in a GB supercell on the failure mode of a FPCTT by using a {001} $\Sigma 5$ twist GB in Al. Second, we apply our *ab initio* local-energy and local-stress scheme [7-9] to FPCTTs of Al GBs, aiming to extract energy-strain or energy-separation relations, independent on the bulk-region size.

We dealt with FPCTTs of 70-atom and 50-atom supercells of the $\Sigma 5$ GB in Al. The bulk-region size in the former cell is 1.4 times longer than the latter. For the 70-atom cell, the energy-strain curve shows spontaneous failure with catastrophic energy release just after the maximum stress, which we name Type A. For the 50-atom cell, the energy increases gradually even after the maximum stress and continuously becomes that of relaxed fracture surfaces, which we name Type B, although the stress-strain curves are almost common in both the cells. The Type-B failure occurs by the lack of accumulated strain energies for creating fracture surfaces even after the maximum stress, because the accumulated strain energy is nearly proportional to the bulk-region size. We clarified that the failure mode in a FPCTT depends on the relationship among 1) the accumulated strain energy depending on the bulk-region size, 2) the work of separation, and 3) the maximum stress of the GB (GB strength). The failure mode of previous FPCTTs of Al tilt GBs with segregated impurities [3-5] can be reinterpreted from this viewpoint by considering the impurity-induced changes of the work of separation and the GB strength. In the local-energy and local-stress analysis of the FPCTT of the Al $\Sigma 5$ GB, we observed that local-energy variations of atomic layers against local strain near the interface from the data can be used as embedded functions combined with continuum simulations.

[1] M. Kohyama, *Phil. Mag. Lett.* **79**, 659 (1999), [2] G.-H. Lu *et al.*, *Phys. Rev. B* **69**, 134106 (2004), [3] G.-H. Lu *et al.*, *ibid.* **73**, 224115 (2006), [4] Y. Zhang *et al.*, *J. Phys. Condens. Matter* **19**, 456225 (2007), [5] Y. Zhang *et al.*, *Phys. Rev. B* **75**, 174101 (2007), [6] H. Wang *et al.*, *J. Phys. Condens. Matter* **31**, 095001 (2019), [7] Y. Shihara, M. Kohyama and S. Ishibashi, *Phys. Rev. B* **81**, 075441 (2010), [8] H. Wang *et al.*, *J. Phys. Condens. Matter* **25**, 305006 (2013), [9] H. Wang *et al.*, *Modelling Simul. Mater. Sci. Eng.* **25**, 015005 (2017)

Hardness distribution in a heterogeneous nano-structured austenitic stainless steel

C. Watanabe^{1*}, Y. Aoyagi², Y. Todaka³, M. Kobayashi³, H. Miura³

**chihiro@se.kanazawa-u.ac.jp*

¹Faculty of Mechanical Engineering, Kanazawa University, Kanazawa 920-1192, Japan

²Department of Finemechanics, Tohoku University, Sendai 980-8579, Japan

³Department of Mechanical Engineering, Toyohashi University of Technology, Toyohashi 441-8580, Japan

Heavy cold-rolling of a SUS316LN austenitic stainless steel successfully introduced complicated heterogeneous nano-structure consisting of rhombic twin domains surrounded by shear bands, which were further embedded in the conventional lamellar structure. The twinning planes of {111} in the twin domains were nearly parallel to the rolling direction (RD). The average twin spacing was 20~70 nm. The direction of the lamellar was also nearly parallel to the RD, and the average boundary-spacing was about 100 nm. Ultra-fine grains with an average size of 70 nm were well-developed within the shear bands. The cold-rolled steel possessed excellent tensile strength of over 1.5 GPa with reasonable elongation of 10%. Nano-indentation of the above microstructures revealed that the shear bands possessed the highest hardness of 9.1 GPa compared to those of the twin domains (6.6 GPa) and lamellar (7.0 GPa). Microstructural observations using the transmission Kikuchi diffraction technique revealed that the misorientation angle of twin boundaries within the twin domains remained 60° after heavily cold-rolling. Moreover, dislocation density within twin domains might be lower than that of the shear bands. It was suggested that relatively lower hardness of twin domains was ascribed to a lower amount of work hardening than that in the shear bands.

Acknowledgment

This research is financially supported by Japan Science and Technology Agency (JST) (20100115) under Industry-Academia Collaborative R&D Program "Heterogeneous Structure Control: Towards Innovative Development of Metallic Structural Materials", and the authors deeply appreciate this support.

Scanning transmission electron microscopy analysis of the modified layered structure by thermal process in lithium batteries

Yujeong Yang^{1*}, Byoungwoo Kang¹ and Si-Young Choi¹

*yujeong@postech.ac.kr

¹Department of Materials Science and Engineering, POSTECH, Pohang, South Korea

In the lithium-ion battery research, structural change in charge cycle has a great influence on the performance of the active material. Therefore, it is important to study the mechanisms on structural change and control them to improve the stability. In this study, we focused on atomic structural change of the LNMO ($\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$) active material during thermal process, which is to improve cathode performance of Lithium-ion battery.

The scanning transmission electron microscopy (STEM) technique including high-angle annular dark field (HAADF) and annular bright field (ABF) imaging was used to investigate the structural changes in the Li layer at an atomic scale. Furthermore, the STEM-electron energy loss spectroscopy (EELS) technique was employed to analyze the composition and chemical state of the material at the atomic resolution. Through STEM analysis, we have studied structural mechanisms related to the improvement of LNMO materials performance by quenching process.

As a result, the HAADF-STEM image of the pristine implies that the Ni element is randomly invaded into the Li layer by the thermal process. By comparing the ABF-STEM images of the processed and unprocessed samples, it was confirmed that the processed sample had less rearrangement of the cations on the surface and less volume expansion so that the structure was well retained even after cycle. In addition, the STEM-EELS analysis could qualitatively confirm the partial $\text{Mn}^{4+} / \text{Mn}^{3+}$ reduction reaction to compensate for the oxygen loss.

These results indicate that the substituted Ni element acts as a frame when LMNO is charged and Li is removed, which improves the structural stability and reduces oxygen loss caused by a substitution of the transition metal and the Li vacancy, thereby preventing structural collapse. These observations were made with a specific projection to observe the C phase structure, which can identify the disordered structure in the LMNO structure where the C phase and the R phase are mixed.

This study demonstrates that the atomic resolution STEM analysis on structural changes of LNMO through thermal processes will be helpful in understanding the materials performance by improving the structural stability of other layered cathode materials

[1] Yu, H. J.; Ishikawa, R.; So, Y. G.; Shibata, N.; Kudo, T.; Zhou, H. S.; Ikuhara, Y, *Angew. Chem., Int. Ed.* **2013**, *52*, 5969–5973.

[2] Boulineau, A.; Simonin, L.; Colin, J.-F.; Canevet, E.; Daniel, L.; Patoux, S, *Chem. Mater.* **2012**, *24*, 3558–3566.

[3] C. R. Fell, D. Qian, K. J. Carroll, M. Chi, J. L. Jones and Y. S. Meng, *Chem. Mater.*, **2013**, **25**, 1621–1629

[4] H. Zhao et al. / *Green Energy & Environment* **2**, 2017, 174–185

Effect of laser surface remelting on the microstructure and mechanical properties of a Mn-Si series bainite steel

Min Zhang^{1*}, Yuelong Yu¹, Xinxin Zhang¹, Zhunli Tan¹

*zhangm@bjtu.edu.cn

¹ School of Mechanical, Electronic and Control Engineering, Materials Science and Engineering Research Center, Beijing Jiaotong University, Beijing 100044, China

Mn-Si based bainite steels have received intensive interest in wide applications due to the excellent combination of high strength and toughness. In order to further improve the mechanical properties and enlarge the applicable area of bainite steel, we extend laser surface remelting method to provide more studies on the microstructures and mechanical properties survey of a common low alloy high strength Mn-Si series bainite steel. We aim to analyze and understand the structure of interfacial transition layer and the mechanism for performance changes.

A quenched and tempered Mn-Si series steel was treated by laser surface remelting. The microstructures of fusion zone and heat affected zone of rapid-solidified surface were studied by scanning electron microscope and transmission electron microscope. The morphology of the surface is almost martensite instead of bainite/martensite multiphase structure. The volume expansion due to the phase transformation during the rapid melting-solidification process has changed the stress state of the surface and produced a layer of compressive stress on the surface. The interface between fusion zone and heat affected zone was detected in-depth. The hardness, wear-resisting property and electrochemical test were investigated. The experimental results show that laser remelting process can improve the hardness of the present bainite steel. The rate of rolling wear is effectively reduced. The electrochemical test shows better corrosion resistance.

Segregation of Ca dopant at ferrite – strontium titanate interfaces

U. Haselmann¹, G. Haberfehlner², D. Knez³, M. N. Popov⁴, L. Romaner⁴ and Z. L. Zhang^{1,5}

*ulrich.haselmann@oeaw.ac.at

¹Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Jahnstraße 12, 8700 Leoben, Austria

²Institute of Electron Microscopy and Nanoanalysis, Graz University of Technology, Steyrergasse 17, 8010 Graz, Austria

³Graz Centre for Electron Microscopy, Steyrergasse 17, 8010 Graz, Austria

⁴Materials Center Leoben Forschung GmbH, Roseggerstraße 12, 8700 Leoben, Austria

⁵Institute of Material Physics, Montanuniversität Leoben, Jahnstraße 12, 8700 Leoben, Austria

Bismuth Iron Oxide (BiFeO₃) is a perovskite material, which has attracted lots of attention in the past years for being one of the few single-phase multiferroic materials with magnetoelectric coupling at room temperature[1-2]. Of significant importance was the demonstration of electrical controllability of the antiferromagnetic domains[3]. BiFeO₃ has great potential for various applications like new kinds of memory devices[4], spin valves, spintronic devices and sensors [5]. Segregation and diffusion processes of cations in perovskite oxides are a known challenge since they can have a huge influence on the functionality of such devices. While a large variety of studies have been conducted on segregation processes towards surfaces thanks to various surface sensitive but usually also surface limited methods [6], segregation processes against non-surface interfaces require usually cross-sectional transmission electrons microscopy (TEM) techniques and are therefore scarcely studied. [7]

A BiFeO₃ film with Ca doping was grown via pulsed laser deposition on a SrTiO₃ substrate at the growth temperature of 700°C. Analytical scanning transmission electron microscopy (STEM) in atomic resolution revealed, that the Ca, which was homogenously distributed inside the film in the beginning, was concentrated in the first layers of the film close to the interface. Atomic-scale strain analysis revealed that the out-of-plane strain (perpendicular to the interface) is significantly reduced in the Ca-rich interface area. This suggests a strain-driven process. Density functional theory (DFT) simulations were conducted and confirmed that Ca agglomeration at the interface is more favorable energy wise. Additionally, the measured interplanar A-site distances showed an extensive agreement with the distances received from the DFT simulations confirming the applicability of the DFT model.

[1] P. Zubko et al., *Annu. Rev. Condens. Matter Phys.*, vol. 2 (2011), 141–65

[2] H. Liu et al., *Ferroelectrics*, vol. 507 (2017), 69–85

[3] T. Zhao et al., *Nat. Mater.*, vol. 5 (2006), 823–829

[4] J. F. Scott, *Nat. Mater.*, vol. 6 (2007), 256

[5] A. Manzoor et.al, *J. Magn. Magn. Mater.*, vol. 393 (2015), 269–272

[6] Y. Li et al., *Chem. Soc. Rev.*, vol. 46 (2017), 6345–6378

[7] U. Haselmann et al., journal article in preparation

Acknowledgments : We kindly acknowledge the financial support by the Austrian Science Fund (FWF): No. P29148-N36. Our gratitude goes to the group of Prof. Yunbin He from the Hubei University in the PRC for providing the samples.

Quantitative measurement methods of atomic excess at triple junction - Ti segregation in CoSi₂ thin films

H. Zschiesche¹, A. Charai¹, C. Alfonso¹, D. Mangelinck¹

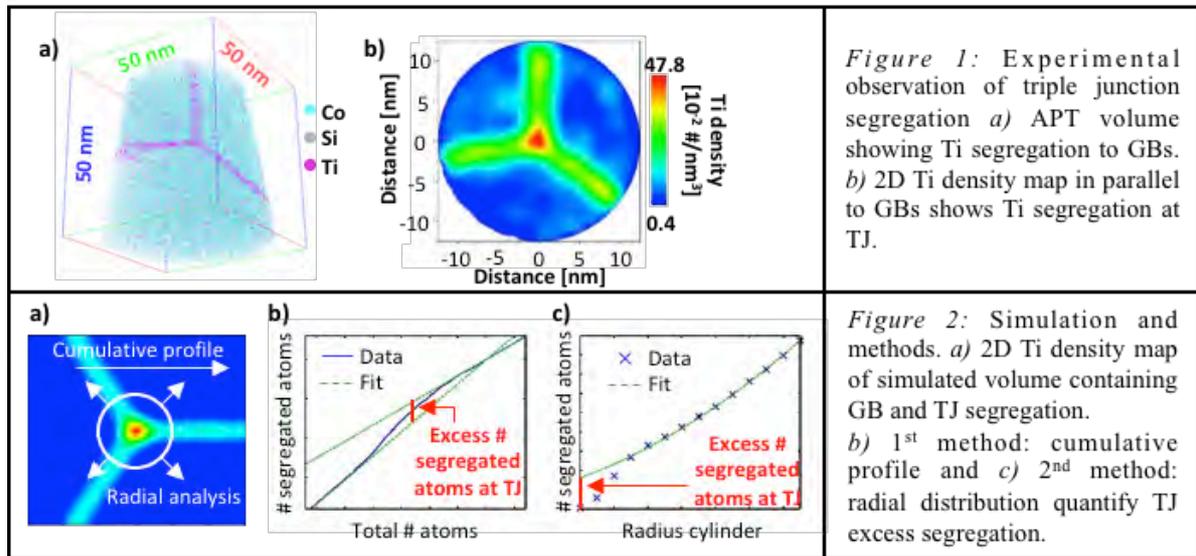
¹ Aix-Marseille Université, IM2NP, CNRS, Faculté de Saint-Jérôme, Case 142, 13397 Marseille Cedex 20, France

Abstract

We present methods to quantify segregation excess at triple junctions of 3D volumes measured by atom probe tomography with atomic resolution. Two different methods are proposed based on a cumulative profile and a radial analysis of the number of segregating atoms. The proposed methods are demonstrated and compared on simulated model systems. Furthermore, they are used for the quantification of Ti triple junction segregation in polycrystalline CoSi₂ thin film which has been measured by atom probe tomography.

Experimental observation of triple junction segregation

Segregation at triple junctions (TJs) can play an important role in diffusion phenomena and grain boundary (GB) motion. However, the experimental characterization of the chemistry at the atomic scale of TJ segregation is challenging. Atom probe tomography (APT) enables to detect single atoms and reconstruct 3D volumes with atomic resolution. This technique was used recently to study Ti segregation at CoSi₂ GBs and to give insights on the role of Ti on the preferential texture of CoSi₂ grown on Si by reactive diffusion. Fig. 1 shows an example of experimental observation of Ti segregation at a TJ between 3 grains of CoSi₂. The 2D concentration map illustrates that Ti is preferentially segregated at the TJ.



Methods to quantify the excess of Ti atoms at TJs

However, methods for quantification of TJ excess need to be developed. In order to fulfil this task, model volumes were constructed with assigned values for GB and TJ segregation (Fig. 2.a) and two methods were tested on the model and experimental volumes. The first method is based on the approach developed by Krakauer et al. [1] for quantification of GB excess: it consists of integrating the numbers of (i) solutes and (ii) all the atoms along a given volume. The excess number of segregated atoms at the TJ can be determined from the step height (Fig. 2.b). Another method is to perform a radial integration of the number of solutes atoms and with a plot of the integrated number as a function of the radius to determine the excess (Fig. 2.c). These two methods will be compared and discussed for the model and real TJ.

[1] B. W. Krakauer, D. N. Seidman. *Physical Review B* **48**, 9 (1993) 6724-6727

List of Participants:

First Name	NAME
Khadidja	ABIB
Esmail	ADABIFIROOZJAEI
Silvère	AKAMATSU
Éric	ALLENO
Dor	AMRAM
Alexandra	ANDREEVA
Sergey	ASTAFUROV
Elena	ASTAFUROVA
Marc	AUCOUTURIER
Quentin	BARRÈS
Carolina	BARUFFI
Jean-Luc	BÉCHADE
Romuald	BÉJAUD
Renaud	BELIN
Bin	FENG
Rémy	BOULESTEIX
Isabelle	BRAEMS
Paul	BRISTOWE
Océane	BUGGENHOUDT
Nathalie	CAPRON
Cyril	CAYRON
Xialoei	CHEN
Ian	CHESSER
Si-Young	CHOI
Ulrich	DAHMEN
Reza	DARVISHI KAMACHALI
Alexander	DESPOTULI
Alexandre	DIMANOV
Sergiy	DIVINSKI
Christophe	DOMAIN
Adrien	EMERY
Vladimir	ESIN
Diana	FARKAS
Svetlana	FEDOTOVA
Bin	FENG
Claude	FOUBERT
Gregory	GERSTEIN
Anne-Françoise	GOURGUES-LORENZON
Denis	GRATIAS
Julien	GUÉNOLÉ
Simone	GUIISO
Olivier	HARDOUIN DUPARC
Jérôme	HAZAN
Pierre	HIREL
Siegfried	HOFMANN
Eric	HOGLUND
Éric	HUG
Hosni	IDRISSI
Seiichiro	II
Yuichi	IKUHARA
Kazutoshi	INOUE

Saki	ISHIHARA
Anastasiia	KHOLTOBINA
Won-Seok	KO
Shigeaki	KOBAYASHI
Masanori	KOHYAMA
Sergey	KOSTYRKO
Stanislav	KRASNITCKII
Aakash	KUMAR
Izabella	KWIECIEN
Frédéric	LANÇON
Melvyn	LARRANAGA
Sylvie	LARTIGUE-KORINEK
Sabine	LAY
Pavel	LEJČEK
Chen	LI
Yong	LI
Lola	LILENSTEN
Luchan	LIN
Yong	LIU
Dominique	MANGELINCK
Arthur	MARCEAUX DIT CLÉMENT
Francesco	MARESCA
Mayerling	MARTINEZ
Philippe	MAUGIS
Jean-Luc	MAURICE
Martina	MAZALOVÁ
Douglas	MEDLIN
Ilyes	MEDOUNI
Fanyan	MENG
Estelle	MESLIN
Yuri	MISHIN
Hiromi	MIURA
Jean-Baptiste	MOLIN
Frédéric	MOMPIOU
Dan	MORDEHAI
Valentina	MOSKVINA
Shamil	MUKHTAROV
Kamilla	MUKHTAROVA
Alexandre	MUSSI
Atsutomo	NAKAMURA
Ayrat	NAZAROV
Mamadou Babacar	NDIAYE
Gahee	NOH
Yutaka	OHNO
Nicholas	ORR
Yu	OSHIMA
Andriy	OSTAPOVETS
Hadjer	OUADDAH
Marina	PANCHENKO
Camille	PERRIÈRE
Thomas	PHILIPPE
Mathis	PLAPP
Dirk	PONGE
Louissette	PRIESTER
Yuanshen	QI

Sylvain	QUEYREAU
Marianne	QUIQUANDON
James	QUIRK
Eugen	RABKIN
Chris	RACE
Oliver	RENK
Joël	RIBIS
Gregory	ROHRER
Lorenz	ROMANER
Aleksei	ROMANOV
Mitsuhiro	SAITO
Shun	SASANO
Maxime	SAUZAY
Thomas	SCHULER
David	SEIDMAN
Anna	SERRA
Tomotsugu	SHIMOKAWA
Bertrand	SICAUD
Mojmir	ŠOB
Kyung	SONG
Jürgen	SPITALER
David	SROLOVITZ
Leonel	STERMANN
Alexander	STRAUMAL
Boris	STRAUMAL
Jun	SUN
Shabnam	TAHERINIYA
Döme	TANGUY
David	TINGAUD
Kristina	TSOY
Sadahiro	TSUREKAWA
Naoki	UEMURA
Masayuki	URANAGASE
Aleksandra	VAKAEVA
Laurent	VAN BRUTZEL
Nathalie	VAST
Philippe	VERMAUT
Justine	VORONKOFF
Thomas	WALTHER
Hao	WANG
Weicheng	WANG
Chihiro	WATANABE
Jiake	WEI
Yujeong	YANG
Rong	YU
Min	ZHANG
Wenzheng	ZHANG
Zaoli	ZHANG
Huan	ZHAO

177 Participants from 20 Countries

France	58
Russia	30
Japan	22
China	11
Germany	11
USA	9
Israel	6
South Korea	6
UK	5
Austria	4
Czech Rep.	3
Azerbaijan	2
Belgium	2
Switzerland	2
Algeria	1
Denmark	1
Netherlands	1
Poland	1
Senegal	1
Spain	1

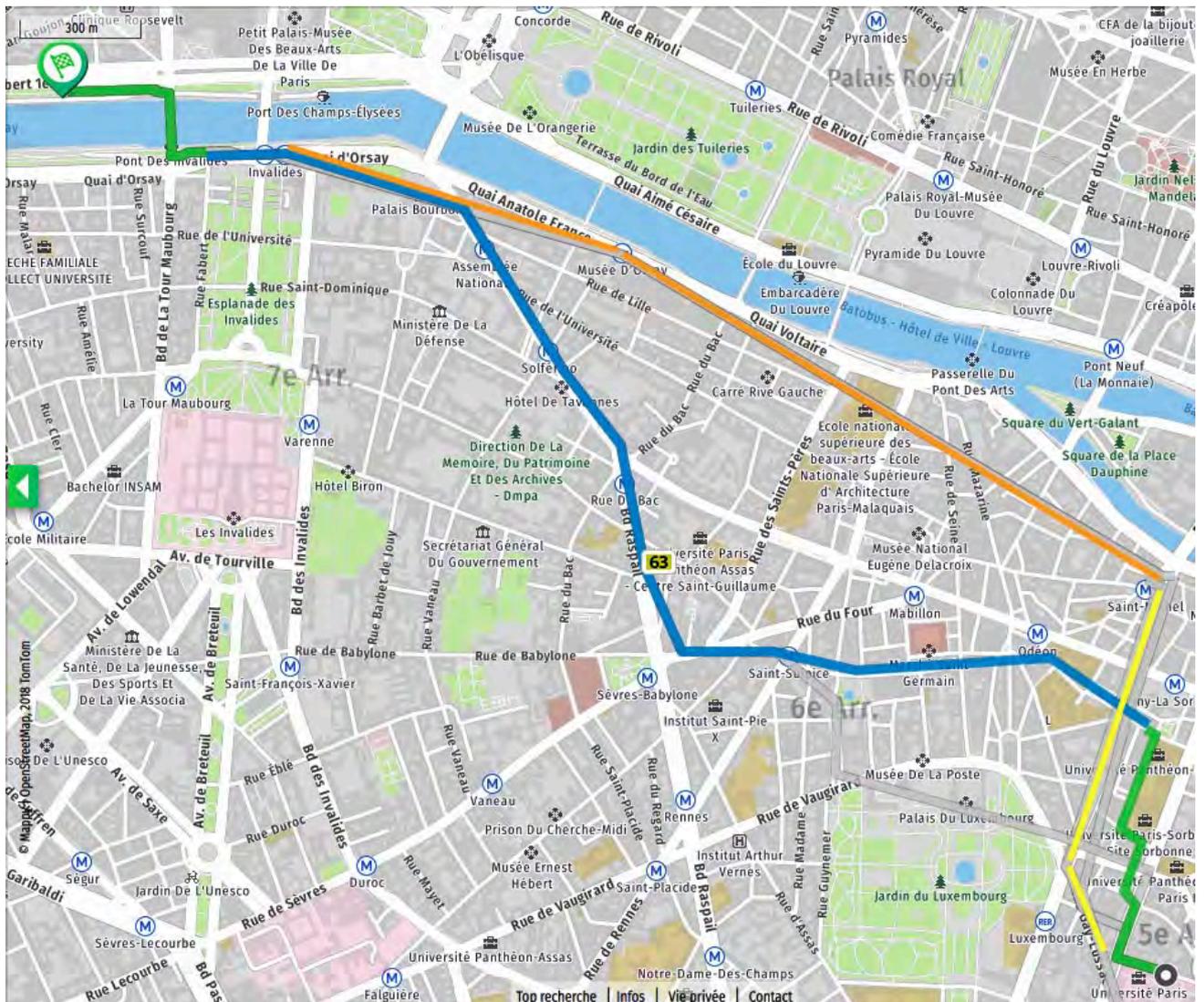
Gala dinner

Bateaux Mouches 'Port de la Conférence'

Access from the iib Conference venue

1) Get to RER C Saint-Michel Notre-Dame, by foot, or by Bus 21 (at stop Luxembourg, rue Gay Lussac, direction Gare Saint Lazare, get off at "Saint Michel Saint Germain"). Take the **RER C**, "Saint-Michel Notre-Dame", Direction "Gare de Saint-Quentin en Yvelines (Montigny-le-Bretonneux)" or "Invalides". Get off at the station **INVALIDES**. Cross the Seine river by the Invalides bridge and turn left.

2) Take bus 63 at stop "Cluny", rue des Écoles, in front of the Sorbonne University, direction "Porte de la Muette", get off at the station **PONT des INVALIDES**. Cross the Seine river by the Invalides bridge and turn left.



Sponsoring

The conference is supported by the SF2M,
Société Française de Métallurgie et de Matériaux.

The organizers express their warm thanks to the companies and
associations that provided financial support to the IIB Conference:

- **École Polytechnique**
- **Eloïse – Electron Optics Instrument Service**
- **Fermi – Fédération pour l'Enseignement et la Recherche sur la Métallurgie en Ile de France**
- **Minos – Materials Innovation for Nuclear Optimized Systems**
- **Nanomegas – Advanced tools for electron diffraction**
- **Nanosaclay – LABEX en nanosciences et nanotechnologies**
- **Société Française des Microscopies – French Microscopy Society**

