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The effect of interface stress on the grain boundary grooving in nanomaterials: Application to the thermal degradation of Cu/W nano-multilayers

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ABSTRACT

The phenomenon of non-equilibrium grain boundaries and interphase boundaries is very important for materials science. They can be found in materials after sever plastic deformation, rapid quenching etc. In the present work, the influence of interface stresses on the energy of Cu/W interphase boundaries during the thermal degradation of Cu/W nano-multilayers is revealed. As rationalized on the basis of a modified Young equation, the large interface stress in the as-deposited NML decreases the thermodynamic driving force for the thermal grooving of W/W GBs. The experimentally derived interface stress linearly decreases with increasing annealing temperature. The onset of NML degradation, as initiated by grooving, only sets in after complete relaxation of the interface stress at around 650°C. The thus obtained fundamental knowledge may be exploited to tailor the thermal stability of immiscible NML systems and other types of immiscible nanomaterials by controlling the interface stress level during material synthesis.

The phenomenon of non-equilibrium grain boundaries (GBs) is very important for materials science. They can be found in materials after sever plastic deformation (SPD) [1,2], rapid quenching etc. The plastic deformation is accompanied by the formation of defects, such as dislocations, which interact with non-equilibrium GBs. The structural difference between GBs in non-equilibrium and equilibrium state has been observed by TEM already in 1970ies [3]: Pumphrey and Gleiter directly measured how the lattice dislocations can be absorbed at room temperature by the GBs in Ni–5 wt.% Al alloy. During *in situ* heating up to 300°C the absorbed lattice dislocations delocalized and relaxed inside the GB layers [3]. Later the idea of non-equilibrium GBs has been extensively used in order to describe the unique properties of nanograined materials manufactured by SPD [1,2]. The additional defects formed during plastic deformation increase the GB energy in comparison with equilibrium values [4]. This fact can be observed, for example, using GB grooving phenomenon in multiphase materials, i.e. the high-energetical GBs tends to be substituted by two interphase boundaries (IBs) of lower energies [4]. Along with GBs, non-equilibrium IBs with the increased energies are also expected in deformed materials. Moreover, the energies of IBs and GBs can be varied by the elastic deformation as well, providing an additional energy to the boundaries.

Nano-multilayers (NMLs) are functional nano-architectures, consisting of a sequence of alternating nanolayers of two dissimilar materials, typically of immiscible metallic systems. This class of nanomaterials is extremely promising due to its unique mechanical, magnetic, optical and radiation tolerance properties [5]. However, these properties are intrinsically related to the multilayer microstructure; therefore, a control of the thermal stability of the NML structure is of significant technological importance. Towards higher temperatures, the microstructure stability can be strongly compromised by the thermodynamic driving force to minimize the energies of internal boundaries, such as high-energetical IBs and GBs. One possible pathway to minimize the energy of the NML system is the grooving of GBs upon annealing, which modifies the thermal, optical, electrical, mechanical properties and may eventually lead to a complete degradation of the multilayer microstructure, forming a nanocomposite (Cu/Mo [6], Cu/W [7], Cu/Co [8]).

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In Cu/W NMLs, the energies of W/W GBs [9] are generally higher than the energies of two Cu/W IBs [10], hence thermally activated grooving of W/W GBs is thermodynamically favored in as-deposited Cu/W NMLs already upon the low-temperature annealing. However, the onset of the multilayer degradation upon annealing, as initiated by GB grooving, was observed only at temperatures as high as 700 – 800°C. As demonstrated in Ref. [11], the NML degradation is rate-limited by the mobility of W along IBs and GBs. Prior to NML degradation in the temperature range of 400 – 600°C, the Cu/W NML system first releases the accommodated residual stresses in the Cu and W nanolayers (while maintaining the multilayer structure) [7]. As shown in this work, the driving force for grooving of W/W GB is predicted to decrease by the presence of a high Cu/W interface stress. Hence, the NML degradation process, as initiated by grooving of W GBs, is thermodynamically unfavorable in the presence of high Cu/W interface stress levels. Experimental estimates of the Cu/W interface stresses in the Cu/W NMLs were derived as function of the annealing temperatures (30, 400, 500, 600°C). The observed decrease of the Cu/W interface stress magnitudes with increasing temperature is discussed, in relation to the grooving process and the thermal degradation of the Cu/W NMLs.

Cu/W nano-multilayers were deposited at room temperature on 10×10 mm^2 epi-polished α-Al_2O_3 (0001) single-crystalline wafer substrates by magnetron sputtering in an ultrahigh vacuum chamber (base pressure $< 10^{-8}$ mbar) from two confocally arranged, unbalanced magnetrons equipped with targets of pure W (99.95%) and pure Cu (99.99%). The sapphire substrates were ultrasonically cleaned using acetone and ethanol; possible surface contamination was removed by Ar^+ sputter cleaning for 5 min applying an RF Bias of 100 V at a working pressure of 1.6×10^{-2} mbar. The RF Bias was maintained during the NML deposition at a working pressure of approximately 5×10^{-3} mbar. First, a 25 nm thick W buffer layer was deposited on the sputter-cleaned substrate. Next, NMLs consisting of 20 repetitions of a Cu/W building block were deposited on top. Three NML configurations were prepared: 3 nm Cu/3 nm W (3Cu/3W), 5 nm Cu/5 nm W (5Cu/5W), 10 nm Cu/10 nm W (10Cu/10W). Isothermal annealing was conducted in high vacuum conditions ($< 10^{-5}$ mbar) during 100 min in the range of 400–800°C with a heating rate of 20 K/min.

Imaging of cross-sectional cuts was performed by high-resolution scanning electron microscopy (HR-SEM) using a Hitachi S-4800 instrument.

A Bruker D8 Discover X-ray diffractometer operating in Bragg-Brentano geometry was used to derive residual stresses at room temperature. Different reflections were recorded using Cu K$\alpha_{1,2}$ radiation at 40 kV / 40 mA. Stress analysis was carried out using the Crystallite Group Method (CGM) [12]. The details of the residual stress analysis are presented in Supplementary material, Part I.

As mentioned above, the onset of the NML degradation process is associated with the thermal grooving of W/W GBs (Fig. 1b) with grooving angles according to Young's equation [13]:

$$\cos\left({}^{\varphi}\!/_{2}\right) = \frac{\gamma_{W/W}}{2\gamma_{int}}, \tag{1}$$

where $\gamma_{W/W}$ and γ_{int} are the W/W GB and Cu/W IB energies, respectively. Twice the mean value of the (111)Cu/(110)W interface energy corresponds to $2\gamma_{int} \approx 1.7$ J/m^2 [10]. The energies of W/W GBs can vary over a relatively broad range from 0.5 to 3 J/m^2 [9] (at absolute zero). Thus, $\cos(\varphi/2)$ can vary between 1 and ~ 0.2941, resulting in respective grooving angles φ in the range of 0° to ~ 146°. These theoretical estimations correlate well with our experimental observations: grooves with smaller angles grow faster, resulting in the W nanolayer pinch-off and covering by Cu, while other parts of the W nanolayer recrystallize into large particles (after 100 min annealing in the temperature range 650 – 800°C, depending on the thickness of nanolayers) [7,14]. Moreover, the GB and interface energies can decrease with increasing temperature (e.g. [15]), which results in a change of the groove angles of W/W GBs.

However, prior to the grooving of W/W GBs, the Cu/W NMLs first release their residual stresses by Cu surface outflow [7,14]. The grooving stage that marks the onset of NML degradation only commences when the residual stress in the W nanolayers approaches zero [7]. In Fig. 1a the experimental evolutions of the in-plane residual stresses in the Cu and W nanolayers upon heating are shown.

These experimental findings for Cu/W NMLs, poses the question why the grooving of the W/W GBs is only thermally activated in the stress-free state of W and not already at lower temperatures (during the initial stage of stress relaxation). In the following it is postulated that the observed "shift" of the grooving stage towards higher temperatures (and lower residual stresses) arises due to the presence of a non-zero interface stress state, which results in an increase of the Cu/W IB energy.

The interface stress represents the additional work to introduce a unit of elastic strain to a unit area of Cu/W IB by equally straining adjoined nanolayers. It is expressed as the second rank tensor [16]:

$$f_{ij} = \gamma_{int}\delta_{ij} + \partial\gamma_{int}/\partial\varepsilon_{ij}, \tag{2}$$

where ε_{ij} is the interface strain tensor. The interface stress is an additional stress contribution to the NML system (besides the deposition, coherency and thermal mismatch stresses). The magnitude of interface stress can be related to the coherency stress through the coherency strain [17]. The work to create an elastically strained interface of area A is (f_{ij} is referred to principal axes and taken isotropic, i.e. $f_{11} = f_{22} = f$, $f_{12(21)} = 0$; analogous for ε_{ij}):

$$W = (\gamma_{int} + 2f\varepsilon)A, \tag{3}$$

where ε is the interface strain.

In Ref. [7], the interface stress of (111)Cu/(110)W IBs in the as-deposited Cu/W NMLs (which exhibit a preferred Cu{111}<–101>||W{110}<–111> texture) was calculated from experimental data; its magnitude turned out to be relatively large, i.e. $f \approx 11.25$ J/m^2. The positive sign of f denotes its compressive nature in relation to the nanolayer volume: the interface stress is balanced by the bulk stress (strain, both of opposite sign) in the adjoined nanolayers.

Hence the work to create a unit of interface area in the presence of interface stress increases, resulting in a modified Young's equation according to:

$$\cos\left({}^{\varphi}\!/_{2}\right) = \frac{\gamma_{W/W}}{2(\gamma_{int} + 2f\varepsilon)}, \tag{4}$$

The W grains are compressively strained in-plane and, consequently, the W/W GBs experience a tensile out-of-plane strain, as defined by the Poisson ratio. Accordingly, newly formed Cu/W IBs should be subjected to a tensile strain as well; this results in an increase of the energy of newly formed Cu/W IBs, as represented by the term $2f\varepsilon$ in Eq. (4). The relatively high temperature for the onset of NML degradation can thus be rationalized on a purely thermodynamic basis by a lower thermodynamic driving force for the W/W GB grooving in the presence of a high interface stress. Noteworthy, from a purely kinetic viewpoint, the NML degradation process is rate-limited by the mobility of W along phase and grain boundaries. Previous experimental findings have indeed confirmed that the interface stress relaxation in Cu/W NMLs strongly correlates with the thermally activated diffusion of W [11]. The interplay between the W mobility and the interface stress magnitude can rationalize the experimentally observed "shift" of the NML degradation to higher annealing temperatures.

In this work, we experimentally derived the values of interface stress f in Cu/W NMLs from the previous reported Cu and W

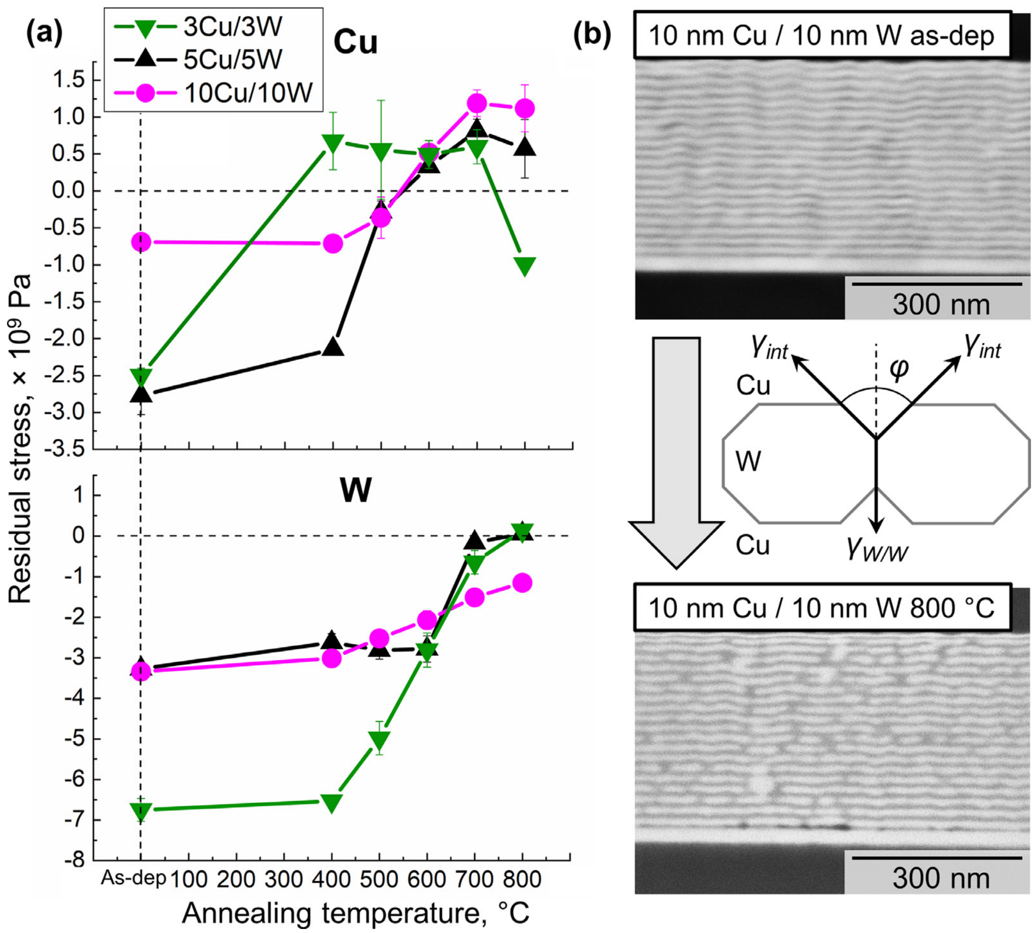

Fig. 1. (a) The evolution of residual stresses in NMLs upon thermal treatment, originally presented in Fig. 9 in Ref. [7] ; (b) schematics of W/W GB grooving and HR-SEM images of 10Cu/10W NMLs in the as-deposited state and after 800°C annealing with pinched-off W nanolayers (the onset of degradation). Error bars are calculated from the linear fit of the strain as a function of $\sin^2\psi$.

residual stress data [7], for three different annealing temperatures below the onset temperature of NML degradation (i.e. 400, 500, 600°C). To this end, the model developed by Ruud et al. [18] was used. This method is based on the stress balance:

$$\sigma_{SC} = {}^{2f}/_{\lambda} + \langle\sigma\rangle, \tag{5}$$

where f is the interface stress; λ is the bilayer thickness; σ_{SC} is the stress, derived from the substrate curvature; $<\sigma> = (\sigma_{Cu} + \sigma_W)/2$ is the average stress in the Cu and W nanolayers, derived by X-ray diffraction. The investigated NMLs are relatively thin: the maximum thickness is in 10Cu/10W NMLs 400 nm, while the sapphire substrate thickness is 500 μm. It may thus be assumed that the forces exerted by a NML film are negligible to produce an appreciable curvature of the substrate and hence $\sigma_{SC} \approx 0$ Pa. The average residual stresses in the Cu and W nanolayers at the different annealing temperatures are plotted in Fig. 1a. In Fig. 2a, the interface stress values were derived from the linear fits of $-<\sigma>$ versus 2/λ, where λ is the Cu/W bilayer thickness. In Fig. 2b, the derived interface stress values, f, in the NMLs after annealing (for 100 min) at different temperatures are presented. It follows that the Cu/W interface stress decreases linearly with increasing annealing temperature, tending asymptotically to zero at a temperature of around 650°C. This temperature nicely coincides with the onset of the NML degradation process (pinch-off of W nanolayers) in the range of 700 – 800°C (e.g. the lower panel of Fig. 1b shows for 10Cu/10W). Indeed, analysis of the bulk microstructure of the 5Cu/5W NML by scanning transmission electron microscopy (STEM) showed that after annealing at 500°C the multilayer microstructure is preserved with no signs of thermal grooving of the W/W GBs (see Supplementary material, Part II).

As postulated above, the residual stress relaxation not only results in a decrease of the Cu/W interface stress, but also lowers the resultant energy of the newly formed Cu/W IBs (i.e. a decrease of the term $2f\varepsilon$ in Eq. (3)). Accordingly, the grooving angle of the selected W/W GBs is established and the groove depth evolves towards nanolayer pinch-off. Additionally, in Ref. [11] by *in situ* high-temperature X-ray diffraction (HT-XRD) analysis we found out that the degradation of 5Cu/5W NML begins at about 100 min of annealing at 675°C, which coincides well with the conditions (~ 650°C of 100 min annealing) for which the interface stress asymptotically approaches zero value. It is presumed that predominantly those W/W GBs are grooved, which can form energetically favorable Cu(111)/W(110) IBs. Other types of GBs are annihilated by recrystallization, as indicated by the conservation of a Cu{111}<−101>||W{110}<−111> crystallographic texture after complete NML degradation [7,14].

Thus, not only the lattice defects produced during plastic deformation can alter the GB and IB energies and in such a way modify the GB grooving behavior. As demonstrated in this work, the elastic residual stresses can also modify the IB energy and, thereby, change the GB grooving conditions. We can also provide showcases of second-order *bulk* phase transitions, such as the transition from paramagnetic to ferromagnetic state [19,20] or chemical ordering [21,22], which exhibit variable conditions for GB grooving. The underlying mechanism(s) for variable grooving angles during such bulk phase transformations could also be related to the gen-

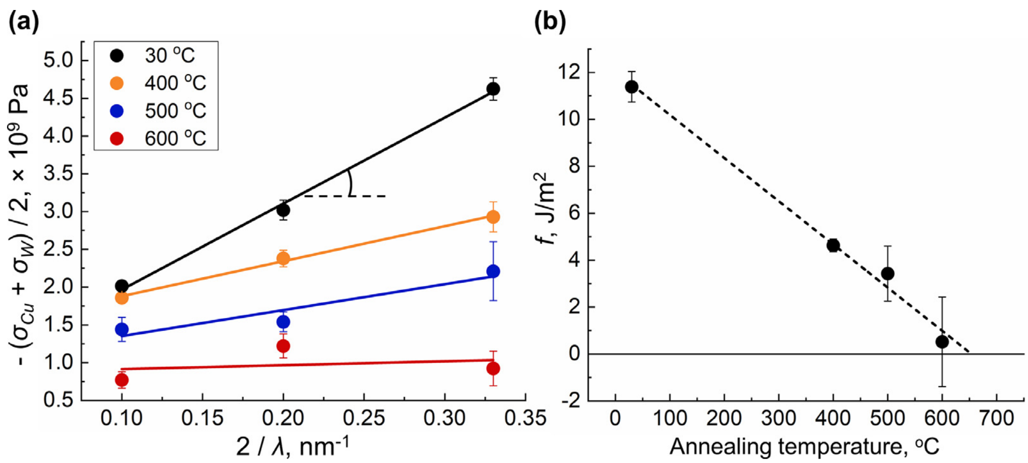

Fig. 2. (a) Linear fits of the Cu and W residual stress versus 2/λ (λ being the Cu/W bilayer thickness) at different temperatures, for deriving the Cu(111)/W(110) interface stress; (b) the interface stress magnitude decreases linearly with increasing temperatures. Error bars in (a) and (b) were derived from the experimental stress values (Fig. 1a) and from the variance of slopes of linear fits in (a), respectively

eration and/or relaxation of elastic stresses during the phase transformation.

In conclusion, the degradation of Cu/W NMLs, as initiated by grooving of W/W GBs, was related to the evolution of the Cu/W interface stress with increasing annealing temperature. High interface stress levels in the Cu/W NMLs obstruct the expected grooving of W/W GBs upon annealing at temperatures ≤ 600°C (for a duration of 100 min). The thermodynamic driving force for grooving of W/W GBs is enhanced for lower magnitudes of the Cu/W interface stress. The interface stress magnitude linearly decreases with increasing temperature and asymptotically approaches zero at around 650°C, which coincides with the experimentally observed onset of the NML degradation (as initiated by grooving). These findings demonstrate that the nature of the GB grooving process in nanomaterials of immiscible material systems (as well as in their respective bulk phase transformations) is not only affected by the defect density, but also by the elastic strain. In Ref. [17] Cammarata et al. showed that magnitude of interface stress can depend on the density of misfit dislocations, i.e. coherency strain. Generally, the deposition parameters can be varied to tailor the stress (strain) magnitudes in Cu and W nanolayers [23]. For example, the coherency strain can be tailored by changing the deposition pressure, bias and/or power, thus affecting the values of the Cu/W interface stress. This implies that the thermal stability of Cu/W NMLs can principally be tailored by tuning the interface stress magnitude during material synthesis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.scriptamat.2021.113866.

References

[1] R.Z. Valiev, R.K. Islamgaliev, I.V. Alexandrov, Prog. Mater. Sci. 45 (2000) 103–189.
[2] X. Sauvage, G. Wilde, S.V. Divinski, Z. Horita, R.Z. Valiev, Mater. Sci. Eng. A 540 (2012) 1–12.
[3] P.H. Pumphrey, H. Gleiter, Philos. Mag. 32 (1975) 881–885.
[4] B.B. Straumal, O.A. Kogtenkova, F. Muktepavela, K.I. Kolesnikova, M.F. Bulatov, P.B. Straumal, B. Baretzky, Mater. Lett. 159 (2015) 432–435.
[5] A. Sáenz-Trevizo, A.M. Hodge, Nanotechnology 31 (2020) 292002.
[6] D. Srinivasan, S. Sanyal, R. Corderman, P.R. Subramanian, Metall. Mater. Trans. A 37 (2006) 995–1003.
[7] A.V. Druzhinin, D. Ariosa, S. Siol, N. Ott, B.B. Straumal, J. Janczak-Rusch, L.P.H. Jeurgens, C. Cancellieri, Materialia 7 (2019) 100400.
[8] M. Hecker, J. Thomas, D. Tietjen, S. Baunack, C.M. Schneider, A. Qiu, N. Cramer, R.E. Camley, Z. Celinski, J. Phys. D Appl. Phys. 36 (2003) 564–572.
[9] S. Ratanaphan, T. Boonkird, R. Sarochawikasit, H. Beladi, K. Barmak, G.S. Rohrer, Mater. Lett. 186 (2017) 116–118.
[10] C.P. Liang, J.L. Fan, H.R. Gong, X. Liao, X. Zhu, S. Peng, Appl. Phys. Lett. 103 (2013) 211604.
[11] F. Moszner, C. Cancellieri, M. Chiodi, S. Yoon, D. Ariosa, J. Janczak-Rusch, L.P.H. Jeurgens, Acta Mater. 107 (2016) 345–353.
[12] B.M. Clemens, J.A. Bain, MRS Bull. 17 (1992) 46–51.
[13] P.G. de Gennes, Rev. Mod. Phys. 57 (1985) 827–863.
[14] C. Cancellieri, F. Moszner, M. Chiodi, S. Yoon, J. Janczak-Rusch, L.P.H. Jeurgens, J. Appl. Phys. 120 (2016) 195107.
[15] D. Scheiber, O. Renk, M. Popov, L. Romaner, Phys. Rev. B 101 (2020) 174103.
[16] R.C. Cammarata, Prog. Surf. Sci. 46 (1994) 1–38.
[17] R.C. Cammarata, K. Sieradzki, F. Spaepen, J. Appl. Phys. 87 (2000) 1227–1234.
[18] J.A. Ruud, A. Witvrouw, F. Spaepen, J. Appl. Phys. 74 (1993) 2517–2523.
[19] E.I. Rabkin, V.N. Semenov, L.S. Shvindlerman, B.B. Straumal, Acta Metall. Mater. 39 (1991) 627–639.
[20] B.B. Straumal, O.A. Kogtenkova, A.B. Straumal, Y.O. Kuchyeyev, B. Baretzky, J. Mater. Sci. 45 (2010) 4271–4275.
[21] O.I. Noskovich, E.I. Rabkin, V.N. Semenov, B.B. Straumal, L.S. Shvindlerman, Acta Metall. Mater. 39 (1991) 3091–3098.
[22] B.B. Straumal, O.I. Noskovich, V.N. Semenov, L.S. Shvindlerman, W. Gust, B. Predel, Acta Metall. Mater. 40 (1992) 795–801.
[23] L. Romano-Brandt, E. Salvati, E. Le Bourhis, T. Moxham, I.P. Dolbnya, A.M. Korsunsky, Surf. Coat. Technol. 381 (2020) 125142.