DOI: 10.1002/adem.201000312

ENGINEERING MATERIALS

Structure and Properties of Nanograined Fe–C Alloys after Severe Plastic Deformation**

By Boris B. Straumal,^{*} Sergei V. Dobatkin, Alexei O. Rodin, Svetlana G. Protasova, Andrei A. Mazilkin, Dagmar Goll and Brigitte Baretzky

The microstructure and properties of several Fe–C alloys are studied in a) the as-cast state, b) after a long annealing time at 725 °C, and, c) after high-pressure torsion (HPT) The grain size after HPT is in the nanometer range. Only Fe₃C (cementite) and α -Fe remain in the alloys after HPT. Less stable Hägg carbide and retained austenite disappear after HPT, and phase composition closely approaches the equilibrium corresponding to the HPT temperature and pressure. This HPT behavior differs from that associated with ball-milling, which can lead to the formation of metastable or amorphous phases. Therefore, severe plastic deformation opens the way to produce materials with very stable phase structure and thus ensures the stable properties of nanograined steel during its life-time.

E-mail: straumal@mf.mpg.de

Prof. B. B. Straumal, Dr. S. G. Protasova, Dr. A. A. Mazilkin Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, 142432 (Russia)

Max-Planck-Institut für Metallforschung Heisenbergstraße 3, 70569 Stuttgart, (Germany)

A.A. Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, Leninsky prosp. 49, 119991 Moscow, (Russia)

National Research University MISIS, Leninsky prosp. 4, 119991 Moscow, (Russia)

Hochschule Aalen, Beethovenstraße 1, D-73430 Aalen, (Germany)

[**] The authors thank the Russian Foundation for Basic Research (contracts 09-03-00784, 09-03-92481 and 09-08-90406), the Israel Ministry of Science (contract 3-5790), and Ukrainian Fundamental Research State Fund (contract X28.7049). They also greatly appreciate Dr. A. Nekrasov for stimulating discussions of magnetic properties. Prof. R. Valiev and Dr. Yu. Ivanisenko are heartily acknowledged for the fruitful discussions on severe plastic deformation.

Some years ago, we observed that severe plastic deformation (SPD) leads to the extremely quick decomposition of the supersaturated solid solution in Al-based alloys.^[1,2] During SPD, the phase composition closely approached the equilibrium state at SPD pressure and temperature. We concluded that SPD can be considered as "hot deformation at room temperature", i.e., a balance between deformation-induced grain refinement and deformation-accelerated formation of equilibrium phases. Quite recently it has been discovered in in situ synchrotron experiments that enormous amount of crystal defects (for all, vacancies) forms during SPD.^[3] They can be responsible for the accelerated diffusion needed for the transformation of metastable into stable phases during SPD. Therefore, we decided to investigate in this work the structural changes in Fe-C alloys during high pressure torsion (HPT) for two reasons: first, due to the enormous importance of Fe-C system, and, second, due to the miraculous phenomenon of "cementite disappearance" in steels during SPD, which has to be clarified.^[4–12]

Results

In Figure 1, the concentration dependence of the lattice parameter in α -Fe (ferrite) after HPT is shown compared with lattice parameter of non-deformed pure α -Fe.^[13] After HPT the lattice parameter of the α -Fe solid solution does not depend on the total carbon concentration in the Fe–C alloys. The lattice parameter is about 0.28667 nm. The solubility of carbon in α -Fe at 680 °C is 0.018 wt.% C.^[14] The addition of 0.018 wt.% C to pure α -Fe increases the lattice parameter of α -Fe by 7 × 10⁻⁵ nm.^[15] In our case, the lattice parameter after HPT is about 4×10^{-5} nm higher than that of pure α -Fe. This

^[*] Prof. B. B. Straumal, Dr. B. Baretzky

Karlsruhe Institute for Technology (KIT), Institute for Nanotechnology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, (Germany)

Prof. B. B. Straumal

Prof. S. V. Dobatkin

Dr. A. O. Rodin

Dr. D. Goll



COMMUNICATION



Fig. 1. Dependence of lattice parameter a in α -Fe (ferrite) after HPT on carbon concentration. The lattice parameter of non-deformed pure Fe is taken from ref.^[13].

means that the carbon concentration in α -Fe after HPT is about 0.01 wt.% C and does not exceed the carbon maximum solubility in the ferrite (about 0.02 wt.% at 740 °C). Within the framework of experimental error, this is more or less equal to the solubility at room temperature.^[14] In other words, HPT does not lead to the formation of supersaturated carbon solid solution in α -Fe. The splitting of the (200) x-rays diffraction line typical for tetragonal martensite lattice was not observed either before or after HPT. This means that both hypoetectoid and hypereutectoid Fe–C alloys do not contain martensite.

In Figure 2 the bright field TEM image of the as-cast Fe-1.7% C alloy and respective selected area electron diffraction (SAED) pattern are shown. Transformed austenite grains contained the troostite lamellar colonies with interlamellar spacing of 100-400 nm. The boundary between two troostite colonies is visible in Figure 2a. This boundary contains the cementite layer. A white iron-enriched zone is visible along this GB cementite layer. Inside the bright ferrite grains, the fine cementite lamellae appear dark. The presence of ferrite and cementite in the structure is supported by the SAED pattern (Fig. 2b). In Figure 3 the bright-field TEM image of another location in the coarse grained as-cast Fe-1.7 wt.%C alloy is shown together with the respective SAED pattern. This illustrates the presence of retained austenite and a small amount of Hägg carbide in the as-cast alloys. Reflections of cementite were also detected in this SAED pattern but are not indicated for the reasons of clarity. TEM of the as-cast alloys with 0.25, 0.45, 0.60, 1.3, and 1.5 wt.% C revealed the presence of ferrite, cementite and retained austenite in all studied alloys. Only the amount of these phases is different in various alloys, in conformity with Fe-C phase diagram.^[16] The amount of Hägg carbide in the as-cast alloys is very small; the respective diffraction spots are not present in all studied locations. According to the LM and TEM, the grain size of ferrite (in hypoeutectoid alloys), retained and transformed austenite (in all alloys) scattered from 200 to 700 µm. TEM and LM also do not show any presence of martensite in the as-cast state of material. Neither split (200) spots (typical for tetragonal martensite lattice) in the SAED patterns nor typical martensite grain morphology (needles, plates) were discov-



Fig. 2. a) Bright-field TEM image of the coarse grained as-cast Fe–1.7% C alloy, and, b) corresponding electron diffraction pattern. Fine cementite lamellae appear dark inside of bright ferrite grains.

ered in LM. Electron diffraction, similar to XRD did not show any presence of graphite in all samples studied.

Figure 4 shows the LM microstructures of the Fe–C alloys with 0.3, 0.6, 1.3 and 1.7 wt.% C after annealing for 950 h at 725 °C (i.e., below the eutectoid temperature). The long annealing time was used in order to produce the equilibrium α -Fe + Fe₃C structure. The structures of hypoeutectoid and hypereutectoid alloys became very similar after long annealing. All samples contain very coarse ferrite and cementite grains. Only the amount of cementite increases with increasing carbon content, according to the Fe–C phase diagram.^[16]

Severe plastic deformation by HPT produces the nanometer range grain structure in the Fe–C alloys. Figure 5 shows bright- (Fig. 5a) and dark-field (Fig. 5b) TEM micrographs of the Fe–0.3 wt.% C alloy. SAED pattern (Fig. 5c) contains only α -Fe and Fe₃C spots. The TEM micrographs and SAED patterns of Fe alloys with 0.45, 0.60,





Fig. 3. a) Bright-field TEM image of another location in the coarse grained as-cast Fe-1.7% C alloy, and, b) corresponding electron diffraction pattern. Retained austenite and small amount of Hägg carbide are present.

1.3, 1.5 and 1.7 wt.% C after HPT are very similar to those shown in Figure 5. Both the ferrite grains and cementite particles are visible in the DF image (Fig. 5b) as the reflections of these phases lie closely to each other. Dislocation density is $> 10^{14}$ m⁻² in all samples. Ferrite grain size after HPT is about 100 nm, which increases slightly with increasing carbon content. Ferrite grains are not equiaxial; they are slightly elongated parallel to the deformation direction. Cementite grain size in all studied alloys is about 30 nm. Their shape is more equiaxial than that of ferrite grains. Fe₃C grains are more or less uniformly distributed over the specimen. The spacing between cementite particles decreases with increasing carbon content. It is about 50-100 nm in Fe-0.3 wt.% C alloy and about 10-50 nm in the Fe-1.7 wt.% C alloy. Only two phases, namely α -Fe and Fe₃C are present after HPT in all studied alloys. No signs of retained cementite, graphite or other iron carbides are present in the SAED patterns.

In Figure 6a to c the XRD spectra for the Fe-1.7 wt.% C alloy are shown. The initial as-cast alloy (Fig. 6a) contains three phases. First, a strong peak of α -Fe with body-centered cubic (bcc) lattice is present (marked by a filled square). Second, peaks of retained austenite (face-centered cubic, γ -Fe) are detected (marked by triangles). Third, the weak and broadened peaks of cementite are also present (marked by arrows). Some very weak peaks (like those at $2\theta = 42.23$, 55.3 and 66.48°) can be attributed as diffraction from the Hägg carbide Fe₅C₂. Figure 6b contains the data for the Fe–1.7 wt.% C alloy annealed for 950 h at 725 $^{\circ}$ C in the α + Fe₃C two-phase region of the Fe–C phase diagram. The spectrum contains only two phases, namely ferrite and cementite. No peaks of retained austenite and Hägg carbide are present. Figure 6c contains the diffraction spectrum for the Fe-1.7 wt.% C alloy after HPT. Similar to the results in Figure 6b, only two phases (ferrite and cementite) remained after HPT in the sample and retained austenite and Hägg carbide disappeared. However, all peaks are broadened even in comparison with the as-cast state due to the fine grain size (and/or residual stresses) in samples after HPT. XRD did not show any presence of graphite in all studied samples.

The lines of ferrite ($H_{eff} = 330 \text{ kOe}^{[17]}$), Hägg carbide χ -Fe₅C₂ with hyperfine fields of $185 \pm 3 \text{ kOe}$,^[18] cementite Fe₃C ($H_{\rm eff}$ =210±5 kOe^[17]) and retained austenite (no hyperfine field)^[17] were found in the Mössbauer spectra of the as-cast alloys (Fig. 7a). The Mössbauer spectra after HPT contain only the lines of ferrite and cementite Fe₃C (Fig. 7c and 7d). Retained austenite and Hägg carbide disappeared both after long annealing (Fig. 7b) and after HPT (Fig. 7c and d). Other iron carbides like ϵ -Fe₂C with hyperfine fields of $170\pm3,\,237\pm3$ and 130 ± 6 kOe, $^{[19,20]}$ Fe₄C or Fe₆C were not observed either before or after HPT. This fact supports the data from XRD and TEM. The amount of carbides before and after HPT calculated based on Mössbauer measurements increases linearly with increasing carbon content. However, the amount of carbides in the as-cast Fe-C alloys is much higher than that in the HPT alloys. This indicates decrease of the cementite amount after HPT. The samples after HPT became rather brittle, which made it possible to break them in situ in the Auger spectrometer chamber. The carbon concentration along GB fracture surfaces fluctuates between 10 to 70 wt.% in the layer of about 1 to 3 nm thickness. This reveals the strong grain boundary carbon adsorption, but not the continuous cementite GB layers.

Discussion

It has been observed recently that after HPT of Al–Zn alloys with 10, 20 and 30 wt.% Zn, the Zn- supersaturated (Al) solid solution decomposes and closely approaches the equilibrium state corresponding to the room temperature.^[1,2] The decomposition of the supersaturated (Al) solid solution proceeds parallel to the drastic grain refinement. No metastable phases conventionally produced at the Al–Zn alloys decomposition (Guinier-Preston I and II zones,





Fig. 4. Light micrographs of the Fe–C alloys with a) 0.25, b) 0.6, c) 1.3, and, d) 1.7 wt.% C annealed at 725 °C for 950 h.



Fig. 5. a) Bright-, and, b) dark-field TEM micrographs of the Fe–0.3 wt.% C alloy after HTP. c) Electron diffraction pattern revealing α -Fe and Fe₃C spots.

rhombohedral distorted fcc α'_R -phase or distorted fcc α'_m -phase) were observed after SPD. We concluded that HPT is nothing else than "hot" deformation at room temperature. In other words, the vacancy production during HPT enhances the diffusion to such a high extent, that the equilibrium at room temperature phases appears parallel to the drastic grain refinement. The high vacancy concentration during HPT has been revealed recently in situ using the synchrotron radiation.^[3]

In the case of Fe-C alloys, ferrite and graphite are equilibrium phases at room temperature. However, cementite becomes equilibrium at rather low pressures (0.1-0.5 GPa, depending on the temperature).^[21-23] In our case the pressure during HPT was much higher, 5 GPa, ensuring the thermodynamic stability of cementite. Other iron carbides become stable above 5 GPa. For example, ε -carbide Fe₇C₃ becomes stable above 5.9 GPa.^[23] Therefore, such carbides do not appear in our alloys after HPT. However, it may be the reason why the HPT of the U13 steel containing 1.37 wt.% C at 12 GPa resulted in appearance of ε -carbide Fe₇C₃ and Hägg carbide Fe₅C₂ at the cost of cementite.^[9]

In early experiments on the severe plastic deformation of steels, Korznikov *et al.* ^[24] observed the disappearance of the cementite peaks from XRD spectra and assumed that, similar to ball-milling, SPD leads to the formation of the supersaturated carbon solid solution in α -Fe. Later is was observed that cementite becomes fine but does not completely disappear from the SPD-treated steel.^[8,1,13,25] Nevertheless, we ask why the amount of cementite decreases after SPD?

Nanograined materials contain a large number of interfaces (grain and interphase boundaries). Up to 10% of atoms can be positioned in these interfaces. In all two- or multicomponent systems the interface segregation takes place. This means that the composition of interfacial layers is generally not equal to the overall composition of the bulk material. Normally, the interfaces are enriched by one of the components. In certain cases thin thermodynamically stable layers of an intergranular phase may form.^[26] Conventional experimental methods usually applied for the investigation of bulk phases are generally not able to detect the input of GB segregation or thin GB phases. For example the XRD peaks are caused by rather large areas of coherent scattering. If the particles of a phase become too small, the X-ray peaks





Fig. 6. X-ray diffraction spectra for the Fe–1.7 wt.% C alloy: a) initial as-cast alloy. b) after annealing at 725 °C for 950 h, and, c) after HPT at 5 GPa, 5 torsions. (110) ferrite peak is marked by the square. Crosses mark the Hägg carbide Fe_5C_2 . Triangles mark the retained austenite. Arrows mark the peaks of cementite Fe_3C .

broaden and finally "sink" in the background. In other words, the amount of bulk phases in the polycrystalline alloy can strongly differ from that predicted by the equilibrium phase diagram if: i) the grain size is in the nanometer range and the portion of atoms, which are positioned not in the bulk but at the interfaces, is high; or, ii) strong interface segregation, i.e., there is a big difference between interface composition and overall bulk composition. Fe-C alloys are a good example of a system with strong GB segregation. The carbon atoms strongly segregate in the ferrite GBs. The concentration of carbon atoms in the ferrite GBs measured in the hypoeutectoid steels lies between 0.2 and 0.5 monolayer.^[27] Our AES measurements for the hypereutectoid alloy with 1.7 at.% C also reveal several tens of percent of carbon in the ferrite GBs. It can be seen that cementite particles become very fine, but do not completely disappear from the steel (Fig. 5). On the other hand, carbon also does not form the supersaturated bulk solid solution in ferrite. Its concentration does not exceed the equilibrium bulk solubility limit in the α -Fe (Fig. 1). However, the magnetic data reveal that the overall amount of the bulk cementite phase after HPT becomes lower than the equilibrium phase diagram predicts.^[28] The magnetization of the samples after HPT is much higher than the I_s values of the as-cast coarse-grained Fe–C alloys. This means that the large amount of carbon has "disappeared" in the ferrite GBs and cannot form bulk cementite. As a result, the amount of cementite in the nanograined HPT alloys is much lower than in the as-cast or coarse-grained Fe-C alloys. This is the reason of the apparent disappearance of bulk cementite after HPT. About one third of bulk cementite disappeared after HPT.^[28] The respective carbon amount formed GB segregation layer and does not input into the overall magnetization value. After HPT the grain size in the studied Fe–C alloys is about 100 nm. If we suppose that the GB thickness is about 0.5 nm, the total volume of GB layers would be about 1.5 at.%. The magnetization of Fe-1.7 wt.% C alloy after HPT is nearly equal to the magnetization of coarse-grained alloy with 1.2 wt.% C.^[28] This means that ferrite/ferrite GBs contain about 0.5 wt.% C. The estimation of the resulting carbon concentration would be about 0.3 carbon monolayers. This value obtained from the magnetic measurements corresponds well both with our Auger data and measurements.^[27]

Conclusions

The following conclusions can be drawn. i) After high pressure torsion (HPT) of Fe-C alloys, the non-equilibrium (metastable) phases disappear from the alloys. The phases which are equilibrium at temperature and pressure of HPT appear instead. It is an important difference from ball-milling which can lead, similar to the ion implantation, to the formation of metastable or amorphous phases. Therefore, severe plastic deformation opens the way to produce materials with very stable phase structure and thus ensures the stable properties of nanograined steel during its life-time. ii) HPT leads to the strong grain refinement of Fe-C alloys. Carbon actively segregates in the numerous ferrite/ferrite grain boundaries (GB) and triple junctions. The formation of new GB segregation layers during SPD consumes carbon and leads to the apparent disappearance of bulk cementite. Bulk cementite, indeed dissolves, however, not in the bulk ferrite but in ferrite/ferrite GBs.





Fig. 7. Mössbauer spectra of the Fe–C alloys. Squares mark the ferrite peaks. Arrows mark the peaks of cementite Fe_3C . Crosses mark the Hägg carbide Fe_5C_2 . Triangle mark the retained austenite. a) As-cast Fe–0.6 wt.% C alloy. The area under the spectrum components corresponds to the 10% of Fe_3C_2 and Fe_5C_2 and 5% of retained austenite. b) As-cast Fe–0.6 wt.% C alloy after long anneal. The area under the spectrum components corresponds to the 8% of Fe_3C_2 . For an Fe_5C_2 . For an Fe_5C_2 and Fe_5C_2 and Fe_5C_2 . Triangle mark the retained austenite. b) As-cast Fe–0.6 wt.% C alloy after long annealing. The area under the spectrum components corresponds to the 8% of Fe_3C_2 and Fe_5C_2 . For Fe_5C_2 . The retained austenite the spectrum components corresponds to the Fe_5C_2 . The retained austenite the spectrum components corresponds to the Fe_5C_2 . Triangle mark the retained austenite the spectrum components corresponds to the Fe_5C_2 . Triangle mark the retained austenite the spectrum components corresponds to the Fe_5C_2 . Triangle mark the retained austenite the spectrum components corresponds to the Fe_5C_2 . Triangle mark the retained austenite the spectrum components corresponds to the Fe_5C_2 . Triangle mark the retained austenite the spectrum components corresponds to the Fe_5C_2 . Triangle mark the retained austenite the spectrum components corresponds to the Fe_5C_2 . Triangle mark the retained austenite the spectrum components corresponds to the Fe_5C_2 . Triangle mark the retained austenite the spectrum components corresponds to the Fe_5C_2 . Triangle mark the retained austenite the spectrum components corresponds to the Fe_5C_2 . Triangle mark the retained austenite the spectrum components corresponds to the Fe_5C_2 .

Experimental

Both hypo- and hypereutectoid Fe-C alloys with carbon concentration of 0.05, 0.10, 0.20, 0.25, 0.45, 0.60, 1.3, 1.5 and 1.7 wt.% were prepared from high purity 5N Fe and C by vacuum induction melting in the form of cylindrical 12 mm diameter ingots. The carbon content was measured by atomic absorption spectroscopy in a Perkin-Elmer spectrometer. 2 mm thick discs were subjected to HPT at room temperature in a Bridgman anvil-type unit under a pressure of 5GPa and for 5 torsions. Samples for structural and magnetic investigations were cut from the HPT-deformed discs at a distance of 3 mm from the sample center. One set of as-cast samples with 0.25, 0.60, 1.3 and 1.7 wt.% C was additionally annealed for 950 h at 725 °C in order to achieve the equilibrium α + Fe₃C structure. Light microscopy (LM) was performed with a Zeiss Axiophot microscope. Transmission electron microscopy (TEM) investigations were carried out on a JEM-4000FX microscope at accelerating voltage of 400 kV. X-ray diffraction (XRD) data were obtained on a Siemens diffractometer (Co K_{α} radiation). Mössbauer experiments were performed using a Perseus spectrometer with Co⁵⁷ source in the rhodium matrix at room temperature in the velocity interval from -10 to $10 \text{ mm} \cdot \text{s}^{-1}$ with 256 registration channels. This allowed the effective magnetic field to be defined with an error of less than 5 kOe. Spectra were analyzed using the least-square method for the superposition of Lorentz lines corresponding to the absorption of various phases.

Auger-electron spectroscopy (AES) of HPT Fe–1.7 wt.% C alloys was performed using a PHI 680 Auger spectrometer.

Received: October 11, 2010 Final Version: February 10, 2011 Published online: March 10, 2011

- B. B. Straumal, B. Baretzky, A. A. Mazilkin, F. Phillipp, O. A. Kogtenkova, M. N. Volkov, R. Z. Valiev, *Acta Mater.* 2004, 52, 4469.
- [2] A. A. Mazilkin, B. B. Straumal, E. Rabkin, B. Baretzky, S. Enders, S. G. Protasova, O. A. Kogtenkova, R. Z. Valiev, *Acta Mater.* 2006, 54, 3933.
- [3] A. R. Kilmametov, G. Vaughan, A. R. Yavari, A. LeMoulec, W. J. Botta, R. Z. Valiev, *Mater. Sci. Eng.* A 2009, 503, 10.
- [4] X. Amilis, J. Nogués, S. Suriñach, J. S. Muriños, M. D. Baró, *Phys. Rev. B* 2001, 63, 052402.
- [5] L. Del Bianco, A. Hernando, Phys. Rev. B 1997, 56, 8894.
- [6] M. Li, R. Birringer, W. L. Johnson, *Nanostruc. Mater.* 1993, 3, 407.



- [7] H. G. Read, W. T. Reynolds, Jr, K. Hono, T. Tarui, Scr. Mater. 1997, 37, 1221.
- [8] Yu. Ivanisenko, I. MacLaren, X. Sauvage, R. Z. Valiev, H.-J. Fecht, *Acta Mater.* 2006, 54, 1659.
- [9] V. A. Shabashov, L. G. Korshunov, A. G. Mukoseev, V. V. Sagaradze, A. V. Makarov, V. P. Pilyugin, S. I. Novikov, N. F. Vildanova, *Mater. Sci. Eng. A* 2003, 346, 196.
- [10] Yu. Ivanisenko, W. Lojkovski, R. Z. Valiev, H.-J. Fecht, *Acta Mater.* 2003, *51*, 5555.
- [11] X. Sauvage, Y. Ivanisenko, J. Mater. Sci. 2007, 42, 1615.
- [12] W. Lojkovski, Y. Ivanisenko, H.-J. Fecht, Trans. Indian Inst. Met. 2005, 58, 993.
- [13] D. E. Thomas, J. Sci. Instr. 1948, 25, 440.
- [14] M. Hasebe, H. Ohtani, T. Nishizawa, Met. Trans. A 1985, 16, 913.
- [15] G. K. Williamson, R. E. Smallman, Acta Cryst. 1953, 6, 361.
- [16] Binary Alloy Phase Diagrams, (Eds: T. B. Massalski, J. L. Murray, L. H. Bennett, H. Baker ASM), International, Materials Park, OH 1993.
- [17] V. S. Litvinov, S. D. Karakishev, V. V. Ovchinnikov, Mössbauer Spectroscopy of Fe-Based Alloys, Metallurgy, Moscow 1978.

- [18] G. Le Caer, J. M. Dubois, J. P. Senateur, J. Solid State Chem. 1976, 19, 19.
- [19] R. A. Arents, Yu. V. Maksimov, I. P. Suzdalev, V. K. Imshennik, Yu. F. Krupyanskiy, *Fiz. Met. Metalloved.* 1973, 36, 277.
- [20] Yu. V. Maksimov, I. P. Suzdalev, R. A. Arents, S. M. Loktev, *Kinet. Katal.* **1974**, 15, 1293.
- [21] J. E. Hilliard, Trans. AIME 1963, 227, 429.
- [22] T. P. Ershova, E. G. Ponyatovskii, Dokl. Chem. Proc. Acad. Sci. USSR 1963, 151, 724.
- [23] Yu. A. Kocherzhinski, O. G. Kulik, Sov. Powder Metall. Met. Cer. 1996, 35, 470.
- [24] A. V. Korznikov, Yu. V. Ivanisenko, D. V. Laptionok, I. M. Safarov, V. P. Pilyugin, R. Z. Valiev, *Nanostruct. Mater.* **1994**, 4, 159.
- [25] Yu. Ivanisenko, I. MacLaren, R. Z. Valiev, H.-J. Fecht, Adv. Eng. Mater. 2005, 7, 1011.
- [26] S. V. Divinski, M. Lohmann, Chr. Herzig, B. Straumal,
 B. Baretzky, W. Gust, *Phys. Rev. B* 2005, *71*, 104104.
- [27] R. G. Faulkner, R. B. Jones, Z. Lu, P. E. J. Flewitt, *Philos. Mag.* 2005, *85*, 2065.
- [28] B. B. Straumal, A. A. Mazilkin, S. G. Protasova, S. V. Dobatkin, A. O. Rodin, B. Baretzky, D. Goll, G. Schütz, *Mater. Sci. Eng. A* 2009, 503, 185.