Grain Boundary Segregation and Amount of Bulk Carbides in Severely Deformed Fe–C Alloys

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Abstract. The microstructure, phase composition, Mössbauer spectra, grain boundary segregation and magnetic properties of binary 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 studied in the as-cast state, after a long annealing at 725°C and after high-pressure torsion (HPT) at the ambient temperature and 5 GPa with 5 anvil rotations (shear strain about 6). The grain size after HPT was in the nanometer range. Only Fe₃C (cementite) and α -Fe remain in the alloys after HPT. It was also shown that the less stable Hägg carbide (Fe₅C₂) and retained austenite disappear, and phase composition closely approaches the equilibrium corresponding to the HPT temperature and pressure. Measurements of saturation magnetization and Mössbauer effect reveal that the amount of cementite decreases after HPT. The reason for partial cementite dissolution is the formation of the carbon-rich segregation layers in the ferrite grain boundaries.

Introduction

The unique properties of the nanostructured materials are of great importance for various advanced applications. Severe plastic deformation (SPD) techniques for preparing nanograined polycrystals, such as equal channel angular pressing (ECAP) and high-pressure torsion (HPT) do not involve changes in the material geometry, in contrast to the conventional processes of high deformation like rolling or wire drawing [1–4]. Comprehensive investigation of nanograined polycrystals is crucial especially for the alloys, which are most important for technological use. Iron–carbon system plays a fundamental role in structural applications. The Fe–C system is very rich on the stable and metastable phases. SPD can lead to their spectacular evolution. One of these processes reported in a number of experimental works is the paradoxial cementite dissolution [1, 2, 5–9]. The aim of this study is to investigate thoroughly structural changes in Fe–C alloys during HPT in a broad interval of carbon concentration and discuss the question of cementite disappearance during the SPD processing of the material.



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 cut from the cast ingots in order to investigate the as-cast state. For HPT treatment 0.4 mm thick discs were cut from the cast ingots, then ground and chemically etched. They were subjected to HPT at room temperature in a Bridgman anvil-type unit under a pressure of 5 GPa and for 5 torsions. Shear strain was about 6. 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 during 950 h at 725°C (i.e. below the eutectoid temperature) in order to achieve the equilibrium α +Fe₃C structure. Light microscopy (LM) was performed with Zeiss Axiophot microscope. For the metallographic investigations the samples were ground by SiC grinding paper, polished with 6, 3 and 1 µm diamond pastes and etched for 5-10 s with a 5 wt. % HNO₃ solution in ethyl alcohol. 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 Siemens diffractometer (Co K_{α} radiation). XRD spectra were measured in a short 20 interval (30–70°) with fine angular step of 0.04° and the intensity was collected for 30s in each point. As a result the signal/noise ratio was above 2 even for the very weak peaks of iron carbides. Calculation of the grain or particle size (D) from the X-ray peak broadening was done using the Scherer's formula: $D = 0.9\lambda/\beta \cos(\theta)$, where λ is the X-ray wavelength, θ is the diffraction angle and β is the full-width at half maximum of the diffraction line. Magnetic measurements were performed in a vibrating sample magnetometer (VSM). Discs of 3 mm-diameter and 0.15 mm thickness were cut for the magnetic investigations. The magnetic field in VSM was applied parallel to the sample plane. 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 mm/s with 256 registration channels. It allowed defining the effective magnetic field with an error of less than 5 kOe. Spectra were analyzed using the less square method for the superposition of Lorentz lines corresponding to the absorption of various phases. Augerelectron spectroscopy (AES) of HPT Fe-1.7 wt. % C alloys was performed using a PHI 680 Auger spectrometer. After HPT the samples became rather brittle and were broken in situ in the spectrometer chamber. The spectra were measured from the fracture surfaces immediately after the cleavage contained oxygen, carbon and iron peaks. Oxygen peaks disappeared after about 60 s of ion etching; the carbon concentration also decreased within this period and then remained at a low but constant level during further etching.

Results

The lattice parameter of the α -Fe (ferrite) solid solution in samples after HPT is about 0.28667 nm and does not depend on the total carbon concentration in the alloys, which is about $4 \cdot 10^{-5}$ nm higher than that for pure α -Fe [10]. The addition of 0.018 wt.% C to pure α -Fe (being the solubility of carbon in α -Fe at 680°C [11]) increases the lattice parameter of α -Fe by $7 \cdot 10^{-5}$ nm [12]. This means that the carbon concentration in α -Fe after HPT is about 0.01 wt.% C. It does not exceed the carbon maximum solubility (about 0.02 wt.% at 740°C). Within the framework of experimental error it more or less corresponds to the solubility at room temperature [11]. In other words, HPT does not lead to the formation of supersaturated carbon solid solution in α -Fe. XRD reveals that both hypoetectoid and hypereutectoid Fe–C alloys do not contain martensite (i.e. body-centered tetragonal supersaturated solid solution of carbon in α -Fe), since the splitting of (200) line typical for tetragonal martensite lattice was not observed either before or after HPT.



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The XRD measurements show that the initial as-cast alloy contains a strong peak of α -Fe with body-centered cubic (bcc) lattice is present [13]. This peak ($2\theta = 52.48^{\circ}$) has slightly shifted from the pure Fe position due to the diluted carbon atoms, as discussed above. Second, peaks of retained austenite (face-centered cubic, γ -Fe) are detected. Third, rather weak and broadened peaks of cementite are also present. Some very weak peaks (like those at $2\theta = 42.23^{\circ}$, 55.3°, and 66.48°) can be attributed as diffraction from the Hägg carbide Fe₅C₂. Fig. 2b contains the data for the Fe – 1.7 wt. % C alloy annealed during 950 h at 725°C in the α +Fe₃C two-phase region of the Fe–C phase diagram. The spectrum contains only two phases, namely ferrite and cementite. All peaks are well separated from each other and very narrow, much narrower than those in the as-cast state. It means that after a very long annealing both ferrite and cementite grains became large and crystallographically perfect. No peaks of retained austenite and Hägg carbide are present. After HPT only two phases (ferrite and cementite) remained after HPT in the samples and retained austenite and Hägg carbide disappeared. However, all peaks are broadened even in comparison with the as-cast state. This fact witnesses that the fine grain size and/or residual stresses are present in samples after HPT. XRD did not show any presence of graphite in all studied samples.

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 [13, 14]. Only the amount of these phases is different in various alloys, in conformity with Fe–C phase diagram [15]. The coarse grained as-cast Fe–C alloys contained the troostite lamellar colonies with interlamellar spacing of



Fig. 1. Dependence of the saturation magnetization J_s on carbon concentration for the as-cast, long annealed (coarce-grained) and HPT-treated alloys.



100–400 nm. The boundaries between two troostite colonies contained the cementite layer. TEM revealed the presence of retained austenite and a small amount of Hägg carbide in the as-cast alloys. Reflections of cementite were also detected in the SAED patterns. 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 μ m. TEM and LM also do not show any presence of martensite in the as-cast state of material. Neither splitted (200) spots (typical for tetragonal martensite lattice) in the SAED patterns nor typical for martensite grain morphology (needles, plates) were discovered in LM. Electron diffraction, similar to XRD did not show any presence of graphite in all samples studied.

The structures of hypoeutectoid and hypereutectoid alloys became very similar after long annealing for 950 h at 725°C (i.e. below the eutectoid temperature). This long annealing was performed in order to achieve the equilibrium α -Fe+Fe₃C structure. All samples contain very coarse ferrite and cementite grains. Only the amount of cementite is different which increases with increasing carbon content, according to the Fe–C phase diagram [15].

Nanometer range grain structure is obtained in the alloys as a result of the severe plastic deformation by HPT [13, 14]. SAED patterns contained only α -Fe and Fe₃C spots. Both the ferrite grains and cementite particles were visible in the DF image as the reflections of these phases lie closely to each other. Dislocation density was > 10¹⁴ m⁻² in all samples. Ferrite grain size after HPT is about 100 nm. It increases slightly with increasing carbon content. Ferrite grain size in all studied alloys is about 30 nm; it confirms the estimations made using the X-ray line broadening. 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

Fig. 1 shows the dependence of saturation magnetization J_s on carbon concentration. Saturation magnetization decreases with increasing carbon concentration for all studied samples. All experimental points are very close to the straight line connecting the saturation values for pure Fe ($J_s = 2.16$ T [16]) and Fe₃C ($J_s = 1.24$ T [17]). However, J_s for the HPT alloys decreases with increasing carbon content slower than that of as-cast alloys. In turn, J_s for the as-cast alloys decreases with increasing carbon content slower than that of coarse-grained alloys annealed at 725°C for 950 h. The dependence of a $\mu_0 H_c$ product (H_c is the coercivity and μ_0 is the permeability of free space) on carbon concentration was measured in [14]. The coercivity of nanostructured samples after HPT is higher than that of coarse-grained as-cast alloys. The $\mu_0 H_c$ value of hypoeutectoid as-cast alloys increases almost linearly with carbon content. In the concentration interval between 0.6 and 1.7 wt. % C, $\mu_0 H_c$ remains almost constant [14].

In Fig. 2 the Mössbauer spectrum of the as-cast alloys and alloys after HPT with are shown. The lines of ferrite ($H_{eff} = 330$ kOe [18]), Hägg carbide χ -Fe₅C₂ with hyperfine fields of 185±3 [18], cementite Fe₃C ($H_{eff} = 210\pm5$ kOe [18]) and retained austenite (no hyperfine field) [18] were found. Effective magnetic field and the fraction of subspectra are presented in the Table 1. The Mössbauer spectra after HPT contain only the lines of ferrite ($H_{eff} = 330$ kOe [18]), and cementite Fe₃C ($H_{eff} = 210$ kOe). Retained austenite and Hägg carbide disappeared after HPT. Other iron carbides like ε -Fe₂C with hyperfine fields of 170±3, 237±3 and 130±6 kOe [19, 20], Fe₄C or Fe₆C were not observed either before or after HPT. This fact supports the data of XRD and TEM. The amount of carbides before and after HPT increases linearly with increasing carbon content. However, the values for the as-cast Fe–C alloys lie much higher than those for the HPT alloys. This indicates decrease of the cementite amount after HPT.





Fig. 2a. Mössbauer spectrum of the as-cast Fe– 0.6 wt. % C alloy. Area under the spectrum components corresponds to the 10% of Fe₃C and Fe₅C₂ and 5% of retained austenite.





spectrum components corresponds to the 4% of Fe_3C .



Fig. 2b. Mössbauer spectrum of the as-cast Fe–0.6 wt. % C alloy after long anneal. Area under the spectrum components corresponds to the 8% of FeeC and FeeCa



Fig. 2d. Mössbauer spectrum of the Fe-1.5 wt. % C alloy after HPT. Area under the spectrum components corresponds to the 12% of Fe₃C.

Before	0.45 %C		0.6 %C		1.7 %C	
HPT						
Phase	% area	H _{eff} , kOe	% area	H _{eff} , kOe	% area	H _{eff} , kOe
α-Fe	81	330	82	330	78	330
γ-Fe	4	-	3	-	5	-
χ -Fe ₅ C ₂	3	190	4	188	3	198
Fe ₃ C	12	207	11	210	14	208
After HPT	0.45 %C		1.5 %C		1.7 %C	
Phase	% area	H _{eff} , kOe	% area	H _{eff} , kOe	% area	H _{eff} , kOe
α-Fe	96	330	88	330	85	330
Fe ₃ C	4	210	12	210	15	210

Table 1. Effective magnetic field and the fraction of Mössbauer subspectra before and after HPT





The samples after HPT became rather brittle, which made it possible to break them *in situ* in the Auger spectrometer chamber (Fig. 3). The carbon concentration along GB fracture surfaces fluctuates between 10 to 70 wt. % in the layer of about 1 to 3 nm thickness. It reveals the strong grain boundary carbon adsorption, but not the continuous cementite GB layers.

Discussion

After HPT stable phases appear and metastable phases disappear. In the 90s the nanocrystalline materials started to be produced by various methods. It was generally believed at that time that all technologies for the synthesis of nanocrystalline materials lead to the formation of structures which are very far from the equilibrium. Particularly, the metastable or unstable phases were assumed to be formed during the synthesis of nanocrystalline materials, like for example supersaturated solid solutions, metastable intermetallics, amorphous phases, etc. Later it became clear that various synthesis methods are crucially different and lead to very different structures and phase compositions of nanomaterials. The Fe–C system is very convenient to analyze these differences. The experiments on the ball milling of Fe–C alloys (steels) unambiguously showed that cementite can completely disappear from the ferrite-cementite structure after a long milling [1, 2, 5–7, 21–25]. As a result, a non-equilibrium supersaturated solid solution of carbon in α -Fe was formed. In an early work on SPD deformation of Fe–C alloys Korznikov et al. [26] observed the disappearance of the cementite peaks from XRD spectra and assumed that, similar to the ball milling, SPD leads to

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Fig. 11. Scheme of magnetization temperature dependence for mixture of two ferromagnetic phases (Fe₃C and α-Fe) with different Curie temperatures of 210°C and 770°C, respectively [9]. The number of anvil rotations by HPT is given for each curve. The derivative break at 210°C becomes invisible with increasing rotations number.

the formation of the supersaturated carbon solid solution in α -Fe. The assumption that cementite disappeared from steels after HPT in [9, 26] was also based on the temperature dependence of magnetization J_s (pearlitic UIC 860V steel with 0.6-0.8 wt. % C [9] and highcarbon steel with 1.2 wt. % C [26] were studied). In the coarse-grained α -Fe+Fe₃C alloys the input of cementite into the $J_s(T)$ dependence be clearly seen, and the derivative break at 210°C can be observed quite well (Fig. 11). Curie temperature of cementite (210°C) is lower than that of α -Fe (770°C). However, by increasing number of anvil rotations by HPT (i.e. with decreasing grain size), the Fe₃C input into $J_s(T)$ curve flattened and disappeared (Fig. 4). The first hypothesis of the authors [9, 26] was that cementite dilutes and disappears during HPT, although neither the carbonsupersaturated

ferrite nor martensite was observed in the samples. Later the same authors found by careful electron diffraction studies that cementite is present after HPT, but the Fe₃C lamellae are broken into very fine particles [7, 27]. These extremely fine (few nanometers) Fe₃C particles were not detected before by conventional TEM and low-statistics XRD analysis [9, 26]. Cementite becomes paramagnetic close to 210°C. It is good visible in the $J_s(T)$ curve when the cementite forms large lamellae or particles. Yet, with increasing number of anvil rotations by HPT, the size of the cementite particles decreases drastically. The magnetic field caused by surrounding ferromagnetic α -Fe penetrates into paramagnetic Fe₃C to a certain depth and magnetizes it. This depth can be roughly estimated by the thickness of the domain wall. It is about 40 nm for α -Fe [16]. When the size of cementite particles decreases below a few dozens of nanometers, they are fully magnetized by the surrounding α -Fe, and the input of Fe₃C into $J_s(T)$ curve flattens (Fig. 4). The refinement of cementite lamellae to the very fine particles was observed also in another mode of SPD, namely by deep drawing of steel wires with a true strain above 4 [28–30]. Also in this case neither cementite disappeared from the steel nor was it diluted in the matrix. Later, when using the field ion microscopy, carbon atoms from the "disappeared" cementite were found to segregate in the ferrite cell and GBs [31].

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 [3, 4]. The decomposition of the supersaturated (Al) solid solution proceeds parallel to the drastic grain refinement. No metastable phases conventionally

consult comment contact produced at the Al–Zn alloys decomposition (Guinier-Preston I and II zones, 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.

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 [32–34]). 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 [34]. 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 [8].

It has been already mentioned above that during the manufacturing process of nanostructured materials, amorphisation may happen, the supersaturated solid solutions may appear and the metastable phases may be formed [35]. However, there are indications that physical properties of the same material with the same grain size in a nanometer range depend on the preparation technique. The most reliable data on the formation of metastable phases came from the ball milling experiments. Particularly, the ball milling of steels leads to the dissolution of cementite or formation of amorphous solid solution in steels in a reliable and reproducible manner [21–25]. Implantation of carbon ions into iron also produces strongly nonequlibrium structures in the surface layers of the samples [36]. In other words, ball milling also called mechanical alloying can be compared with a kind of mechanical implantation of one material into another. The HPT (also called compression shear) or deep drawing are principally different from the ball milling. The results of this work, as well as our previous data on HPT of Al-based alloys [3, 4], demonstrate that HPT or deep drawing lead simultaneously to (a) the formation of a highly non-equilibrium nanometer grain structure and (b) the disappearance of non-equilibrium phases and the formation of phases which are in equilibrium at the HPT temperature and pressure. The careful experiments and analysis of previous publications on HPT demonstrate that this deformation mode leads to the grain refinement but cannot lead to the disappearance of equilibrium phases (e.g. dissolution of cementite) or formation of non-equilibrium ones (ϵ or Hägg iron carbides). This is the most important difference between HPT and ball milling, as two technologies for manufacturing nanostructured materials.

However, what is really behind the widespread idea of the cementite dissolution during SPD of steels?

Role of grain and interphase boundaries. Nanograined materials contain a large amount 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 [37–40]. Such layers can also be called multilayer segregation. However, the investigations of GB segregation and GB phases need special sophisticated methods like high resolution electron microscopy, AES, field ion microscopy, etc. which allow very local areas of a material to be studied. 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 broaden and finally "sink" in the background. Similarly, all layers which are thinner than the equilibrium layer of a domain wall do not input into the overall bulk magnetisation [14]. In other words, the amount of bulk phases in the polycrystalline alloy can strongly differ from that predicted by the equilibrium phase diagram if: (a) 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; (b) 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 monolayers [41]. 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. 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 [13, 14]. However, the magnetic data (Fig. 8) reveal that the overall amount of the bulk cementite phase after HPT becomes lower than the equilibrium phase diagram predicts. Both ferrite and cementite are ferromagnetic. The saturation magnetisation of ferrite is however, much higher than that of cementite: J_s (ferrite) = 2.16 T [164] and J_s (Fe₃C) = 1.24 T [17]. Therefore, the magnetization of a two-phase mixture decreases linearly with increasing cementite content. However, if the ferrite grain size decreases, a certain amount of carbon would not be used for the formation of bulk cementite, but for the segregation layers in the ferrite-ferrite GBs. As a result the amount of cementite would decrease, and the overall magnetization of the HPT alloy would increase in comparison with the coarse-grained one, and the deviation to the top from the line connecting J_s points for pure Fe and Fe₃C would be observed. A decreasing grain size of ferrite would increase such positive J_s deviations and exactly this behaviour is observed in Fig. 1. The long-annealed samples have very large ferrite and cementite grains and few GBs. Their J_s points form the lower straight line in Fig. 1. They almost coincide with a line connecting points for pure Fe and Fe₃C. The as-cast alloys have smaller grains and their J_s values are higher than those of corresponding coarse-grained counterparts (Fig. 1). The samples after HPT possess the smallest grains (100 nm for ferrite and 30 nm for cementite). The magnetization of these samples is much higher than J_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. The diagram in Fig. 1 demonstrates how the amount of "disappeared" cementite can be estimated. The J_s value for the HPT alloy with 1.7 wt. % C is equal to that of coarse-grained alloy with 1.15 wt. % C (marked with a cross). This means that about one third of bulk cementite disappeared after HPT. The respective carbon amount formed GB segregation layer and does not input into the overall magnetization value.

Measurements of the Mössbauer effect also allow the amount of "disappeared" cementite to be estimated semi-quantitatively. The comparison of the area under respective components of the Mössbauer spectra before and after HPT (Fig. 10) also undoubtedly demonstrate that the amount of bulk cementite decreased after HPT. The formation of the network of GBs and cell boundaries in the ferrite enriched by the carbon atoms was also observed in the careful investigations of HPT-treated carbon steel UIC-860 by means of the field ion microscopy [31].

Conclusions

- 1. Severe plastic deformation of Fe–C alloys by high pressure torsion leads to the disappearance of the non-equilibrium (metastable) phases and to the formation of the phases which are equilibrium at temperature and pressure of HPT treatment. It is an important difference from the ball milling which can lead, similar to the ion implantation, to the formation of metastable or amorphous phases.
- 2. HPT leads to the grain refinement. Carbon strongly segregates in the numerous ferrite GBs. Consumption of carbon by these GB segregation layers causes of the bulk cementite amount to decrease.



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Section "Grain Boundary Diffusion, Segregation and Stresses"



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