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Nanocrystalline steel obtained by mechanical alloying of iron and graphite subsequently compacted by high-pressure torsion

Christine Borchers [a,*], Clemens Garve [a], Marie Tiegel [a], Martin Deutges [a], Andreas Herz [a,b], Kaveh Edalati [c], Reinhard Pippan [d], Zenji Horita [c], Reiner Kirchheim [a,c]

[a] Institut für Materialphysik, Universität Göttingen, 37077 Göttingen, Germany
[b] Institute of Materials Engineering and Institute of Micro- and Nanotechnologies, Chair Materials for Electronics and Electrical Engineering, TU Ilmenau, 98693 Ilmenau, Germany
[c] International Institute for Carbon-Neutral Energy Research (WPI-I^{2}CNER), Kyushu University, Japan
[d] Erich-Schmid-Institute of Materials Science, Jahnstrasse 12, 8700 Leoben, Austria

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ABSTRACT

Steel powders obtained by mechanical alloying of iron and graphite were compacted by high-pressure torsion. During high-pressure torsion, mean grain sizes rise from about 10 nm after mechanical alloying to about 20 nm. Vickers hardness reaches values of more than 10 GPa. Differential scanning calorimetry revealed superabundant vacancies present in concentrations up to 10^{-3}. The results are discussed in terms of strain, strain rate, energy input and deformation mechanisms.

1. Introduction

Nanocrystalline (NC) materials with grain sizes below 100 nm are of great technological interest. Because of the reduced grain size they exhibit different thermodynamic, mechanical, electrical and magnetic properties than their coarsely crystalline counterparts [1]. Nanostructured iron alloys are for example used as NC powder cores for high frequency applications [2], as nanoparticles for ultrahigh density magnetic recording [3], as biodegradable cardiovascular stents [4], as heat- and radiation resistant reactor materials [5], or as a nanoscale activator for persulfate to oxidize hazardous organic compounds [6].

It has been shown that NC iron with grain sizes between 5 and 15 nm can be prepared by mechanical alloying (MA) of iron and graphite powders [7]. The origin of this remarkably small grain size is the interaction of solute elements, carbon in the case mentioned, with the grain boundaries in iron generated by MA, as described in the defactant concept [8,9]: According to a theory originating from Gibbs [10], an excess of a different substance at boundaries can reduce their energy, leading to a reduced driving force for their annihilation. However, in view of applicability powders are not always a choice material. It would in many cases be wishful to have bulk NC materials [11] with grain sizes in the range mentioned above.

Severe plastic deformation (SPD), a type of metal processing known for over 2000 years [12], is an effective means to fabricate ultrafine-grained metals and alloys [13,14]. During SPD, heavy deformations are forced onto the feedstock material, inducing defects in high densities. During SPD of coarse-grained material, a saturation of the microstructure is reached, with typical grain size values of 10–1000 nm, depending on process temperature and the presence or absence of alloying elements [15–17]. SPD including torsion and pressure, commonly called high pressure torsion (HPT) was first reported by Bridgman in 1943 [18], and is thoroughly reviewed by Zhilyaev and Langdon [19]. HPT of carbon steels of various compositions has been reported repeatedly; see e.g. [20–26]. Korznikov and co-workers [20] as well as Ivanisenko et al. [21,22] analyzed the changes of high carbon steel (carbon content 1.2 wt.% and 0.6–0.8 wt.%, respectively) under HPT and found complete dissolution of cementite and the evolution of structural components with a mean size of 10–20 nm, whereas Zrnik et al. [23], Bayramoglu et al. [24] as well as Ning et al. [25] found structural components with a mean size of 100–200 nm in AISI 1045 (0.45 wt.% C) after HPT, and Todaka et al. elongated grains of a size of about (300 × 600) nm^2 in projection in pure iron

* Corresponding author.
E-mail address: chris@ump.gwdg.de (C. Borchers).

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after HTP [26]. Application of HPT for consolidation of powders was also reported; see e.g. [27–32]. Quite different kinds of powders were compacted, including Ti [27], $Al_{90}Fe_5Nd_5$ [28], Co [29], α-Al_2O_3 [30], Cu [31], as well as Fe 1-wt.% C [32], where the Co, Cu, and Fe – 1 wt.% C were subjected to MA prior to HPT.

It is the aim of this work to demonstrate the mechanical and thermal behavior of NC Fe–C powder obtained by MA of iron and graphite after having been subjected to high-pressure torsion.

2. Experimental

The MA Fe–C powder was obtained by ball-milling iron powder with a purity of 99.99% mixed with 0.4 wt.% graphite powder (99.99% purity) for 100 h in a Fritsch planetary mill Pulverisette 6. Fig. 1 shows the microstructure of the powder obtained by scanning electron microscopy (SEM, Fig. 1(a)), and transmission electron microscopy (TEM, Fig. 1(b) and (c)). Powder particles exhibit a size of around 10 μm, and the microstructure is NC, with a mean grain size of about 10 nm, as can be seen from the dark-field micrograph Fig. 1(c) [7,33]. This powder was subjected to high-pressure torsion with an applied pressure p of 6 GPa, a torsion rate of 2π min^{-1}, with different evolution numbers N and different nominal temperatures as given in Table 1. Details of the employed HPT facility can be found in [34].

The compressed samples were characterized by XRD using a Siemens D5000 with Cu-Kα-radiation as well as a Philips X'Pert with Co-Kα-radiation; microstructural investigations were performed with SEM using a Philips SEM 515 operated at 5 kV, and with TEM using a Philips CM 12 operated at 120 kV and a FEI Titan 30–300 ETEM operated at 300 kV. Sample preparation for SEM was done by cutting a rectangular strip out of the HPT pellet by spark erosion as sketched in Fig. 2, where a photograph of the pellet, as compared to a 1-€-cent-coin (16.25 mm Ø) is also shown. One narrow side of the strip was subsequently polished by hand. Sample preparation for TEM was done utilizing focused ion beam (FIB) milling in a FEI Nova 600 NanoLab.

Vickers hardness measurements were performed with a Fischer Ultra-Mikro-Indenter at the points marked with arrows and denoted 1–5 in Fig. 2(b) with the indents vertical to the torsion axis and an applied force of 1000 mN. Sample 3 was subjected to tensile testing performed with a universal testing machine Zwick 1474. The sample was a rectangular block with a cross sectional area of 1.8 mm^2. Sample 3 was also subjected to differential scanning calorimetry (DSC) with a Perkin-Elmer DSC-7 at a heating rate of 5 K min^{-1}.

3. Results

After HPT under all four conditions listed in Table 1, compact pellets were obtained, as shown in Fig. 2, and it was possible to cut rectangular strips out of the pellets without the sample disintegrating. XRD measurements, see Fig. 3 where an XRD spectrum of sample 1 is shown, yielded a bcc structure with a lattice constant of 0.287 nm, that of pure iron; this result was equally obtained for samples 1–3 subjected to XRD. Fig. 4 shows SEM micrographs of sample 3 (N = 50, T = 300 K). Fig. 4(a): overview of the polished narrow side of the rectangular strip, which is positioned in the middle of the micrograph. The polished side looks smooth and coherent; in particular the original powder particles cannot be distinguished. Fig. 4(b): close-up of the region marked with an arrow in Fig. 4(a). At the outer edge of the pellet, original powder particles can be distinguished quite well; the particle size of 10–20 μm evident from Fig. 1(a) is still apparent, however the particles seem to be somewhat flattened from HPT. SEM micrographs of the other samples exhibit quite a similar appearance.

Fig. 5 shows TEM micrographs of all four samples: (a) bright field and (b) dark field of sample 1, (c) bright field and (d) dark field of sample 2, (e) bright field and (f) dark field of sample 3, (g) bright field and (h) dark field of sample 4. Sample 1, N = 2, shows a NC microstructure with a mean grain size of 21 nm [35] with strongly elongated grains as can be seen in the dark field image Fig. 5(b). The inset diffraction image demonstrates the predominance of ferrite, but it does exhibit faint cementite rings. There is an eye-catching band about 100 nm wide running from the upper left side to the lower middle of the micrograph Fig. 5(a), where the dark spots are much smaller than in the rest of the micrograph. Sample 2, N = 10, shows a NC microstructure with a mean grain size of 16 nm [35], also with strongly elongated grains as can be seen in the dark field image Fig. 5(d). Here too, the inset diffraction image demonstrates the predominance of ferrite, but it exhibits faint cementite rings as well. Sample 3, N = 50, shows a NC microstructure with a mean grain size of 23 nm [35], with less prevalent elongation of the grains than in case of samples 1 and 2, as can be seen in the dark field image Fig. 4(f). However, the bright spots arranged like pearls on a necklace in the dark field image demonstrate that grains of similar orientations tend to arrange in sequential colonies. The inset diffraction image also shows faint cementite rings. This diffraction image is obtained from a larger area of the sample than the other ones, i.e. many more grains contributed to the diffraction rings, which is why they are less disrupted than in the other cases. Sample 4, N = 10, T = 523 K, exhibits NC grains with a mean size of 20 nm [35], as can be seen in the right panel of Fig. 5(h). The other half shows a dark field image gained with the faint cementite rings that can be seen in the diffraction image set into Fig. 5(g); the scale bar is identical for both halves. Cementite particles seem to be much smaller than ferrite grains, i.e. only a few nm, and their volume fraction can be estimated to be around 1%.

The results of hardness measurements are given in Table 2 (to convert Vickers hardness H_V to GPa multiply by 9.81×10^{-3} m s^{-2}). The hardness of sample 4 could only be determined at two places because the pellet broke. In Fig. 6(a), the result of tensile testing is displayed. The stress/strain curve of the rectangular sample shows an ultimate tensile strength (UTS) of about 80 MPa at a strain of about 0.8%. Fig. 6(b) shows the fracture surface after failure. Fracture has occurred at powder particle–particle interfaces, which is confirmed by a comparison with Fig. 4(b).

The results of DSC heating are shown in Fig. 7. Three exothermic peaks can be seen, one of which at 427 K, the next at 639 K, and the third one at 740 K.

4. Discussion

4.1. Microstructure

It is well known that grain sizes saturate during HPT of coarse-grained bulk material [15,16,19,36]. The most important factors influencing the saturation grain size are composition and temperature, and to a lesser extent the strain rate [16]. Reports about HPT of Fe–C found in the literature are not abundant, but can be found nonetheless: Ivanisenko et al. also studied compacts obtained by HPT of MA Fe–C powder, however with 1 wt.% C, and after HPT performed under a pressure of 1.4 GPa and a temperature of 813 K; they found a grain size of 70 nm [32]. In other studies, carbon steel with different carbon contents was subjected to HPT, and the grain size was 200 nm after HPT of Fe-0.45 wt.% C at 7 GPa and 673 K [23], 120 nm after HPT of Fe-0.45 wt.% C at 6 GPa and 623 K [25], 10 nm after HPT of Fe-0.6–0.8 wt.% C at 7 GPa and 300 K [21], and 20 nm after HPT of Fe-1.2 wt.% C at 10 GPa and 300 K [20]. The larger grain sizes as compared to the