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Yinyin Zhang, Sergio Sao-Joao, Sylvie Descartes, Guillaume Kermouche, Frank Montheillet, et al.. Microstructural evolution and mechanical properties of ultrafine-grained pure  $\alpha$ -iron and Fe-0.02%C steel processed by high-pressure torsion: Influence of second-phase particles. *Materials Science and Engineering: A*, 2020, 795, pp.139915. 10.1016/j.msea.2020.139915 . hal-02927805

**HAL Id: hal-02927805**

**<https://hal.science/hal-02927805>**

Submitted on 22 Aug 2022

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# Microstructural evolution and mechanical properties of ultrafine-grained pure $\alpha$ -iron and Fe-0.02% C steel processed by high-pressure torsion: Influence of second-phase particles

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## Abstract

A Fe-0.02wt%C, containing cementite particles, and a pure  $\alpha$ -iron were subjected to unconstrained high-pressure torsion and their microstructural refinement with strain are examined by electron backscatter diffraction (EBSD) and transmission Kikuchi diffraction EBSD (TKD-EBSD), based on which the influence of second-phase particles on grain refinement mechanisms is investigated. Both materials are refined rapidly by formation of subgrain boundaries and grain boundaries at low and medium strains. The single-phase iron generates a higher density of geometrically necessary dislocations and forms small grains in the deformation inhomogeneity regions. However, at a higher strain of  $\sim 12.3$ , the cementite particles facilitate to overcome the saturation microstructure that occurred in pure iron and promote further grain refinement. Continuous dynamic recrystallization (CDRX) by transforming subgrain boundaries to grain boundaries is the major grain refinement mechanism before  $\epsilon_{vm} \sim 12-13$ . Geometric dynamic recrystallization (GDRX) is also operating during ultrahigh strains ( $\epsilon_{vm} \sim 12-30$ ), particularly prevalent in the cementite-containing specimen. Mechanical properties of the HPT-processed microstructures are examined by nanoindentation and micropillar compression.

**Key words:** high-pressure torsion; grain refinement; second-phase particles; CDRX; GDRX

# 1 Introduction

Severe plastic deformation (SPD) has been developed and improved rapidly over the past thirty years and has become an important tool to achieve ultrafine-grained and nanocrystalline metallic materials in bulk form that provide exceptionally high strength, superplasticity at elevated temperatures, and activation of hydrogen storage [1-3]. Among the basic SPD techniques such as equal-channel angular pressing (ECAP), high-pressure torsion (HPT), accumulative roll bonding (ARB), multi-axial forging, and twist extrusion, HPT is prominent for its remarkably efficient grain refinement and formation of high angle grain boundaries [4, 5]. It has been successfully applied to various materials ranging from pure metals, single-phase alloys to multiple-phase alloys, composites and intermetallics [2, 6-8]. Müller et al. [8] recently reported an ultrahigh-strength structure produced by HPT in a Fe-0.1wt%C martensitic steel, where the lamella width was reduced to  $27 \pm 5$  nm after an equivalent strain of 15, and it revealed an ultimate tensile strength of  $2.4 \pm 0.1$  GPa, the highest tensile strength ever reported in such low carbon steel. However, saturation of grain refinement for metallic materials often takes place during HPT once the strain reaches a critical value, beyond which grain size keeps constant with increasing strain. Such phenomenon was reviewed by Pippan et al. [9], who attributed that to grain boundary migration at large strains. A lot of efforts have been devoted to overcoming saturation and gaining more control on grain sizes. Edalati et al. [6, 7] examined empirically a broad range of single-phase alloys and they showed a dramatical reduction in minimum grain size achievable comparing to their pure metal counterparts. For instance, grain size of pure aluminium processed by HPT at room temperature was stabilized at  $\sim 1900$  nm, whereas Al-8.8at%Mg was able to be further refined to  $\sim 140$  nm in grain size under identical condition [6]. They rationalized that the additional grain refinement by alloying was induced by atomic-size and modulus mismatch that increased stress locally required for the edge dislocation motion and thus eliminated dislocation recovery, recrystallization and grain boundary migration. Except for alloying, another effective strategy to overcome the grain refinement limit may be introduction of second-phase particles to stabilize grain boundaries. A copper matrix nanocomposite Cu+0.5wt.%Al<sub>2</sub>O<sub>3</sub> processed by HPT yielded nanograins  $\sim 80$  nm, much finer than that of pure Cu where the grain size often saturated at submicrometers [10]. Using powders, with natural or artificial oxide layer, as starting material, Bachmaier et al. [11] produced bulk nanocrystalline nickel matrix composite using HPT; the

limit of the grain size was reduced from ~200 nm to ~30 nm, which was driven by the nanometer-sized dispersoids of nickel oxides.

However, mechanisms of grain refinement driven by addition of second-phase particles has not been fully understood [9]. More specifically, whether the second-phase particles facilitate or retard formation of high angle boundaries (HABs) during SPDs is still unclear. This can be seen by various, sometimes contradict, results reported in the literature [12-19]. For example, in alloys containing coarse second-phase, i.e. micrometer size, the grain refinement often occurred at a dramatically higher rate and thus more refined grains were achieved eventually comparing to their single-phase counterparts; whereas nano-sized dispersoid-containing alloys exhibited retardation of forming HABs, leading to less refined microstructure ultimately [12, 13, 15, 18]. Nevertheless, recent studies demonstrate submicron second-phase particles also enabled to gain further refined grains during high velocity impact, during which dynamic recrystallization was driven by particle-simulated nucleation [17]. Barlow et al. [14] and Markushev et al. [16] showed in aluminum and high-strength aluminum alloys that contain nanometer-sized dispersoids, nanostructured material with subgrains or less were developed rapidly during cold-rolling and HPT. A main reason for the complexity of second-phase particles during SPDs is that various factors including cohesion between the particles and matrix, particle deformability, size, shape, volume fraction, distribution, as well as deformation condition such as temperature play an important role during SPDs of the alloys and composites. Although effects of particles on static recrystallization of a deformed microstructure during annealing have been extensively studied and relatively better understood in terms of on recrystallization kinetics, microstructure, and texture, there is a need of such thorough research in the field of severe plastic deformations where continuous dynamic recrystallization was believed to occur [20, 21].

In the present work, using model materials, *viz.* a high purity  $\alpha$ -iron and a Fe-0.02%C containing cementite precipitates, influence of particles on microstructural refinement mechanisms and mechanical properties during SPD were explored by imposing unconstrained HPT. The well-controlled model materials permit to rule out possible effects induced by alloying elements such as oxygen, chromium, nickel etc. that are often contained in commercial grades that have been widely applied in literature [22]. The single-phase  $\alpha$ -iron was served as reference. Two materials were strained to various rotations of 90°, 180°, and 360° such that microstructural observations

were carried out from a wide range of strains (i.e.  $\varepsilon_{vm} = 2-30$ ). Size and distribution of the second-phase particles with increase in strain were carefully tracked. Electron backscatter diffraction (EBSD) and Transmission Kikuchi Diffraction-EBSD (TKD-EBSD) were used to characterize microstructural features and microstructural evolution with strain, based on which deformation mechanisms of pure  $\alpha$ -iron and Fe-0.02%C were revealed. Statistical measurements and close investigations of the microstructures from low to large strains were performed and influence of cementite particles on grain refinement mechanisms was discussed. In addition, mechanical properties of HPT-processed microstructures were examined by nanoindentation and micropillar compression.

## 2 Materials and experimental

### 2.1 Pure iron and Fe-0.02% C steel

The high-purity  $\alpha$ -iron (<15 ppm carbon) and Fe-0.02%C (“Fe-200”, representing 200 ppm carbon) were fabricated using a custom-built high-vacuum cold-crucible melting procedure [23]. The desired amount of carbon, i.e. 0.02 wt% in the present study, was introduced by induction heating. The 200-ppm carbon was to achieve cementite precipitates and, in the meantime, to avoid formation of pearlite that possesses a distinct lamellar morphology. The ingots were then hot forged and swaged into bars with a diameter of approximately 12 mm. The pure iron bar was annealed at 800 °C for 2 hours to eliminate the effects of previous deformation processes and result in a homogeneous microstructure consisting of equiaxed grains of ~1 mm in size. The Fe-200, however, was heated up to 1000 °C and dwelled for 10 minutes to ensure a complete austenitic transformation and followed by air cooling to room temperature. Fig. 1 shows microstructure of the Fe-200 after heat treatment. It is a dual phase microstructure, consisting of iron matrix and needle-shape second-phase particles that have higher carbon content (Fig. 1D); mean grain size of the matrix measured by EBSD map (not shown) is ~150  $\mu\text{m}$ . Given that this material comprises only Fe and C, the second phase can be identified as cementite. They are mainly distributed in the grain boundaries (Fig. 1B) and gathered as clusters in the grain interiors (Fig. 1A and 1C). The volume fraction measured by image analysis is ~0.3-0.4%, close to theoretical calculation, i.e. 0.3%, where 200 ppm carbon was assumed to be fully transformed to cementite. Therefore, it is reasonable to believe that thermomechanical equilibrium has been

reached when the material was cooled down slowly in air such that almost all the carbon atoms are in form of cementite. Indeed, carbon solubility in coarse-grained ferrite at room temperature is close to zero [24, 25]. Average length of the needles is ~2400 nm and their mean free path, that is average distance between surfaces of particles along any random straight line [26], is ~33  $\mu\text{m}$ . The bars after the heat treatment were machined into cylinders of  $6 \pm 0.1$  mm in diameter, then sliced into disks and polished down to 500-530  $\mu\text{m}$  thick using P2500 sandpaper for the purpose of performing HPT.

## 2.2 High pressure torsion tests

Torsion tests were carried out by a custom-built unconstrained HPT test rig at room temperature (20 - 25  $^{\circ}\text{C}$ ) [27, 28]. The disks were placed between two WC-Co anvils with flat surfaces that were scratched by P320 sandpaper to promote high friction between the anvils and specimen. Prior to HPT tests, the disks and anvils were bathed in acetone and alcohol, respectively, for 10 minutes using ultrasonic cleaning. A mean compressive pressure of ~1 GPa was loaded first and kept constant throughout the following rotation process, which was carried out at 0.5 revolutions per minute (RPM) to angles of 90 $^{\circ}$ , 180 $^{\circ}$ , and 360 $^{\circ}$ . The sample thickness evolution during HPT was calculated by measuring the vertical displacement using inductive sensors, and the torque was measured by a static torque sensor.

Assuming adherence between the anvils and specimen is perfect, i.e. no sliding occurs, and deformation is homogeneous throughout thickness at any point along radius, also giving the strain component associated with thickness change is negligible with respect to shear strain, equivalent von Mises strain  $\varepsilon$  and stress  $\sigma_r$  at the external radius can be calculated by the Fields and Backofen method [29]:

$$\varepsilon = \frac{\varphi}{\sqrt{3}} \frac{r}{h} \quad (1)$$

$$\sigma_r = \frac{\sqrt{3}T}{2\pi r^3} (3 + N + M) \quad (2)$$

where  $\varphi$  is rotation angle in radians,  $r$  outer radius,  $h$  sample thickness,  $T$  torque,  $N = \frac{\partial \ln T}{\partial \ln \dot{N}}$  and  $M = \frac{\partial \ln T}{\partial \ln N}$  are the coefficients specifying the logarithmic dependences of the torque on rotation and rotation rate, respectively. Here  $M$  was set equal to zero considering that the materials were undergoing deformation at room temperature [29].

### 2.3 Microstructure characterizations

Locations for microstructural observations were selected from the specimens deformed to 90°, 180°, and 360° to examine microstructural evolution as a function of strain during HPT. Fig. 2A-B show typical top view of a disk processed by HPT where three distinct zones can be identified. An adhesion zone at the center is characterized by the anvil imprints on the surface; next to it is sliding zone where scratches along torsion direction are visible; the outermost zone is a layer of material that has been extruded out of the contact due to outward material flow during unconstrained HPT [5, 27, 28, 30]. The area of adhesion zone often reduces with rotation angle, for instance, for the Fe-200, it was ~6 mm in diameter at 0°, 3.8 mm at 90°, 3.4 mm at 180°, and 3.3 mm at 360°. The interesting areas are selected from the adhesion zones where equivalent von Mises strain can be better estimated using equation (1). Two of them are from the 90° sample and located at the edge and half radius of the adhesion zone, corresponding to  $\varepsilon_{vm} \sim 3$  and 5, respectively; the other two are from edges of adhesion zones of 180° and 360° samples with  $\varepsilon_{vm} \sim 13$  and 30, respectively. As shown in Fig. 2C,  $r_z$  cross-sections were cut across the disk diameters and then polished using a cross-section polisher (IB-19530CP, Jeol, Japan) operating at a voltage of 6 kV. EBSD maps were acquired in a field emission scanning electron microscope (Zeiss Supra 55-VP, Zeiss, Germany) with an accelerating voltage of 20 kV and a step size of 30 nm. In order to reveal more details on microstructural refinement at the large strains of  $\varepsilon_{vm} \sim 13$  and 30, thin foils in  $\theta_z$  plane (Fig. 2C) were made using the standard lift-out technique on a focused ion beam-scanning electron microscope (FIB-SEM, Helios NanoLab DualBeam, FEI, US). TKD-EBSD was then performed using the Zeiss Supra 55-VP microscope with an accelerating voltage of 30 kV and a step size of 10 nm. The index rate of the EBSD and TKD-EBSD maps ranged from 70% to 90% depending on the strain level of the material and techniques.

## 2.4 Measurements of mechanical properties

Hardness of the above microstructures were studied by an MTS DCM nanoindenter equipped with a Berkovich diamond tip. Indentation tests were performed on  $rz$  cross sections that were prepared by firstly cutting across the disk diameter, followed by metallographic polishing and vibratory polishing for 5 hours. A grid matrix of  $4 \times 280$  indents, with a  $10 \mu\text{m}$  spacing in both horizontal and vertical directions, was indented starting from the center of the disk. Hardness values were calculated by Oliver and Pharr method [31].

Micro-pillar compression tests of the HPT-processed materials were conducted and conical-shaped pillars were milled from the  $rz$  plane using the FIB-SEM and with a typical dimension of  $3\text{-}4 \mu\text{m}$  in diameter and  $5\text{-}6 \mu\text{m}$  in height, leading to an aspect ratio of  $\sim 1.7$ . The pillars were compressed in the Zeiss Supra 55-VP microscope equipped with an Alemnis indentation setup [32]. The compression was carried out with a  $15 \mu\text{m}$ -diameter tungsten carbide flat punch at a constant loading rate of  $0.01 \mu\text{m/s}$ . At least three repeatable tests were obtained for each microstructure.

## 3 Results and discussion

### 3.1 Stress-strain curves and distributions of the cementite particles during HPT

Fig. 3A plots measured torque and sample thickness versus rotation angle up to  $360^\circ$  over the torsion process, which are then substituted into equations (1) and (2) to drive stress-strain curves. For both samples, the torque increases rapidly at the beginning of rotation, then raises gradually until it reaches a steady plateau at  $\sim 200^\circ$  of rotation. However, the torque of Fe-200 surges faster than that of iron after rotation commences and achieves a higher stable-state value of  $\sim 31 \text{ Nm}$ . The sample thickness decreases during the rotation as material is extruded out of the anvils; iron thickness reduces faster and is  $\sim 60 \mu\text{m}$  thinner than that of Fe-200 after  $360^\circ$  of rotation. Fig. 3B shows the stress-strain curves of iron and Fe-200 during HPT; similar to their torque evolution, von Mises stress grows rapidly at the beginning of the rotation until it comes to steady-state values of  $\sim 1000 \text{ MPa}$  for the Fe-200 and  $\sim 900 \text{ MPa}$  for the iron. It is important to note that



because the  $r$  in equation (1) is set as 3 mm without considering the sliding occurred between anvil and sample, the strains plotted in Fig. 3B are overestimated. Strains of the interested microstructures presented later are calculated using their actual  $r$ , and thus are lower than the plot in Fig. 3B.

Since size and distribution of the second-phase particles are often found critical in monitoring microstructural evolution during SPDs [12, 13], evolution of the cementite size and distribution during HPT were investigated thoroughly by backscatter scanning electron (BSE) micrographs; at least 100 measurements were taken at each strain level and their mean values are reported here. As shown in Fig. 4A, length of the needles reduces quickly from  $\sim 2.4 \mu\text{m}$  to  $\sim 1.6 \mu\text{m}$  at the onset of deformation (i.e.  $\varepsilon_{\text{vm}} \sim 0.2$ ), then keeps decreasing gradually to  $\sim 1.3 \mu\text{m}$  at  $\varepsilon_{\text{vm}} \sim 5.9$ , finally shortens to  $0.6 - 0.8 \mu\text{m}$  at ultrahigh strains of  $\varepsilon_{\text{vm}} > 10$ . Combining with the fact that magnitude of the standard deviations of the cementite size diminishes greatly with strain (Fig. 4A), the needle-shape cementite particles have been fragmented into small pieces by HPT. Distribution of the cementite particles inside the Fe-200 is examined by mean free path, one of the most frequently used definition to evaluate interparticle spacing in dispersion alloys, which is described as the average distance between the surfaces of particles along any random straight line in the material [26]. In the present study, Fullman's formula is used to calculate the mean free path  $\lambda$  [26]:

$$\lambda = \frac{1-F_v}{N_L} \quad (3)$$

where  $F_v$  is volume fraction of particles;  $N_L$  the number of particles per unit length on any straight line. From Fig. 4A, the free mean path between the cementite particles reduces over the HPT test, with a much higher rate at the low to medium strain, i.e.  $0 < \varepsilon_{\text{vm}} \leq 5.9$ ; the final mean free path is  $\sim 3.8 \mu\text{m}$  at the strain of  $\sim 28.7$ , nearly nine times lower than that in the initial state. This suggests the second-phase particles become more homogeneously distributed during HPT. The sharp decrease in  $\lambda$  at the beginning is also partly induced by the rapid reduction in sample thickness during the early stage of torsion (see Fig. 3A). Fig. 4B-D exhibit typical BSE morphology of the cementite under medium and ultrahigh strains, from which size and distribution change with strain can be easily seen.

Those observations are consistent with previous literatures on fragmentation and homogenization of the second-phase particles in two-phase alloys and composites subjected to HPT [19, 33, 34]. For instance, after 10 HPT revolutions of a Al-2%Fe alloy, the precipitates Al<sub>6</sub>Fe started being fractured and brought down the mean particle size from 240 nm to 130 nm, yet the size distribution still had a significant degree of scatter; after 1000 revolutions, further fragmentation decreased dramatically the large particles and rendered a relatively uniform distribution of nanometer-sized dispersoids with 40 nm in diameter [19].

However, the present result seems not following well early studies conducted by Ivanisenko et al. [35] who observed extensive dissolution of cementite in a pearlitic steel during constrained HPT process, resulting in a pure solid solution with a mean grain size of ~10 nm after 5 revolutions (corresponding to a shear strain of  $\gamma = 300$ ,  $\epsilon_{vm} \sim 173$ ). By contrast, in the present work, the volume fraction of cementite keeps constant throughout the strain span of 0 - 28.7. It appears controversial at first glance, yet discrepancies between those two studies regarding HPT process and materials account for it. First, unconstrained and constrained HPT were performed in the present study and Ivanisenko's work, respectively; compressive stress distribution during the former often declines much more significantly along radius with respect to that in the latter [36-38]. Coupling with the fact that a higher mean compressive pressure of 7 GPa (1 GPa in the present work) was applied in the constrained HPT, it permitted a higher shear strain of ~300. The lowest shear strain that the authors started to examine cementite dissolution was ~94, i.e.  $\epsilon_{vm} \sim 54$ , much higher than the maximum strain here. Therefore, it is possible that the strain here is not high enough to simulate dissolution of the cementite phase. Second, starting materials are different; Ivanisenko used a commercial pearlitic steel (0.8 wt%C) consisting of alternating nanolamellae of ferrite and cementite with widths of 210 nm and 40 nm, respectively, whereas in the present study only 0.02 wt%C is introduced into iron and its typical microstructure is equiaxed grains plus 0.3-0.4 vol% needle-shape cementite. The former promoted a high density of cell structures between cementite layers, which were later occupied by dissolved carbon atoms. However, such mechanism does not apply to the present material whose deformation modes will be examined in the following sections. In addition, even though strain-induced dissolution could possibly occur around the cementite particles, the diffusion path of the carbon atoms is too short to be detected by the present technique here. Indeed, using atom probe tomography (APT) technique, Sauvage and Ivanisenko found that dissolution-induced carbon

content increase ( $\leq 2$  at.%) in the adjacent ferrite extended by only  $\sim 8$  nm after straining to  $\varepsilon_{vm} \sim 36$  [39]. Therefore, it is reasonable to state that one important difference of the present work is cementite particles serving as second-phase particles throughout the HPT test.

### 3.2 Statistical measurements of the microstructural evolution during HPT

To achieve overview of grain refinements in the single-phase iron and particle-containing Fe-200, several grain characteristics with a function of strain were examined and presented in Fig. 5. No statistical data from lower strains ( $\varepsilon_{vm} < 2$ ) are reported here due to technical difficulties. According to initial grain sizes of the iron ( $\sim 1$  mm), Fe-200 ( $\sim 150$   $\mu\text{m}$ ), and the disk thickness prior to HPT (i.e. 500-530  $\mu\text{m}$ ), it is likely that the iron disk is a single crystal or contains few HABs, the Fe-200 disk comprises only 3-4 grains along the thickness. Therefore, small step sizes used for EBSD to identify subgrain boundaries often cover an area that is not large enough to obtain statistically reliable data of HABs. In addition, microstructural heterogeneity at low strains by HPT is not uncommon [27], which also has been widely observed in other SPD methods such as ECAP [40], suggesting one EBSD map is probably not representative. For those reasons, in the present study explicit microstructure observations focus on  $\varepsilon_{vm} \sim 2.6$  and beyond. In Fig. 5A, the grain thickness is the HAB intercept in normal direction. The average grain thickness of both iron and Fe-200 drops fast over low to medium strains and turns into relatively stable state at ultrahigh strains. However, the Fe-200 holds larger grains at low to medium strains yet is further refined to smaller grains during ultrahigh strains, leading to a grain size of  $\sim 120$  nm, around half of that in the iron (i.e.  $\sim 224$  nm). Accordingly, two important messages regarding effect of the cementite particles are delivered. First, Fe-200 effectively overcomes saturation microstructure that is seen in the single-phase iron subjected to HPT. Second, the cementite particles likely retard grain refinement at low strains. More details on deformation mechanisms of those two materials are examined and discussed in Sections 3.3-3.6. The steady-state grain size of the iron here agrees well with previous reports. For example, using automated crystal orientation mapping (ACOM) in transmission electron microscope, the average grain thickness of a high purity iron (99.99999%) after 1 turn of HPT was around 220 nm [27]. In another study, with dark-field images acquired from TEM, the average steady-state grain sizes of Fe (99.96% purity), Fe (99.94%) and Fe (99.88%) after 20 turns of HPT at room temperature were 350 nm, 340 nm, and 230 nm, respectively [22]. Those slightly higher values are probably

because their specimens were taken from  $r\theta$  planes that often display pancake-like grains, yet cross sections generally show elongated structure. Descartes et al. [27] investigated HPTed iron from both  $rz$  and  $r\theta$  planes using TEM and showed larger grain sizes from the  $r\theta$  view. It is important to mark that considering its much larger starting grain size, more drastic grain size reduction must have occurred at low strains of  $\varepsilon_{vm} < 2.6$  in iron. However, early state of grain refinement via plastic deformation has been well documented in the literature and will not be the focus of the current work [21, 41, 42].

Grain aspect ratios that manifest grain fragmentation during HPT were measured and their average values as a function of strain are plotted in Fig. 5B. It reduces rapidly in the Fe-200 from low to medium strains, achieving a low aspect ratio of 1.64 at  $\varepsilon_{vm} \sim 12.3$ , then keeps low throughout ultrahigh strains, i.e. 1.52 at  $\varepsilon_{vm} \sim 28.7$ . Nevertheless, for the iron, the aspect ratio starts decreasing from medium strain and it is as high as  $\sim 2.16$  at  $\varepsilon_{vm} \sim 12.9$ ; contrary to that in Fe-200, it declines fast at ultrahigh strains, ending up with  $\sim 1.23$  at  $\varepsilon_{vm} \sim 29.2$ . The first distinction between the two materials resides in the medium strain ( $\varepsilon_{vm} \sim 5-6$ ) where Fe-200 shows a bloom of small grains revealed by sharp reduction in the grain thickness (Fig. 5A) and length (i.e. aspect ratio in Fig. 5B), whereas iron is more on thinning of the grains (Fig. 5A-B). The second contrast is in the ultrahigh strain regime ( $\varepsilon_{vm} > 10$ ), where the iron undergoes a significant decrease in the aspect ratio, turning the elongated grains to equiaxed grains, while the aspect ratio of the Fe-200 grains keeps relatively constant.

Another important microstructure feature that controls grain refinement process is formation of HABs during HPT. According to large grain sizes obtained after heat treatment ( $\sim 1$  mm and  $\sim 150$   $\mu\text{m}$  for iron and Fe-200, respectively) and small areas of the EBSD maps ( $16 \times 15$   $\mu\text{m}$ ), it is reasonable to assume there are no original HABs caught by the EBSD scans, that is, HABs observed here are formed over HPT. As shown in Fig. 5C, for both materials, once undergoing HPT process, the HAB population surges to over 30% at a low strain of  $\varepsilon_{vm} \sim 3.0$ , and further escalates to around 80-85% when strain increases to  $\varepsilon_{vm} \sim 12-13$ , then keeps relatively stable and reaches the highest point of 90% at the maximum strains. This result is consistent with the high efficiency of forming HABs through HPT [5]. Zhilyaev et al. [43] processed pure nickel using HPT and ECAP and their orientation imaging microscopy (OIM) results showed that the HPT nickel had a larger amount of HABs ( $\sim 68.1\%$ ) than that ECAP nickel ( $\sim 60\%$ ). Despite the

similar trend shown in Fig. 5C, differences between the two materials are prominent. At low strain of  $\epsilon_{vm} \sim 3.0$ , the iron contains 41% of HABs, around 19% higher than that in the Fe-200, which agrees with its smaller grains at that moment (Fig. 5A). But with increase in strain, the Fe-200 generates HABs faster and possesses slightly higher HAB fractions. This is particularly true from low to medium strains, where the Fe-200 improved the HAB population by 50% yet only by 15% in the iron.

### 3.3 Microstructural evolution during HPT at low and medium strains

( $\epsilon_{vm} < 10$ )

Fig. 6 shows typical EBSD maps of the iron and Fe-200 at low and medium strains, i.e.  $\epsilon_{vm} \sim 2-3$  and  $\epsilon_{vm} \sim 5-6$ , from *rz* view. The figure also displays their corresponding grain boundary misorientation distributions at each strain level. In Fig. 6A-C, the iron deformed to  $\epsilon_{vm} \sim 2.6$  and  $\epsilon_{vm} \sim 5.3$  consists predominantly of subgrains and elongated crystallites with their long axis parallel to *r*. It is important to note that HPTed microstructures were not deformed under pure shear but multiple strain components that may be activated due to compression, shear, as well as sliding between the anvil and the samples. Hence, HPT microstructure is distinct from those processed by classic torsion [44]. Fig. 6A-B also depict strain inhomogeneity regions in the iron, and they appear more frequently with strain, showing as possible deformation bands that are 15-25° to *r*. Interestingly those regions often involve new small grains that are elongated and have a mean grain thickness of  $\sim 290$  nm, which is the same length scale as the subgrain thickness i.e.  $\sim 290$  nm. This suggests the new HABs are originated from subgrain boundaries and evolved into HABs in the strain inhomogeneity regions where higher strain, higher strain rate, and higher strain gradient are introduced [20, 45]. Increased strain inhomogeneity regions at  $\epsilon_{vm} \sim 5.3$  bring more refined grains, which are responsible for the decrease in the mean HAB intercept (Fig. 5A) and increase in HAB frequency (Fig. 5C). The above observations demonstrate that although formation of subgrains is dominant, strain inhomogeneity is critical for grain refinement at low and medium strains in the single-phase iron.

The cementite-containing Fe-200, however, shows distinct features on microstructural refinement after deformed to similar strains by HPT. In Fig. 6D, at  $\epsilon_{vm} \sim 3.0$ , the Fe-200 deforms more homogeneously throughout the sample via formation of subgrains, resulting in a high

fraction of the 2.5-degree boundary and a large percentage of low angle boundaries (LABs) (~67%) (Fig. 6F top). Unlike the substructures in iron, the subgrains here are less elongated and the mean subgrain thickness is around 400 nm. Newly formed HABs are aligned parallel to  $r$ , and only few new grains are formed. Therefore, presence of the cementite precipitates effectively prevents strain inhomogeneity and formation of HABs at a low strain of  $\varepsilon_{vm} \sim 3.0$ . However, with strain increases to  $\varepsilon_{vm} \sim 5.9$ , as shown in Fig. 6E, substantial grain refinement takes place, showing as clusters of fine grains with a mean grain thickness of  $\sim 300$  nm. Microstructures outside the clusters are abundant with subgrains that are approximately 340 nm in thickness. The refined grains and subgrains are relatively equiaxed. This microstructure evolution contributes to a drop in LABs and an increase in HABs (Fig. 6F). Grain refinement taking place selectively in the sample is related to size and distribution of the cementite precipitates, which is around 1.3  $\mu\text{m}$  in length and a mean free path of roughly 7  $\mu\text{m}$  at this strain level (Fig. 4A). It has been widely acknowledged that during SPDs, grain refinement often started near the second-phase particles and then extended outwards, hence the finest grains were observed in the vicinity of particle clusters [13, 46]. Size of the refined clusters is roughly 4-5  $\mu\text{m}$ , slightly lower than the mean free path  $\lambda$ , which could be because the precipitates are not homogeneously distributed yet (Fig. 4B) and grain refinement occurs preferentially between adjacent particles that are close to each other. In addition, similar size and morphology between the new grains and the subgrains indicate that those HABs are likely transformed from earlier subgrain boundaries.

Microstructures are observed more closely by Kernel average misorientation (KAM) maps that provide local average misorientation angle at each pixel of an EBSD map [47]. Indeed, it is directly related to geometrically necessary dislocation (GND) densities introduced by plastic deformation [48]. The selected areas are indicated by rectangles in Fig. 6 and they include typical features observed above such as strain inhomogeneity in iron and refined cluster in Fe-200. From Fig. 7, the single-phase iron displays subgrain boundaries and GNDs in the grain interiors, as well as thick boundaries (marked by white arrows) that are possibly associated with cell blocks; while the Fe-200 forms well-defined subgrain with sharp boundaries. That indicates for the Fe-200, GNDs have been condensed into grain/subgrain boundaries. Local misorientation distributions plotted in Fig. 7E exhibit majority of the substructures in iron have a high local misorientation of  $0.32^\circ$ - $0.37^\circ$ , yet it is only  $\sim 0.17^\circ$  in Fe-200. Therefore, the fine grains produced

in iron at early state of HPT are attributed to the higher density of GNDs that are likely to form subgrain boundaries.

The above contrast between the iron and Fe-200 demonstrates the needle-shape cementite particles are not able to pin dislocations and prevent dislocation consolidation like the finely spaced nano-precipitates often do [12, 16]. For instance, when a dispersion Al-0.2Sc alloy and a single-phase Al-0.1Mg alloy were subjected to ECAP to a strain of  $\varepsilon_{vm} \sim 2$ , a large amount of cell blocks and a high dislocation density were observed in the former due to pinning effect of  $Al_3Sc$  precipitates, yet well-defined subgrain boundaries were in the latter [12]. Distinct features associated with size and distribution of the particles could explain the disagreement. In [12], the  $Al_3Sc$  particles were more or less round and around 20 nm in diameter,  $\sim 100$  nm spacing, leading to a finer inter-particle spacing than the matrix natural cell size (i.e. over 1  $\mu m$  for a single-phase aluminum alloy). In the present work, however, inter-particle spacing of the needle-shape cementite particles is 7  $\mu m$ , much larger than the subgrain size (i.e.  $\sim 340$  nm) at this strain level.

### **3.4 Microstructural evolution during HPT at ultrahigh strains ( $\varepsilon_{vm} > 10$ )**

Once entering ultrahigh strains ( $\varepsilon_{vm} \sim 10$ ), both the single-phase iron and cementite-containing Fe-200 undergo considerable grain refinement and homogenization, leading to uniformly distributed ultrafine grains that keep relatively stable with further increase in strain. From  $rz$  plane shown in Fig. 8A, the iron microstructure evolves into ultrafine grains with a mean grain thickness of  $\sim 224$  nm, which is about the same thickness as its subgrains that mainly exist in the relatively large grains. Considering the sample thickness reduced from  $\sim 276$   $\mu m$  to  $\sim 216$   $\mu m$  over this period (Fig. 3A), the subgrains at  $\varepsilon_{vm} \sim 5.3$  ought to be thinned to  $\sim 226$  nm from  $\sim 290$  nm, which matches well the measured grain thickness at  $\varepsilon_{vm} \sim 13.0$  (i.e.  $\sim 224$  nm). This suggests grains are thinned by a combination of sample thickness reduction and transformation of previous subgrain boundaries into grain boundaries; no additional new grain boundaries along  $r$  is formed from  $\varepsilon_{vm} \sim 5.3$  to  $\varepsilon_{vm} \sim 13.0$ . Such grain thinning with sample thickness can be considered as a mere result of grain boundary convection, that is commonly observed when a polycrystal is deformed at room temperature where grain boundary mobility is negligible, grain and subgrain boundaries move due to movement of the material [49]. Moreover, the refined grains remain elongated yet with a much lower aspect ratio of around 2.16 compared to that at lower strains (e.g. 3.22 at

$\varepsilon_{vm} \sim 5.3$ ). This demonstrates fragmentation of elongated grains is an important refinement process during straining from  $\varepsilon_{vm} \sim 5.3$  to  $\varepsilon_{vm} \sim 13.0$ . Due to substantial decrease in LABs and increase in HABs during this deformation (Fig. 8C top and Fig. 6C bottom), we believe fragmentation could take place through transforming some of those subgrain boundaries to grain boundaries. Meanwhile, continuous formation of subgrain boundaries and grain boundaries that are parallel to  $z$  axis also occurs to bring down the aspect ratio.

At the maximum strain  $\varepsilon_{vm} \sim 29.2$ , in Fig. 8B, the grain thickness keeps constant at  $\sim 224$  nm, regardless of the sample thickness continuously decreases from  $\sim 216$   $\mu\text{m}$  to  $\sim 157$   $\mu\text{m}$  (Fig. 3A), which implies the transverse thickness of the grains has reached steady state. However, the average aspect ratio reduces remarkably to  $\sim 1.23$ , which is likely driven by converting LABs that divide the elongated grains at  $\varepsilon_{vm} \sim 13.0$  to HABs. This process is consistent with the increased HAB fraction (i.e. 88%) shown in Fig. 8C bottom, where the misorientation profile is approaching a random distribution [50]. For those reasons, we believe the single-phase iron has attained steady state at a strain of  $\varepsilon_{vm} \sim 29.2$ , which confirms the statistical observations in Section 3.2.

The cementite-containing Fe-200, however, achieves ultrafine grains via a different approach. From Fig. 8D, at  $\varepsilon_{vm} \sim 12.6$ , the grains are refined to  $\sim 190$  nm in thickness (along  $z$  axis), and an aspect ratio of  $\sim 1.64$ , both of which are lower than those of iron deformed to a similar strain (Fig. 8A). Such microstructure leads to a higher fraction of HABs (i.e. 85%) and a higher population of HABs around the misorientation of  $\sim 45^\circ$  (Fig. 8F&C top). The more refined microstructure from  $\varepsilon_{vm} \sim 5.9$  to  $\varepsilon_{vm} \sim 12.6$  demonstrates grain refinement that starts from vicinity of cementite particles has been extended throughout the specimen by evolving subgrain boundaries to grain boundaries, as well as continuous formation of new subgrain and grain boundaries. Thickness of the refined grains is about the same size as that of the subgrains. This agrees well with previous observation on how grain refinement proceeded in a metal matrix composite of Al-SiC under HPT [46]. In addition, when following the above approach to examine the role of sample thickness reduction, grains inside the refined clusters at  $\varepsilon_{vm} \sim 5.9$  should be further thinned to  $\sim 246$  nm, which is much larger than the measured value here. This is distinct from that observed in the single-phase iron at a similar strain and it indicates additional



new grain boundaries parallel to  $r$  direction are significant from  $\varepsilon_{vm} \sim 5.3$  to  $\varepsilon_{vm} \sim 12.6$  in the Fe-200.

When strain increases to  $\varepsilon_{vm} \sim 28.7$ , the microstructure is further refined, leading to an average grain thickness of  $\sim 120$  nm, 40-50% smaller than the iron microstructure at  $\varepsilon_{vm} \sim 29.2$ . This illustrates the cementite particles help to overcome the grain refinement limit observed in pure iron. In the meantime, the average aspect ratio of the grains reduces slightly from  $\sim 1.64$  to  $\sim 1.52$ , indicating fragmentation of the elongated grains continues during this period. The role of sample thickness reduction was examined, and it indicates the grain thickness should be  $\sim 166$  nm, higher than the actual value, suggesting extra new grain boundaries along  $r$  continue to form in the ultrahigh strain regime. In Fig. 8F, the distribution of grain boundary misorientations is comparable to Mackenzie plot. Even though the grain sizes keep decreasing so that we could not directly identify whether the current microstructure has entered steady state, the grain boundary misorientation may give a clue. Wetscher and Pippan [51] deformed nickel using HPT up to an accumulative strain of 64, and they found the grain boundary misorientation distribution approached Mackenzie plot and no further shift to higher misorientation angles. Ivanisenko et al. [52] applied OIM to Armco iron after strained to  $\gamma=210$  and 420 ( $\varepsilon_{vm} \sim 121$  and 242, respectively) by HPT; the grain boundary misorientation spectra between  $2.5^\circ$ - $62.5^\circ$  displayed a Mackenzie-like distribution and the highest HAB fraction achieved was  $\sim 86\%$  ( $\sim 50\%$  stated in [52] due to inclusion of the boundaries less than  $2^\circ$ ). Hence, the high fraction of HABs (i.e. 91%) and Mackenzie-like distribution of GB misorientations obtained in the present work demonstrate the Fe-200 microstructure at  $\varepsilon_{vm} \sim 28.7$  should be close to, if it does not enter, the steady state.

Fig. 9 shows typical microstructures of the single-phase iron and cementite-containing Fe-200 by KAM maps of small areas that are randomly selected from Fig. 8. Comparing to that at lower strains (Fig. 7), the local misorientation at ultrahigh strains appears homogeneous in the grain interiors, indicating relatively homogeneous distribution of GNDs. From Fig. 9A-B, the iron exhibits similar features at  $\varepsilon_{vm} \sim 13.0$  and 29.2, which is confirmed by their misorientation plots (Fig. 9E) that show an identical peak value at  $0.38^\circ$ . It is worth to note that higher local misorientation values often show up at subgrain boundaries, indicated as arrows in Fig. 9. Remarkably, the cementite-containing Fe-200 at  $\varepsilon_{vm} \sim 12.3$  generates a high density of large local misorientation that is uniformly distributed in the grain interiors (Fig. 9C). This contributes to the

significant shift of misorientation distribution to high angles, as seen in Fig. 9E. Apparently, it is the cementite particles that trigger substantial GND formation at  $\varepsilon_{vm} \sim 12.3$ . However, they are cleaned up with further strain to  $\varepsilon_{vm} \sim 28.7$ , bringing the misorientation distribution back to smaller angles (Fig. 9D-E). Therefore, those GNDs at  $\varepsilon_{vm} \sim 12.3$  are condensed into subgrain boundaries to convert them to grain boundaries, leading to further refined grains at  $\varepsilon_{vm} \sim 28.7$ .

### **3.5 Ultrahigh-strained microstructures observed from $\theta z$ plane using TKD-EBSD**

More features of microstructures at ultrahigh strains are revealed by using TKD-EBSD technique from  $\theta z$  planes that provide distinguish characteristics regarding grain elongation, fragmentation, as well as possibility of texture formation. Fig. 10 shows EBSD maps of the single-phase iron at strains of  $\varepsilon_{vm} \sim 13.0$  and  $\sim 29.2$ , that comprise elongated grains with long axis parallel to the shear direction  $\theta$  and an average grain thickness of  $\sim 135$  nm and  $\sim 121$  nm, respectively. Apparently, the grain thickness measured from TKD-EBSD maps is lower than those from conventional EBSD (e.g. 121 nm vs. 224 nm at  $\varepsilon_{vm} \sim 29.2$ ), which is mainly due to difference in spatial resolution of those two techniques. It has been demonstrated in a number of publications that spatial resolution of TKD-EBSD is in a range of 2-10 nm, which is approximately an order of magnitude better than conventional EBSD [53, 54]. Therefore, some small grains with a few tens of nanometers and less are not indexed by the conventional EBSD technique, resulting in higher values. Even so, the general trend derived from both techniques is similar, i.e. the grain thickness of the single-phase iron keeps relatively constant after entering the ultrahigh strain regime. In this section, focus is on grain boundary characteristics and texture analysis.

An interesting feature, as shown in the rectangles, is formation of equiaxed grains by grain boundary impingement, known as geometric dynamic recrystallization (GDRX). This is a model introduced by McQueen and it has been successfully applied to interpret microstructural refinement by conventional hot rolling and torsion [55-57]. In Fig. 10A, four grains with  $\langle 001 \rangle // z$  crystal orientation are formed by this mechanism, where the serrated grain boundaries pinch off when they get in contact. Those grains are often equiaxed. With increase in strain, Fig. 10B shows some grains with their opposite grain boundaries serrated and pushed close to each other. Fine grains by pinching off of serrations are found, yet most grain boundaries are straight

with no evidence of forming serration. Therefore, GDRX does not dominate in the pure iron during HPT and hence majority of the grains are highly elongated. Fig. 10C shows {110} pole figure of the final microstructure, where  $\theta$  is shear direction and  $z$  is normal direction. Given that the maximum intensity is 3.93 in the pole figure, the present microstructure can be identified as randomly distributed grain orientations.

Fig. 11 shows grain orientation maps of the cementite-containing Fe-200 at  $\varepsilon_{vm} \sim 12.3$  and 28.7 from  $\theta z$  plane. The microstructures are characteristic of elongated grains with the long axis parallel to the shear direction  $\theta$ . Compared to iron, Fe-200 possesses much finer grains, with the grain thickness of  $\sim 100$  nm at  $\varepsilon_{vm} \sim 12.3$  and  $\sim 88$  nm at  $\varepsilon_{vm} \sim 28.7$ . Again, the lower values than those from conventional EBSD are due to nature of the two techniques. As grains have been significantly thinned, a lot of small grains are obtained by grain boundary impingement and it is more prevalent with increase in strain. From Fig. 11A, those small grains are often ranging from 30-80 nm in thickness, with a mean value of around 50 nm, which is half of the overall average grain thickness, i.e. 100 nm. The serrated grain boundaries approach to each other during thinning of the grains until opposite serrations meet and pinch off, resulting in refinement of the microstructure. With straining to  $\varepsilon_{vm} \sim 28.7$ , more grains are extremely thinned, as seen in Fig. 11B, which promotes more grain boundary impingement and thus a higher number of small grains. Based on the above observations, GDRX is a crucial process to fragment the strongly elongated microstructure along the primary shear direction in Fe-200. It is worth to note that, to the authors' knowledge, it is for the first time that GDRX was experimentally observed as an important grain refinement mechanism during HPT, thanks to the EBSD characterizations from multiple views as well as the high resolution TKD-EBSD technique. In Fig. 11C, the {110} pole figure of the Fe-200 at the strain of  $\sim 28.7$  indicates even a weaker texture than iron at a similar strain (Fig. 10C), demonstrating that cementite particles further facilitate randomization of texture formation during HPT.

A requirement for GDRX to occur is that grain thickness has to be thinned to a critical value which is of the order of subgrain size [55-57]. Even though in the pure iron at  $\varepsilon_{vm} \sim 13.0$  and  $\sim 29.2$ , the subgrain sizes measured along shear direction  $\theta$  are  $\sim 250$  nm and  $\sim 150$  nm, respectively, higher than the grain thickness, GDRX is not observed frequently. That suggests the above critical condition is a necessary but not a sufficient criterion for formation of ultrafine

grains via GDRX. Similar discovery was also reported in Al-Mg alloys subjected to conventional plane strain compression and rolling, in which formation of equiaxed micron-scale grains by GDRX was determined by not only strain but also processing temperature [56]. A lower limit to the processing temperature was imposed to ensure adequate mobility of grain boundaries to form serrations, yet an upper limit is imposed to eliminate grain growth, resulting in a severely restricted processing window [56]. For the present high-purity iron (i.e. <15 ppm carbon), the grain boundaries in the deformed sample are likely super mobile even at room temperature, evidenced by that steady state has been reached in the ultrahigh strain regime and it contains a constant HAB fraction of ~76% (measured from  $\theta_z$ ). As a result, grain refinement by grain boundary impingement is not favourable. However, in the case of Fe-200 at ultrahigh strains, the concurrence of grain thinning (i.e. from ~100 nm to ~88 nm) and sample thickness reduction (i.e. from 250  $\mu\text{m}$  to 217  $\mu\text{m}$ ) by a similar amount of ~12% demonstrates low mobility of the grain boundaries. This leads to a significant increase in HABs at the maximum strain of  $\epsilon_{\text{vm}} \sim 28.7$ , i.e. from 76% to 84%. Meanwhile, grain boundary serrations are not prevented by the cementite particles (Fig. 11B). That is likely due to the coarse particle size (i.e. ~0.8  $\mu\text{m}$  in length) and low density ( $\lambda \sim 3.8 \mu\text{m}$ ). Blum et al. [55] found similar behaviour in an Al-Mg-Mn alloy containing coarse  $\text{Al}_6\text{Mn}$  particles during hot torsion, in which GDRX proceeded without prohibition of the particles against grain boundary serration, very much like in the particle-free Al-Mg alloy. Therefore, GDRX becomes an important grain refinement mechanism in the Fe-200 at ultrahigh strains.

Remarkably, the GDRX occurred here during HPT that was conducted at room temperature is distinct from that during conventional thermomechanical processes. In the latter, GDRX is often active at low strains to fragment the initial grains [55, 57]. During hot deformation, original grain boundaries are highly mobile and they progressively serrated while grains are flattened or elongated. Meanwhile, subgrains form and when the grain thickness reduces to about one to two times the subgrain size, the serrated grain boundaries start coming into contact and eventually pinch off. Nevertheless, during the HPT here, grain refinement through GDRX mechanism was only found at ultrahigh strains ( $\epsilon_{\text{vm}} > 10$ ) and it becomes more significant with increase in strain. Moreover, grain thickness here appears lower than the subgrain size, and pinching off of grain boundaries requires strong grain thinning. The disparate characteristics are believed to be originated from mobility of grain boundaries. In hot working, elevated temperature initiates

mobile grain boundaries that then form serrations with a high magnitude; while large strains imposed by HPT at room temperature enable to bring low-mobility boundaries close to each other by extremely thinned grains.

### **3.6 Influence of cementite particles on grain refinement mechanisms**

Based on the comprehensive observations on microstructural evolution from both  $r_z$  and  $\theta_z$  views, grain refinement mechanisms of the single-phase iron and cementite-containing Fe-200 are shown of great contrast due to the presence of cementite particles. In this section, deformation mechanisms of those two materials during HPT are discussed, based on which how cementite particles facilitate the further grain refinement is revealed.

For both single-phase iron and cementite-containing Fe-200, the major mechanism to form the ultrafine grains is consistent well with continuous dynamic recrystallization (CDRX) model. This model was originally introduced to describe microstructural refinement of high stacking fault energy metals, such as aluminum and ferritic steels, submitted to high temperature deformations like pure torsion, rolling and uniaxial compression [58-60]. The essence of CDRX is that dislocations produced by strain hardening accumulate progressively into subgrain boundaries (i.e. LABs), which transform the LABs into HABs gradually [60]. According to microstructural observations in Sections 3.3 and 3.4, this is particularly true for both materials before ultrahigh strains. Prevalent formation of subgrain boundaries and progressive transformation to grain boundaries are essential deformation mechanism. However, at low and moderate strains, the iron shows slight greater ability to produce GNDs and to convert subgrains to grains in strain inhomogeneity regions, leading to more refined grains. Fe-200, on the other hand, manifests a much higher capacity to generate GNDs at an ultrahigh strain of  $\varepsilon_{vm} \sim 12.3$  (Fig. 9C), leading to drastic formation of substructures and later transformation to grains. Coarse second-phase particles facilitating grain refinement during SPDs is not surprising. Apps et al. [13] explored explicitly in an AA8079 aluminum alloy that particles of  $\sim 2 \mu\text{m}$  in diameter helped to achieve UFGs at an effective strain of around 5, much lower than that of 10 in a single-phase Al-0.13% Mg alloy under an identical ECAP processing. Underneath an oscillatory sliding wear contact of a WC-reinforced copper matrix composite, where materials underwent severe shear and compression stresses, a stable layer of nanolamellae  $\sim 20 \text{ nm}$  in width was formed due to

participation of the WC fragments [18]. Those second-phase particles effectively raised strain gradient around themselves to maintain deformation compatibility, leading to a high density of GNDs that readily to form cells and subgrains. That could also interpret greater grain refinement here in the Fe-200.

At ultrahigh strains, CDRX continues to operate in Fe-200 (Fig. 8D-E), but GDRX was found to play an important role in grain refinement (Fig. 11). Strongly elongated grains are fragmented appreciably via GDRX, yet the single-phase iron remains heavily elongated without GDRX occurring prevalently. As discussed in Section 3.5, that is associated with reduced mobility of grain boundaries in Fe-200. In addition, although a random texture of iron is generated by HPT after an ultrahigh strain of  $\varepsilon_{vm} \sim 30$ , an even more random texture is produced in Fe-200 due to the presence of cementite particles.

### **3.7 Mechanical properties of iron and Fe-200 processed by HPT**

Fig. 12A-B plot hardness distribution along radius from center of the disks rotated to  $90^\circ$ ,  $180^\circ$  and  $360^\circ$ . For both iron and Fe-200, at lower rotation angles of  $90^\circ$  and  $180^\circ$ , the hardness firstly increases along the radius, then starts declining when it enters the sliding zones and beyond. After a rotation of  $360^\circ$ , the hardness reaches the highest and keeps approximately constant along the radius in the adhesion zone. Such hardness evolution is typical for metallic materials processed by unconstrained HPT [61]. Apparently, the hardness increases with a higher rate in the cementite-containing Fe-200 than that in the iron at an identical rotation angle. Their strengthening mechanisms are examined through the selected microstructures observed in the previous sections.

Fig. 12C plots hardness values of interested microstructures, marked in Fig. 12A-B, against equivalent von Mises strains. For both materials, hardness increases with strain more rapidly before it arrives  $\varepsilon_{vm} \sim 12-13$ , then raises in a relatively lower rate, with the iron much slower than Fe-200. Fe-200 displays higher hardness than iron at all strain levels. Fig. 12D plots hardness versus inverse root square of the grain sizes. Here, equivalent diameters of the elongated grains are applied. The HPTed iron and Fe-200 follow Hall-Petch relationship well and they share the same slope (see the two dashed lines). That indicates grain refinement and grain boundary strengthening are mainly responsible for the hardness increase introduced by HPT. Indeed, grain

boundary strengthening was also found predominant in HPT-processed irons with various purity levels [22]. In Fig. 12D, contrast between the two materials resides in the higher hardness of Fe-200 for a given grain size. This could be mainly due to dispersion strengthening by the cementite particles. Because volume fractions of the cementite particles keep almost constant throughout HPT, the extra hardness initiated by them does not change with grain size. Solid solution strengthening can be ruled out given that almost all carbon atoms are in the form of cementite here. Thus, the matrix of Fe-200 shows the same hardness as iron prior to HPT (i.e. ~3 GPa); their hardness values are revealed from the extruded material after 90° rotation (see Fig. 12A and 12B). Hardening yielded by GNDs is not principal and could not interpret the result, especially considering iron holds higher GND densities than Fe-200 at low and medium strains (Fig. 7). It is also important to note that it is still challenging to precisely quantify GND densities by existing techniques [22].

Uniaxial compression of micropillars were carried out on the microstructures deformed to ultrahigh strains. Typical dimensions of the pillars (Fig. 13C) that were milled from the  $rz$  cross sections demonstrate it includes at least 20-40 grains, sufficient to avoid influence of local heterogeneity such as grain orientations, and hence can be representative of the material. Fig. 13 shows true stress-strain curves extracted from micropillar compression tests and typical morphologies of those pillars under compression. Yield strength here is defined as stress at a strain of 2% ( $\sigma_{0.02}$ ), following which the iron at  $\epsilon_{vm} \sim 13.0$  and  $\epsilon_{vm} \sim 29.2$  owns a yield strength of 1.10 GPa and 1.05 GPa, respectively, and the Fe-200 strained to  $\epsilon_{vm} \sim 12.3$  and  $\epsilon_{vm} \sim 28.7$  possesses a yield strength of 1.14 GPa and 1.37 GPa, respectively. The iron microstructures show similar yield strength, which is likely due to their similar microstructure size (Fig. 5A and Fig. 8A-B). Higher yield strength of Fe-200, especially at the highest strain, can be interpreted by their finer microstructures (Fig. 5A, Fig. 8D-E). Dispersion strengthening induced by cementite precipitates probably plays a role as well. From Fig. 13D-F, during compression, deformation instabilities may appear on the pillar surfaces and initiate material weakening and eventual failure. But the pillar of the most refined Fe-200 deforms homogeneously during compression (Fig. 13G). Contrast between the two deformation modes is not sharp here. It is worth to note that the anisotropy of HPT-processed microstructure may have an impact on micropillar compression as well. However, because most materials examined in literature were

homogeneous [62], how microstructural anisotropy affects uniaxial microcompression is still an open question.

## 4 Conclusions

Ultrafine grains are produced in the single-phase iron and cementite-containing Fe-200 using unconstrained HPT, based on which their deformation mechanisms and the additional grain refinement induced by cementite particles are evaluated. The microstructures are refined through both CDRX and GDRX. Their deformation mechanisms and mechanical properties are summarized as follows.

- An addition of a low density (0.3-0.4 vol%) of cementite particles enables to overcome saturation microstructure that is often encountered in pure metals subjected to HPT, and further brings down the HAB intercept from ~224 nm to ~120 nm.
- For both iron and Fe-200, the substantial microstructural refinement before an ultrahigh strain of  $\varepsilon_{vm} \sim 12$  is predominantly progressed by CDRX.
- At low and moderate strains, the iron shows slight greater ability to produce GNDs and form HABs through strain inhomogeneity, leading to finer grains. However, the Fe-200 exhibits a much higher capacity to generate GNDs when entering ultrahigh-strain regime at  $\varepsilon_{vm} \sim 12.3$ , contributing to dramatic formation of substructures that later transform to grains.
- During ultrahigh strains of  $\varepsilon_{vm} \sim 12-30$ , GDRX plays an important role in grain refinement from  $\theta_z$  plane in the Fe-200. Grain boundary impingement of the heavily elongated grains results in finer grains with thickness of ~80 nm. That is likely associated with their low grain boundary mobility.
- Both iron and Fe-200 deformed to ultrahigh strains by HPT exhibit as random textures, and cementite particles help to further randomize the texture.
- The most important strengthening mechanism of HPT-processed microstructures is grain refinement and grain boundary strengthening. That applies to both hardness and yield strength measurements.



## Acknowledgements

The authors are grateful to Claude Varillon at the Ecole des Mines of Saint-Etienne for preparation of the high purity iron and Fe-0.02%C. Y. Zhang gratefully acknowledge Lionel Lafarge (INSA Lyon), and Marilyne Mondon and S. G. Insardi (Ecole des Mines of Saint-Etienne) for technical assistance. Y. Zhang is grateful especially to useful discussion with Dr. D. Piot (Ecole des Mines of Saint-Etienne).

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**Figure captions:**

**Fig. 1** (A) SEM micrograph of Fe-200 after heat treatment, showing cluster of the 2<sup>nd</sup> phase particles; (B) and (C) Morphology of the 2<sup>nd</sup> phase particles at grain boundaries and grain interiors, respectively; (D) EDX tests on the 2<sup>nd</sup> phase particles and on the matrix.

**Fig. 2** (A) A typical top-down view of a disk after an HPT test, which results in three distinct regions: adhesion zone, sliding zone and extruded material. The dashed lines indicate area this is in contact with the anvil at the end of torsion. (B) shows a closer view of the surface characteristics of adhesion and sliding zones. (C) A schematic illustration of principal directions for an HPT-processed specimen, where the observation planes of rz and  $\theta z$  are exhibited.

**Fig. 3** (A) Evolution of torque and sample thickness of Fe and Fe-200 during HPT test with a rotation angle of 360°. (B) Their stress-strain curves during HPT derived from the Fields and Backofen method.

**Fig. 4** (A) Evolution of cementite length and distribution with strain; (B) (C) and (D) are BSE micrographs exhibiting typical morphology of cementite at different strain levels.

**Fig. 5** Evolution of the average transvers grain boundary intercept (A), grain aspect ratio (B), and HAB fractions (C) of iron and Fe-200 with strains processed by HPT

**Fig. 6** EBSD grain boundary + band contrast maps of iron at  $\epsilon \sim 2.6$  (A) and 5.3 (B), (C) top and bottom show, respectively, their grain boundary misorientation distributions. The white lines in (A, B) indicate strain inhomogeneity regions. EBSD grain boundary + band contrast maps of Fe-200 at  $\epsilon \sim 3.0$  (D) and 5.9 (E), (F) top and bottom show, respectively, their grain boundary misorientation distributions. The black lines in (A, B, D, E) are HABs ( $\geq 15^\circ$ ), while the red lines

are LABs ( $2^{\circ}$ - $15^{\circ}$ ). The solid lines in (C, F) plot misorientation distribution of a random texture. The rectangles mark typical features of the microstructures and are observed more closely later.

**Fig. 7** KAM maps of iron at  $\varepsilon \sim 2.6$  (A) and  $\varepsilon \sim 5.3$  (B), and Fe-200 at  $\varepsilon \sim 3.0$  (C) and  $\varepsilon \sim 5.9$  (D) taken from the areas marked by rectangles in Fig. 6; (E) plot of local misorientation distributions. The black lines in (A-D) are high angle grain boundaries. The white solid lines in (A) and (B) represent strain inhomogeneity regions. The arrows indicate possible diffusive cell structures.

**Fig. 8** EBSD grain boundary + band contrast maps of iron at  $\varepsilon \sim 13.0$  (A) and  $29.2$  (B); (C) top and bottom shows, respectively, their grain boundary misorientation distributions. EBSD grain boundary + band contrast maps of Fe-200 at  $\varepsilon \sim 12.3$  (D) and  $28.7$  (E); (F) top and bottom shows, respectively, their grain boundary misorientation distributions. The black lines in (A) and (B) are HABs ( $\geq 15^{\circ}$ ), while the red lines are LABs ( $2^{\circ}$ - $15^{\circ}$ ). The solid lines in (C) and (F) plot misorientation distribution of a random texture.

**Fig. 9** KAM maps of iron at  $\varepsilon \sim 13.0$  (A) and  $\varepsilon \sim 29.2$  (B), and Fe-200 at  $\varepsilon \sim 12.3$  (C) and  $\varepsilon \sim 28.7$  (D). (E) a plot of local misorientation distributions. The black lines in (A-D) indicate HABs.

**Fig. 10** EBSD maps of iron at  $\varepsilon \sim 13.0$  (A) and  $\varepsilon \sim 29.2$  (B) from  $\theta z$  plane obtained by TKD-EBSD. (C) is  $\{110\}$  pole figure of (B). The black lines in the EBSD maps mark HABs ( $\geq 15^{\circ}$ ), the white lines LABs ( $2^{\circ}$ - $15^{\circ}$ ). The dashed line rectangles mark evidences of GDRX.

**Fig. 11** EBSD maps of Fe-200 at  $\varepsilon \sim 12.3$  (A) and  $\varepsilon \sim 28.7$  (B) from  $\theta z$  plane obtained by TKD-EBSD. (C) is  $\{110\}$  pole figure of (B). The black lines in the EBSD maps mark HABs ( $\geq 15^{\circ}$ ), the white lines LABs ( $2^{\circ}$ - $15^{\circ}$ ). The dashed line rectangles mark evidences of occurrence of GDRX. The white arrows indicate cementite particles.

**Fig. 12** Hardness distribution of iron (A) and Fe-200 (B) from center of the disk towards the edge. The arrows indicate locations of the interested microstructures. (C) Hardness of the interested microstructures plotted against their equivalent von Mises strains; (D) hardness versus inverse square root of grain size (i.e. equivalent diameter) of the interested microstructures.

**Fig. 13** True stress-strain curves of HPTed iron microstructures (A) and Fe-200 microstructures (B) obtained from micropillar compression; (C)-(G) are characteristic morphology of the initial pillar and those during compression.





























