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High temperature deformation behavior of bulk cementite produced by mechanical alloying and spark plasma sintering

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Abstract

Using the bulk cementite samples produced by mechanical alloying and spark plasma sintering technique, high temperature deformation behaviors of cementite were studied. To avoid decomposition at high temperature, 5 at.% Mn alloyed cementite ($(Fe_{0.95}Mn_{0.05})_3C$) was mostly used. Brittle fracture was observed in the bulk cementite when deformed at a high strain rate at elevated temperatures (studied up to 1273 K). However, compression strain (this true strain larger than 2) was observed at around A_1 temperature (1000 K) at stresses in the range of 100–150 MPa. Specimens were deformed without cracks and without change in hardness. After this superplastic flow, grains are slightly elongated and grain growth was observed. It was demonstrated that the bulk cementite sheets can be deformed cooperatively with low carbon steel sheets and fine layered cementite/low carbon steel laminates could be fabricated by superplastic deformation. As a possible deformation mechanism of lamellae cementite in pearlite, grain boundary sliding was proposed.

Keywords: Cementite; Mechanical properties; Superplasticity; Mechanical alloying MA; Pearlite

1. Introduction

Cementite is one of the most important phases in steels, which plays a critical role in mechanical properties of steels. As a basic phase in steels, the understanding of its mechanical and physical properties is particularly desired. However, since cementite is metastable at all temperatures with respect to graphite and its saturated solution in iron, it is difficult to fabricate single phase cementite specimens with reasonable size for mechanical test. Cementite is known to be substantially harder than ferrite and quite brittle. When cast irons are deformed, large blocks of cementite (either eutectic of hypereutectic) fracture into fine pieces. On the other hand, cementite lamellae in fine pearlite deform plastically during rolling [1] or wire drawing [2]. This change in mechanical behavior of cementite is not well understood. Several reports about mechanical properties of cementite in a ferrite matrix or electrolytically extracted from steels or cast irons have been published [3–7]. However, large errors were inevitable due to the influence of matrix or its small size. As a high temperature deformation, superplastic flow was observed in the cementite base materials (80 vol.% cementite) produced from gas atomized powders [8]. However, high temperature deformation behavior of single phase cementite materials remains to be studied. In our previous study, large bulk cementite samples were successfully fabricated by mechanical alloying (MA) and spark plasma sintering (SPS) method [9]. Various properties of the produced bulk cementite were measured and reported [9–11].

The purpose of the present study is to investigate the change in the deformation mode of cementite from brittle to ductile with temperature, stress and strain rate. The bulk cementite samples were deformed below and above the A_1 temperature by swaging and compression test. Superplastic flow was observed under a certain deformation conditions. A possibility of superplastic deformation of lamellae cementite in pearlite was considered. The cooperative deformation of cementite and ferrite was also examined using cementite/low carbon steel multilayers.

2. Experimental procedures

Pure Fe, graphite and Mn (Fe: >99.9% and <100 μm, C: 99.9% and <5 μm, Mn: 99.9% and <60 μm) were mixed at nominal compositions of $Fe_{75}C_{25}$ or $(Fe_{0.95}Mn_{0.05})_{75}C_{25}$

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and mechanically alloyed for 360 ks in an Ar atmosphere using a horizontal ball mill. The sintering of MA powders were carried out using the spark plasma sintering (SPS) equipment operated at 1173 K for 900 s at a stress of 50 MPa in vacuum. The obtained compact of $Fe_{75}C_{25}$ has 86 vol.% (the rest is ferrite, graphite and voids) and the compact $(Fe_{0.95}Mn_{0.05})_{75}C_{25}$ has 95.5 vol.% (the rest is voids) of cementite phase. The grain size of $Fe_{75}C_{25}$ compact is 0.62 μm and that of $(Fe_{0.95}Mn_{0.05})_{75}C_{25}$ is 0.46 μm. Since the $Fe_{75}C_{25}$ compact (call pure cementite) starts to decompose above 873 K, the experiments above 873 K were done using $(Fe_{0.95}Mn_{0.05})_{75}C_{25}$ compact (call $(Fe_{0.95}Mn_{0.05})_3C$) which is thermally stable up to 1273 K. Compression tests were carried out for prism specimens 4 mm × 4 mm × 6 mm using an Instron type machine with constant cross-head speed of 0.5 mm/min (initial strain rate of$2.14 \times 10^{-3}\,s^{-1}$) at room temperature, 573 and 773 K in air. Swaging was carried out at room temperature, 973 and 1273 K. Compression deformation was carried out using SPS equipment with initial stress in the range of 100–150 MPa at 923 and 973 K in vacuum. Microstructures were characterized by optical microscope, scanning electron microscope (SEM) and transmission electron microscope (TEM). Specimens for optical and SEM observations were etched by the solution of $CuCl_2$:HCl = 1:24 (in wt.) or Nital (HNO_3:C_2H_5OH = 1:19 (in vol.)). Thin foil specimens for TEM observations were prepared by electropolishing with electrolyte of $HClO_4$:C_2H_5OH = 1:9 (in vol.) at 263 K.

3. Results

Compression test done on pure cementite at room temperature and 573 K showed that specimens are fractured within the elastic limit as is shown in Fig. 1. At 773 K strain about 0.1 was observed. To obtain a larger deformation at hydrostatic pressure, bulk cementite specimens were deformed under constrained condition. The specimens of $(Fe_{0.95}Mn_{0.05})_3C$ were cut into rods (diameter: 3 mm, length: 10 mm) and encapsulated with a stainless steel (SUS304) tube (outer diameter: 14 mm, inner diameter: 3 mm). After sealed, the tube was swaged at room temperature, 773 and 1273 K until the outer diameter reduced to 6 mm (initially 14 mm). Fig. 2 shows SEM micrograph of the specimen swaged at 1273 K. It is seen that the bulk cementite specimen was deformed irregularly and cracked severely. The results were more pronounced for the specimens swaged at room temperature and at 773 K. This confirms that bulk cementite specimens are brittle when deformed at high strain rate even at high temperature and under constrained condition.

Kim et al. [8] have reported that a fine-grained cementite base material exhibits superplastic properties. They prepared a fine-grained (linear intercept grain size of 2.1 μm) material containing 80 vol.% cementite from gas atomized Fe–5.25% C–1.5% Cr powder. The tensile elongation as high

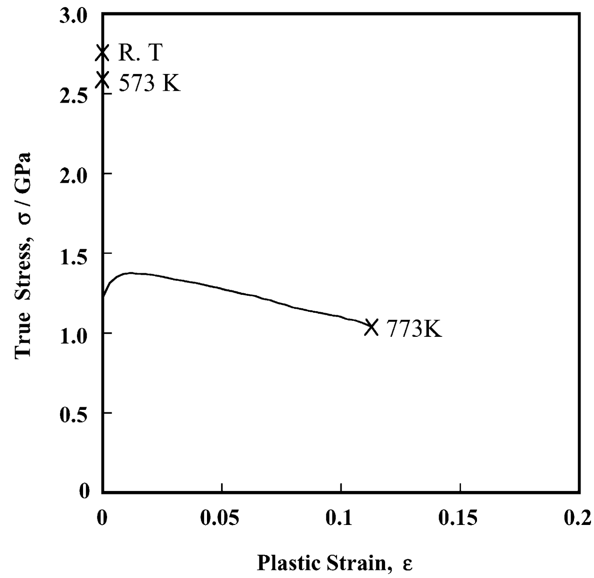

Fig. 1. Compressive stress–strain curves of Fe_3C at room temperature, 573 and 773 K.

as 600% was obtained. At 998 K (below the A_1) the strain rate of $3 \times 10^{-4}\,s^{-1}$ was obtained at the stress of 100 MPa. It is expected that the present bulk cementite may exhibit superplastic flow since the grain size (linear intercept grain size is 0.41 μm) is much smaller than theirs. A preliminary compression test was carried out at 973 K at a constant stress of 100 MPa. Fig. 3 shows a specimen before and after the compression deformation. The initial height of the specimen was 5.3 mm and a final height was 0.76 mm. The obtained compression strain is −1.94 and this is equivalent to a tensile elongation of 600%. In spite of such a large deformation, no cracks were observed either on the surface or in the interior of the material. The hardness of the sample at room temperature did not change by this deformation and maintained the initial hardness of 12 GPa. It is interesting to notice that the present bulk cementite $(Fe_{0.95}Mn_{0.05})_3C$ can

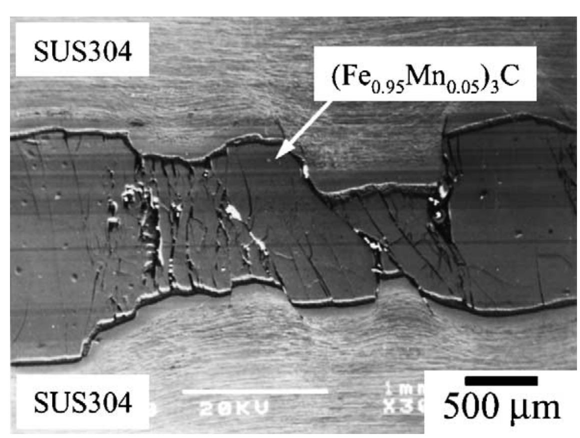

Fig. 2. SEM image of $(Fe_{0.95}Mn_{0.05})_3C$ after swaging at 1273 K. The initial diameter of cementite sample was 3 mm. The stainless steel capsule containing a cementite rod was swaged from ∅ 14 mm to ∅ 6 mm.

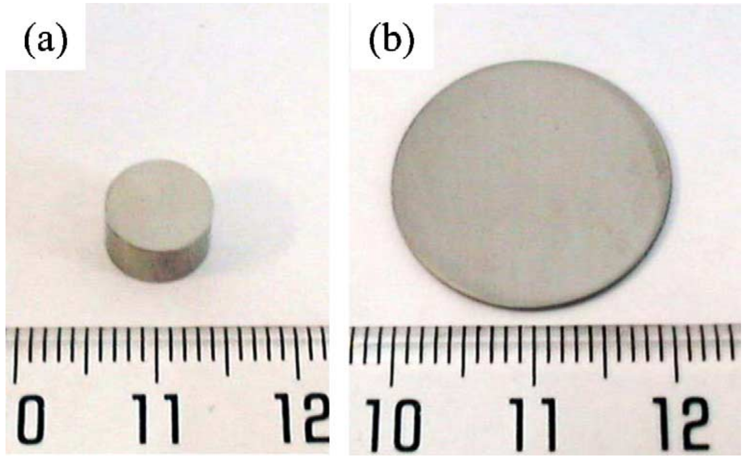

Fig. 3. $(Fe_{0.95}Mn_{0.05})_3C$ specimen before (a) and after (b) compressive deformation at 973 K with initial stress of 100 MPa. (a) Diameter: 8.0 mm, thickness: 5.3 mm and (b) diameter: 21.0 mm, thickness: 0.76 mm.

be deformed by the stress of 0.1 GPa at elevated temperature although it has a yield strength about 4 GPa (estimated from its hardness) at room temperature.

Fig. 4 shows a cross-sectional SEM micrographs from the center of the sample before and after the compression test. After compressive deformation grains are slightly elongated along the direction perpendicular to the compression axis (vertical in the picture) and grain boundaries are deeply etched probably because of small cavities. The TEM observation from the compression direction showed clear grain growth from 0.46 to 1.5 μm, as shown in Fig. 5. Dislocations are scarcely observed in the grains after the compression to the strain of −1.94. No traces of decompositions of cementite were recognized. Since the present samples do not contain second phase (except a few vol.% of voids) to inhibit grain growth and the initial grain size is quite small, the cementite grains can grow with a sufficient rate. From these observations, it can be concluded that the present fine grained bulk cementite specimen deforms at 973 K with stress of 100 MPa mostly by grain-boundary sliding mechanism and partly by a slip deformation mechanism. Recently, it has been reported that after heavy deformation by wire drawing of pearlite, lamellae cementite turns out to be nanocrystalline material [12–14]. This suggests that the deformation mechanism of cementite lamellae in pearlite can be grain boundary sliding.

The deformation of cementite by dislocation gliding has been observed [3,4,15]. More than three slip planes were reported which fulfill the condition for a crystal to be ductile (five independent slip systems). Thus, cementite can be ductile if the proper macroscopic conditions are favorable. However, it seems difficult to explain the observed large strain in cementite lamellae in pearlite during wire drawing by dislocation gliding since the dislocation density in cementite is substantially low compared with that in ferrite [4]. Thus, the deformation mechanism in cementite lamellae during severe deformation is not mainly governed by dislocation gliding. Regarding the superplastic deformation of

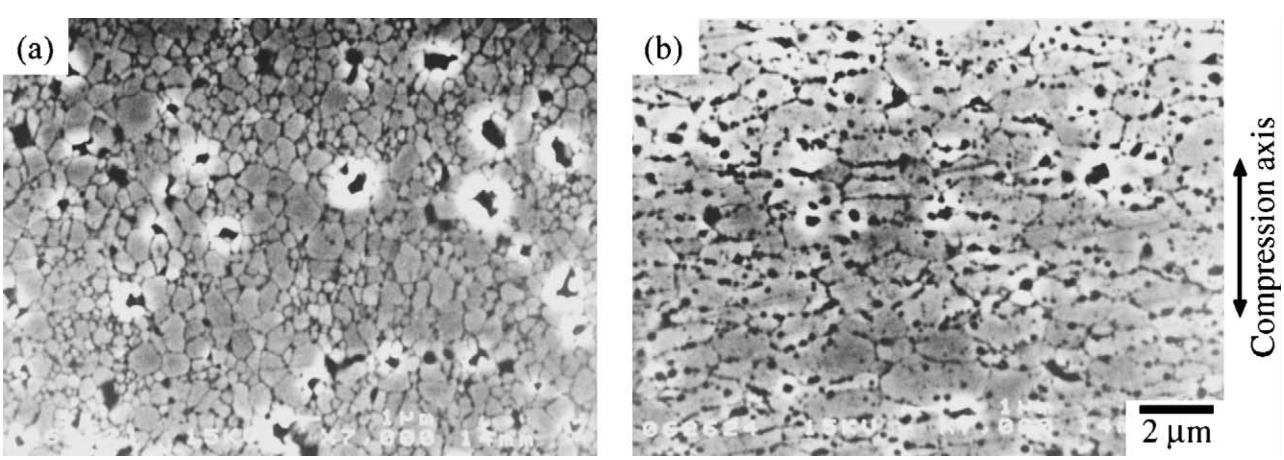

Fig. 4. SEM images of $(Fe_{0.95}Mn_{0.05})_3C$ before (a) and after (b) compressive deformation at 973 K with initial stress of 100 MPa. The height of specimen reduced from 5.3 to 0.76 mm. The specimens were etched by the solution of $CuCl_2$ and HCl.

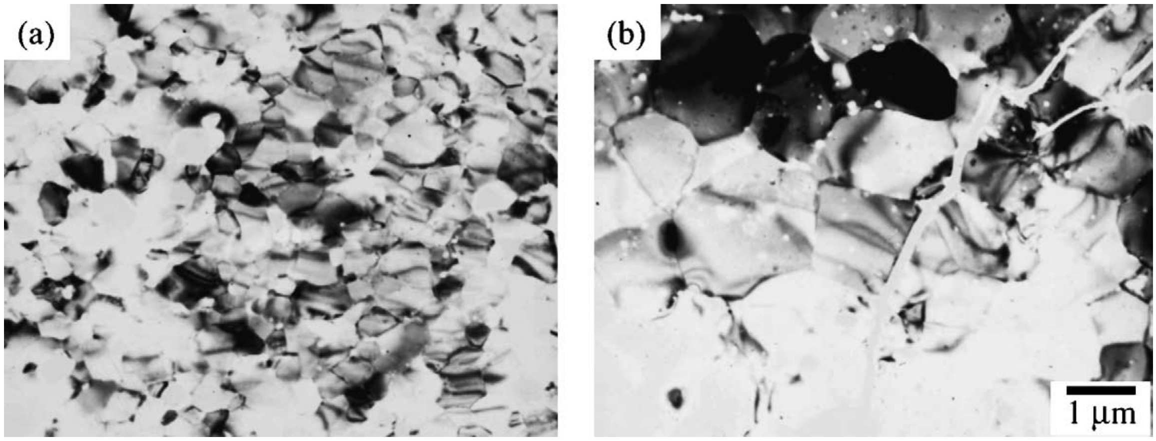

Fig. 5. TEM images of $(Fe_{0.95}Mn_{0.05})_3C$ before (a) and after (b) compression at 973 K with initial stress of 100 MPa. The height of specimen reduced from 4.2 to 0.89 mm.

cementite, Kim et al. [8] proposed the following constitutive equation.

$$\dot{\varepsilon} = K\left(\frac{\boldsymbol{b}}{L}\right)^{p} \sigma^{n} \exp\left(-\frac{Q_c}{RT}\right) \quad (1)$$

where $\dot{\varepsilon}$ is the steady-state creep rate, K (363.8 ($Pa^{-2}\,s^{-1}$) for tension) is a material constant, $\boldsymbol{b}$ the Burgers vector, L the linear intercept grain size, p the grain size component ($\approx$3), σ the flow stress, n the stress exponent ($\approx$2), Q_c the activation energy for plastic flow (200 kJ/mol), R the gas constant and T is the absolute temperature. If we assume that the stress acting on the lamellae cementite in pearlite during severe deformation is 5 GPa and the grain size of cementite is 1 nm, the strain rate obtained from Eq. (1) is $0.14\,s^{-1}$ at 473 K (supposed deformation temperature during wire drawing). The strain rate actually operating during wire drawing is $0.02–2.5\,s^{-1}$ [16] and the estimated value of $0.14\,s^{-1}$ is in this range. This supports the idea that grain boundary sliding is a possible deformation mechanism of lamellae cementite in heavily deformed pearlite.

For the deformation of pearlite, not only the plastic deformation of cementite but also the cooperative deformation of cementite with ferrite should occur since the lamellar structure of pearlite is maintained even after severe deformation by rolling [1] or drawing [2]. To examine the cooperative deformation of cementite with ferrite, bulk cementite samples were deformed with low carbon steel samples using the SPS equipment. Cementite disks of 6 mm in diameter and 0.45 mm thick and low carbon (Fe–0.25% C or Fe–0.15% C) disks of 6 mm in diameter and 0.90 mm in thickness were stacked alternately. After the stacking, the sample is compressed at 873 K at the initial stress of 100 MPa. The result is shown in Fig. 6 where three layers of $(Fe_{0.95}Mn_{0.05})_3C$ and four layers of fine grained (about 1 μm) Fe–0.15 mass% C steel disks were compressed to 66%. It is seen that low carbon steel and cementite deformed uniformly except the side of the specimen. Cracking or necking of cementite layers is hardly observed. Fig. 7 shows a cross-sectional SEM micrograph of cementite and low carbon (commercial Fe–0.25% C) multilayers compressed at 873 K at the stress of 100 MPa. The grain of low carbon steel after compression deformation is almost equiaxed about 5 μm which was about 20 μm initially. The thickness of cementite is about 40 μm which was initially 700 μm. There are no voids or cavities at the cementite/low carbon steel interfaces. The irregularity of the interface corresponds to the grains of cementite instead of the grains of low carbon steel. It seems that the cementite layers which probably deform faster by superplastic deformation than low carbon steel. This difference in a strain rate will arise internal stress and assist the deformation of low carbon steel layers. When the low carbon steel layers deform in a certain extent, recrystallization will take place and the grain

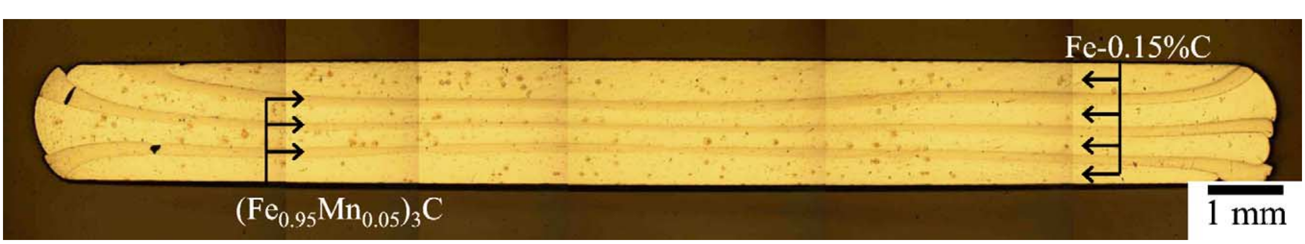

Fig. 6. Optical micrograph of multilayers consisting of three $(Fe_{0.95}Mn_{0.05})_3C$ layers and four Fe–0.15% C steel layers after compressive deformation at 973 K with initial stress of 100 MPa. Specimen height reduced from 5.0 to 1.3 mm.

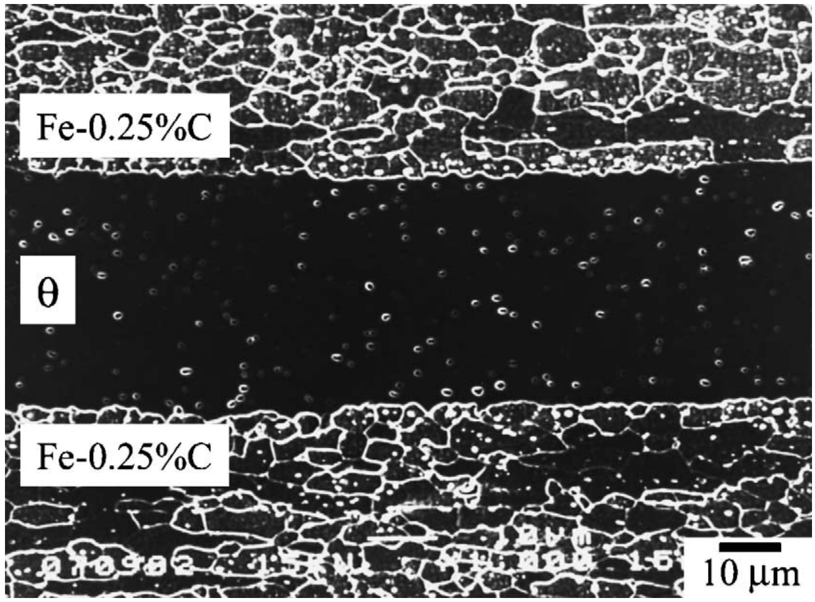

Fig. 7. SEM image of multilayered specimen consisting of $(Fe_{0.95}Mn_{0.05})_3C$ layer and two Fe–0.25% C steel layers produced by compressive deformation at 973 K with initial stress of 100 MPa. Specimen height reduced from 11.1 to 2.2 mm.

size becomes finer. As the grain size of low carbon steel layer reduces, the grain boundary sliding may become a dominant deformation mechanism like cementite layers. This may be the mecahnism of the observed cooperative deformation of cementite/low carbon steel multilayers. It is expected that in pearlite, once cementite lamellae become nanocrystals, the deformation of cementite controlles the deformation of ferrite and both deform cooperatively maintaining the lamellar structure.

4. Summary

In the present study, bulk cementite samples were fabricated by mechanical alloying of the elemental powders and spark plasma sintering of MA powders. The brittleness of bulk cementite at high strain rates was confirmed by applying compression and swaging deformation. However, bulk cementite can be deformed in a large extent by superplastic deformation at stresses in the range of 100–150 MPa at around 1000 K. From the similarity of the previous works on cementite-based materials, it was considered that the deformation mechanism of bulk cementite is grain boundary sliding. As a possible deformation mechanism of lamellae cementite in pearlite, grain boundary sliding after nanocrystalization was proposed. The cooperative deformation of cementite with ferrite was demonstrated using cementite/low carbon steel laminates. It was proposed that similar deformation may occur in pearlite where the lamellar structure is maintained after severe plastic deformation.

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