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# Effects of Chromium Addition on Preparation and Properties of Bulk Cementite

Bao-chao ZHENG, Zhi-fu HUANG, Jian-dong XING, Yi-yang XIAO, Xiao FAN, Yong WANG
(State Key Laboratory for Mechanical Behavior of Materials, School of Materials Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, Shaanxi, China)

**Abstract**: Bulk cementites with the Cr contents of 0, 3.01, 6.03, 8.22, and 11.51 mass% were prepared by mechanical alloying (MA) and spark plasma sintering (SPS). The results indicated that when the Cr content was low (3.01 mass%), the phases were composed of cementite with a small amount of α-Fe at a sintering temperature of 1173 K, but the microstructure became single-phase alloyed cementite as the Cr content was further increased. It showed that micro-addition of Cr was beneficial for promoting the formation of cementite. Furthermore, the mechanical performance of cementite can be greatly affected by the variation of Cr content. The hardness, elastic modulus and elastic recovery presented a remarkably increasing tendency with the addition of Cr, and the maximum micro-hardness and elastic modulus values reached 1070.74 HV and 199.32 GPa, respectively, which were similar to the precipitation phase (cementite) obtained by melting and casting techniques. Moreover, when the Cr content was below 11.51 mass%, the crystal structure of $Fe_3C$-type cementite would not change with increasing the Cr content. A Cr atom replaced an Fe atom in the lattice of the cementite, and voids appeared when Cr was doped into the cementite at content of about 11.51 mass%, causing the relative density to decrease.

**Key words**: mechanical alloying; spark plasma sintering; bulk cementite; relative density; chromium addition

As a strengthening agent, cementite has received much attention because of its importance in the steel and iron industries. In particular, its mechanical performance, size, volume fraction, composition and morphology have important effects on the service properties of steel and iron[1-3]. Cementite usually refers to $Fe_3C$; however, only few investigations are available on the mechanical properties of cementite[4-7], which is far from well-understood. This is because single-phase $Fe_3C$ is thermodynamically unstable and high temperature equilibrium $Fe_3C$ phases in the metastable form are very difficult to obtain; besides, the bulk size of single-phase cementite cannot be produced by traditional melting processes. Therefore, cementite is not completely realized in nature[8,9]. Generally, Cr is added into cast iron to stabilize cementite and promote its formation; as a result, relatively stabilized carbides which are represented as $(Fe, Cr)_3C$-type carbide are generated[10-13]. As a basic phase in steel and iron, an understanding of mechanical properties of cementite is particularly desirable. However, the above-mentioned problems still required not only experimental observations but also related mechanism discussion.

Recently, Umemoto et al.[14-16] successfully fabricated bulk cementite by using mechanical alloying (MA) and spark plasma sintering (SPS) techniques; the size of the single-phase cementite is up to $\phi$15 mm × 10 mm. Meanwhile, various alloying elements, such as Cr, Mn, Mo, V, and Ti, were selected to study the effects of alloying additions on the mechanical, physical and abrasive properties of cementite.

Nevertheless, to date, there is an urgent need for systemic investigation of the mechanical properties of Cr-doped cementite, which is still lack now

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**Biography**: Bao-chao ZHENG, Doctor; **E-mail**: zhengbaochao@126.com; **Received Date**: September 2, 2015
**Corresponding Author**: Zhi-fu HUANG, Professor; **E-mail**: hzf@mail.xjtu.edu.cn

but can indubitably lead to more meaningful results that could explain the relationship between the mechanical properties and Cr addition. Bulk single-phase cementites with different Cr contents were prepared successfully in this paper to discuss the variations of the mechanical performances and crystal structures of these cementites.

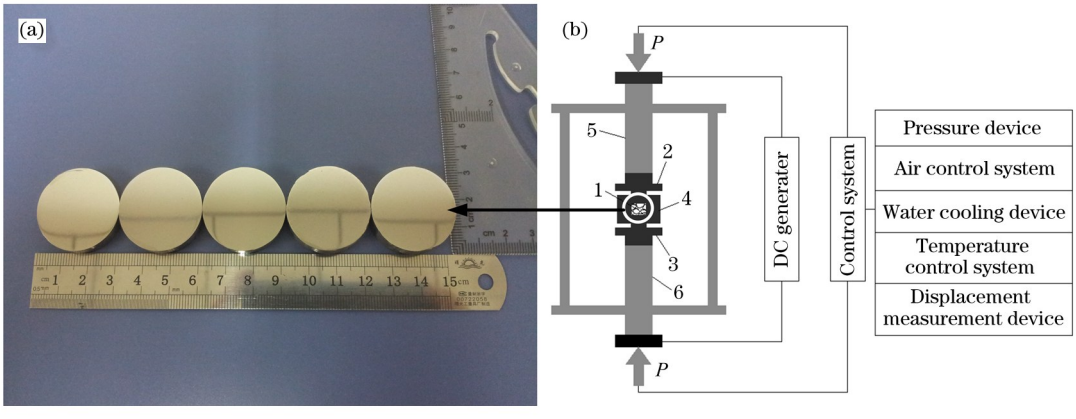
## 1 Experimental Procedures

The bulk cementite samples with different Cr additions were fabricated by MA and SPS. The initial materials included elemental iron powder (99.0 mass% and less than 30 μm in particle size), graphite powder (99.0 mass% and less than 10 μm in particle size) and Cr powder (99.9 mass% and less than 45 μm in particle size). The three powders were mixed in an agate milled jar, and the atomic ratio of Fe and Cr to C was 3 ∶ 1 according to the $(Fe,Cr)_3C$-type molecular formula. The mass fraction of each powder is given in Table 1. Mechanical alloying was carried out by a planetary mill, which has four 5 L agate jars with some agate balls (ϕ10 mm, total mass 500 g) and a ball-to-powder mass ratio of 10 ∶ 1. The mixture powder was protected under vacuum during the milling procedure at room temperature (25 ℃), and then, it was placed under an Ar atmosphere in a glove box. After mechanical alloying, the particle size and morphology of the milled powder changed. This was shown under a scanning electron microscope (SEM) with an energy dispersive spectrometer (EDS), and the phase composition was identified by X-ray diffraction (XRD). Besides, the thermal analysis and amorphous forming ability of the milled powder were measured with aluminium crucibles using a differential scanning calorimeter (DSC).

**Table 1 Chemical compositions of mixture powders** mass%

| Specimen | C | Fe | Cr |
|---|---|---|---|
| A0 | 6.64 | 92.55 | 0 |
| A1 | 6.67 | 90.82 | 3.01 |
| A2 | 6.74 | 86.96 | 6.30 |
| A3 | 6.80 | 84.98 | 8.22 |
| A4 | 6.85 | 81.64 | 11.51 |

After MA, the mixture powder was compacted into a graphite die under a constant pressure of 30 MPa at room temperature and then sintered by the SPS method in vacuum at 1173 K for 300 s. The schematic structure of the SPS sintering furnace is shown in Fig. 1(b). To measure the relative density of the sintered samples by Archimedes′ method, the specimens have to be polished using aluminium abrasive paper (till 1200 grit) into a cylinder with a size of ϕ30 mm×10 mm, then the average relative density of each sample was calculated by ten measured values (Fig. 1(a)). To observe the phase distribution by SEM, the sintering specimen was etched with 4 vol. % nital.




1—Milled powder; 2—Upper pressure head; 3—Lower pressure head; 4—Graphite die; 5—Top electrode; 6—Bottom electrode.

**Fig. 1 SPS bulk samples (a) and schematic of SPS sintering furnace (b)**

Subsequently, micro-hardness measurements were carried out on an HXD-type 1000 Vickers hardness tester with a load of 0.98 N and a dwell time of 10 s following the ASTME 384 standard. Each hardness value was measured ten times and then took the average. The elastic modulus ($E$), hardness ($H$) and $H/E$ ratio (elastic recovery) of the cementite specimens were measured on a nanoindentation instrument with a Berkovich diamond tip. Fifteen indentations were made on each specimen to check reproducibility of the measurement data. Loading and unloading of the indenter was controlled at 5 mN/s for