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Influence of alloy additions on production and properties of bulk cementite

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Introduction

Decades of efforts have been devoted to understanding the structure and mechanical properties of cementite in view of proper controlling the mechanical properties of steels [1–4]. However, there is no report about the properties of bulk cementite, which is essentially important to evaluate the properties of steels. Our recent endeavor has led to successful fabrication of bulk cementite by combining mechanical alloying (MA) with the subsequent spark plasma sintering (SPS) [5]. Cementite bulks with dimensions of up to $\phi 15 \times 10$ mm^3 have been produced. The main results obtained for bulk cementite (Fe_3C) are summarized in Table 1.

In steels alloying additions such as Cr, Mn, Ni, etc., are popularly employed to improve their properties. The alloying additions influence not only the properties of ferrite but also those of cementite. For instance, Cr and Mn highly partition in cementite instead of in ferrite. In contrast, Ni and Si tend to partition in ferrite. Therefore, in the present study, various alloying elements, Cr, Mn, Mo, V, Ti (cementite stabilizer in steels), Ni and Si (ferrite stabilizer in steels) were selected to study the influence of alloying addition to the mechanical and physical properties of cementite.

Experimental details

The fabrication and characterization of bulk cementite has been described in detail in the previous paper [5]. Pure Fe, graphite as well as Cr, Mn, Mo, V, Ti, Ni, and Si

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Table 1
Properties of bulk cementite

Lattice constant	0.45219 nm
	0.50875 nm
	0.67484 nm
Hardness (HV)	~10 GPa
Compression stress	2.8 GPa
Thermal expansion (α)	6.8×10^{-6} K^{-1}(<481 K)
	16.2×10^{-6} K^{-1}(<481 K)
Electricity conductivity (σ)	13 $\Omega^{-1}\,cm^{-1}$ (373 K)
Seebeck coefficient	−3.2 μV/K (673 K)
Specific heat	125.4 J/mol K

(Fe: >99.9% and <100 μm, C: 99.9% and <5 μm, Cr: 99.9% and <60 μm, Mn: 99.9% and <60 μm, Mo: 99.9% and <60 μm, V: 99.9% and <60 μm, Ti: 99.9% and <150 μm, Ni: 99.9% and <150 μm, Si: >99.9% and <10 μm) were mixed at compositions of $(Fe_{1-x}M_x)_{75}C_{25}$ (M = Cr, Mn; $x = 0.1$, 0.2 and 0.3, for M = Mo, Ti, Ni and Si, $x = 0.05$). The MA powders were subsequently subjected to X-ray diffraction (XRD) analysis, optical microscope, scanning electron microscope (SEM) and transmission electron microscope (TEM), and differential scanning calorimetric (DSC) analysis for structural characterization. SPS was carried out at 1173 K for 900 s under 50 MPa to sinter the milled powders. Similar structural characterizations were performed on the sintered compacts. The microhardness of the sintered compacts was measured under a load of 0.98 N for 15 s. The specific heat, C_p, was measured by DSC using Cu as reference. Before the SEM observation, the sintered compacts were polished and etched by 5% Nital for 5 s. The Young's modulus, E, was measured with a specimen size of $30 \times 10 \times 1$ mm^3. E was calculated by the following equation:

$$f = 1.028 \times 10^6 \times \frac{t}{l}\sqrt{\frac{E}{\rho_m}}$$

where f is harmonic frequency of the specimen, t and l, the thickness and length of specimen plate, and ρ_m, measured density of the specimen.

Results and discussion

Analysis of the powders milled for 360 ks revealed that the alloying additions improved the grain refinement of the powder mixture during milling, indicated by the broadening and weakening of XRD peaks corresponding to α-Fe. The formation of cementite from the milled powders was examined after aging the milled powers at 1173 K for 900 s in vacuum, the same condition as for pure cementite. The effect of alloying elements on the formation of cementite is clearly shown by the XRD patterns of the aged samples (with 5 at.% additions) as illustrated in Fig. 1. The additions of Cr, Mn, Mo and V show no negative effect on the formation of cementite phase. Full cementite

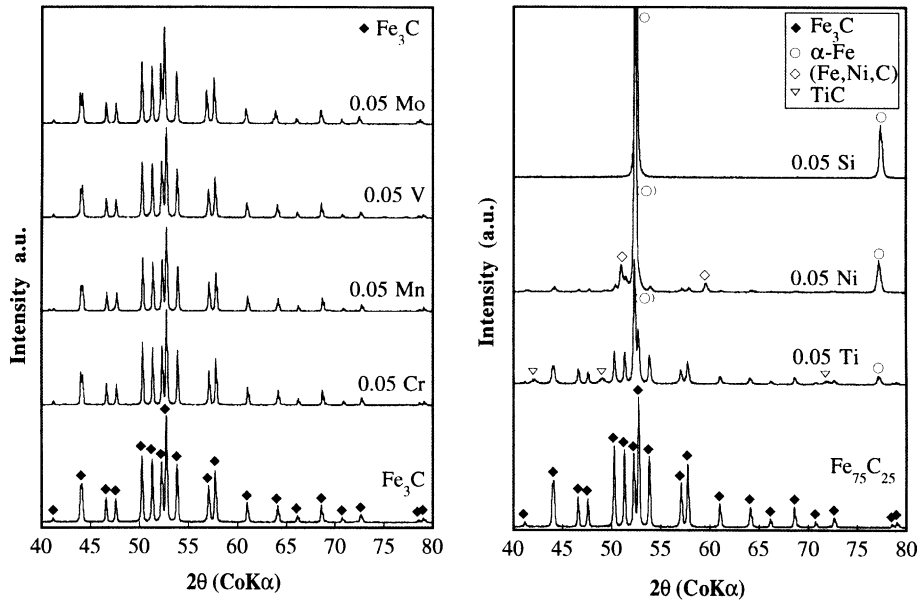

Fig. 1. XRD patterns of $(Fe_{0.95}M_{0.05})_{75}C_{25}$ (M = Cr, Mn, Mo, V, Ti, Ni and Si) powders after ball milling for 360 ks and aging at 1173 K for 900 s.

was obtained for these samples. In contrast, the additions of Ti, Ni and Si show a negative effect on the formation of cementite. 5 at.% Ti leads to the formation of TiC together with α-Fe and cementite. The addition of Ni results in a mixture of α-Fe(Ni), fcc (Fe, Ni, C) solid solution, small amount of cementite and graphite. The extreme case is the Si added sample. Aging leads to the complete suppression of the formation of cementite and results in the formation of an α-Fe(Si) solid solution and graphite.

Based on the aging behavior of the various milled powders, only Cr and Mn were chosen for the intensive investigation on the influence of alloying elements on the properties of bulk cementite. Thermal analysis revealed that the addition of Cr and Mn almost does not alter the formation heat of cementite phase during heating, which was revealed by the similar exothermicity during DSC measurements for various specimens (remaining around 18 kJ/mol). It should be noted that the addition of both Cr and Mn brings the formation reaction of cementite to higher temperature. Cr-addition leads to a linear increase of cementite formation temperature (5 K/%Cr) from 580 K of $Fe_{75}C_{25}$ specimen, while the temperature increase for Mn addition is 1.3 K/%Mn. This phenomenon might be attributed to the lower diffusivity of C in cementite with Cr and Mn addition. Since 30% Cr addition resulted in the formation of a different type of carbide other than cementite (Fe_3C structure), such specimen is excluded from the subsequent investigation.

Fig. 2 shows the typical cross-sections of sintered Fe_3C, $(Fe_{0.8}Cr_{0.2})_3C$ compacts, respectively (0.2 Mn added specimen revealed a similar structure as that of 0.2 Cr added). The Cr and Mn added compacts show fewer voids and no decomposed ferrite

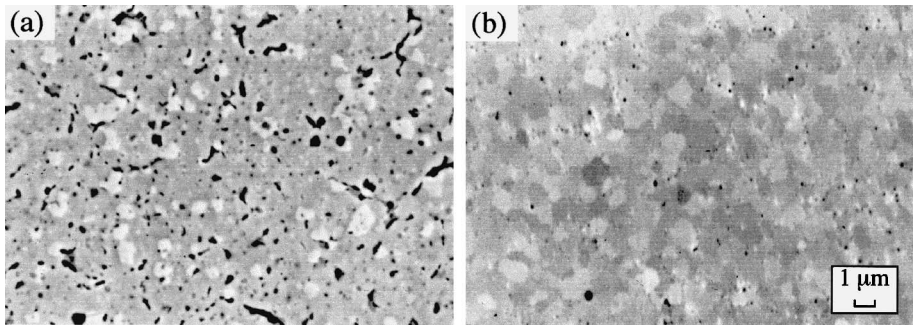

Fig. 2. Cross-sectional SEM micrographs of sintered compacts of cementite (a) (Fe_3C) and (b) $(Fe_{0.8}Cr_{0.2})_3C$.

and graphite. During heating up to 1273 K, the decomposition of cementite completely disappeared in the specimens with more than 5% substitutional additions of Cr or Mn, although pure Fe_3C decomposes partially from 853 K.

The microhardness of the sintered compacts at room temperature were shown in Fig. 3(a). The increase of Cr and Mn additions in sample results in a great increase in cementite hardness from 10 GPa to around 13.5 GPa for 20% additions of Cr, and about 15 GPa for 30% addition of Mn, respectively. This evolution is in good agreement with the previous study on pro-eutectoid cementite [6], while those values for pro-eutectoid are 2–3 GPa higher than the present results. This difference is believed to be due to the difference in specimen size and measuring load. A temperature dependence of hardness similar to that of pure cementite was observed for both Cr- and Mn-added cementites. At 773 K, the hardness dropped to 8.3 GPa for 20% Cr-addition and about 6.0 GPa for 20% Mn-addition, which are still much higher than that of pure cementite (3.3 GPa). The strengthening effect of Cr is larger than that of Mn at higher temperature. It was observed that the hardness at 773 K decreased with increasing the loading time due to creep deformation. The increase in the indentation size by creep deformation was smaller in Cr than Mn.

Young's modulus of cementite (Fe_3C) has been measured by several researchers and compared among specimens produced with various processes [7–11]. It has been reported that cementite shows a lower Young's modulus than pure Fe, irrespective of a higher hardness and strength. This behavior is quite different from most of other carbides, which show a much higher Young's modulus than their pure metal counterparts. Regretfully, the reason to this phenomenon remains unclear at the present stage. At present investigation a flexural vibration method was employed to measure the Young's modulus of bulk cementite with and without alloying additions. Young's modulus of the present pure bulk cementite was measured to be 196 Gpa, which is smaller than that of pure iron measured with the same method (212 GPa). The Young's modulus of cementite measured in the present investigation falls into the range of the previous measurements, which vary from 160 to 212 GPa. The linear increase of Young's modulus with the increase of Cr and Mn content was observed as is shown in Fig. 3(b). The contribution of Cr addition is much larger than that of Mn addition. 20% Cr and Mn additions increase the Young's moduli of cementite to 245 and 227 GPa, respec-

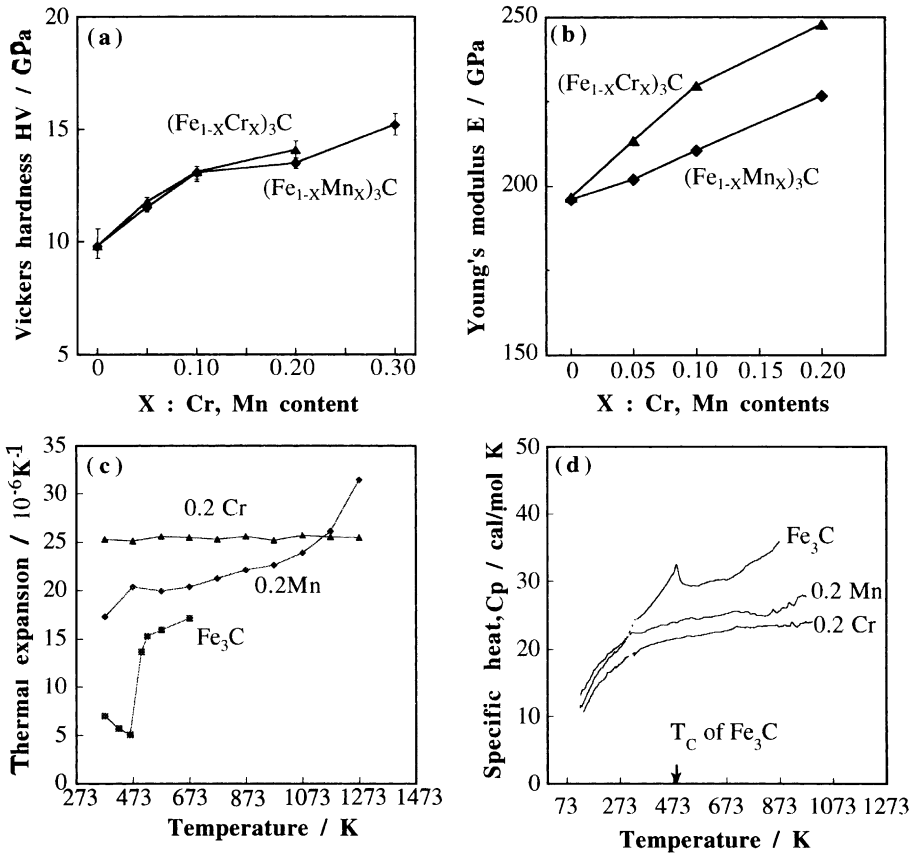

Fig. 3. Effect of alloying additions on (a) room temperature hardness, (b) Young's modulus, (c) thermal expansion coefficients, α, (with 20% Cr and with 20% Mn addition) and (d) specific heat, C_p, (with 20% Cr and with 20% Mn addition. C_p was shown for 1 mol of cementite (3 mol of Fe(Cr, Mn) plus 1 mol of carbon).

tively. It is considered that the additions of Cr and Mn increase the bonding strength in cementite. Again, the addition of Cr shows a stronger influence than Mn does.

The measured thermal expansion coefficient, α, of the Cr- and Mn-added cementite as a function of temperature is shown in Fig. 3(c). In the pure cementite (Fe_3C), the thermal expansion coefficient sharply decreases at temperature below its Curie temperature (481 K). With the addition of Cr or Mn, Curie temperature decreases and decomposition of cementite below 1273 K is completely suppressed. Addition of 20% Mn shows a gradual increase in α with temperature. In the specimen with Mn addition α increases gradually with temperature up to 973 K and increases sharply at above 973 K. The value of α also gradually increase with increasing Mn content in the temperature range RT – 973 K. The case was different in Cr-added specimens. Although 5% Cr addition showed similar curve to that of Mn-added specimen, 20% Cr-added cementite specimens showed an almost constant thermal expansion coefficient, α, around 25.5×10^{-6} K^{-1} between RT and 1273 K. This value of α is almost same as that of Al

and is quite large for a material with an expected high melting point. The reason of this phenomenon remains unclear.

Specific heat, C_p, of cementite was measured as well. Fig. 3(d) demonstrates the specific heat of 20% Cr and Mn added cementite as functions of temperature. A slight decrease in C_p was observed for both Cr and Mn added specimens, while Cr addition resulted in a lower value than Mn did. Since the addition of Cr and Mn decreases the Curie temperature of cementite strongly (from 483 K of pure cementite to 320 K for 0.1 Cr-addition and 150 K for 0.2 Cr-addition), the peak observed on C_p curve of cementite at Curie temperature disappeared for Cr and Mn added cementite.

Discussion

In the present study, the formation of alloyed cementite has been observed for Cr, Mo, V and Mn with the addition larger than 5%. However, in the cases of Si, Ni and Ti, 5% additions of such elements suppressed the formation or enhance the decomposition of cementite during aging. It is well known that in steels Cr, Mn, Mo and V tend to enrich in cementite instead of in ferrite. The partition coefficients of Si and Ni in cementite are known to be <1. When Si is added, only α-Fe solid solution was observed after aged at 1173 K. The addition of Ni suppressed the formation of cementite and resulted in the appearance of a fcc phase, (Fe, Ni, C) solid solution. Therefore, a mixture of α-Fe, fcc (Fe, Ni, C) solid solution, small amount of cementite and graphite was obtained. The addition of 5% Ti formed a mixture of TiC, Fe_3C and α-Fe. Since Ti is a strong carbide former, it formed TiC instead of alloying into cementite.

The increase in hardness and Young's modulus of Cr and Mn-added cementite can be attributed to the increase of bonding strength in cementite. It was previously considered that the addition of cementite stabilizing elements enhances the bonding strength between metal atoms and carbon atoms [12]. However, the recent study by using first principle molecular orbital calculations suggests that the metal–Fe (M–Fe) bondings rather than metal–carbon (M–C) bondings in cementite show strong dependence on solute atom [13]. The bond overlap population, which indicates the bonding strength, of Fe–M is higher than Fe–Fe bounding in the order of Cr, V and Mn, while the M–C bondings are nearly constant irrespective of solute atoms. This calculation predicted that both Cr and Mn additions improve the bonding strength in cementite, while the effect of Cr is stronger than Mn. This is consistent with the measured hardness and Young's modulus in the present study.

Summary

Based on the previous research on the fabrication of cementite bulk through MA and SPS, the influence of Cr, Mn, V, Mo, Ti, Ni and Si additions substitutional to Fe on the structure and properties of cementite bulk has been studied. It has been found that Cr,

Mn, V and Mo can form alloyed cementite and stabilize it while Ti, Ni and Si destabilize or even suppress the formation of cementite. The hardness and Young's modulus of cementite were increased by the addition of both Cr and Mn. Thermal expansion coefficient was increased substantially by Cr or Mn additions. Slight decrease in C_p was observed by the addition of Cr or Mn.

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