Phase transformation and mechanical properties of sintered Fe-Mo-Si-C-(Cu) alloys

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Abstract
Sintered Fe-Mo-Si-C alloys, prepared from pre-alloyed Fe-0.85Mo powder, fixed 4wt. % silicon carbide powder and varied graphite powder contents, showed microstructures similar to those of ductile cast irons, i.e., the microstructural feature consisted of a black particle enveloped with matrix consisting of ferrite halo and pearlite. The varied added-graphite content caused morphological change from black nodular to black vermicular particles. With increasing added-graphite content resulted in the decrease of black nodular/vermicular particle fraction, the increase of pearlite fraction and the slight change of ferrite fraction. The black nodular particles were either graphite or Fe-Mo-Si-C/graphite core-shell particles whereas black vermicular particles were totally composed of carbon. With 2 wt.% copper addition, the morphologies of black nodular and vermicular particles in sintered Fe-Mo-Si-C-Cu alloys were not affected, but one component of the matrix changed from pearlite to duplex structure consisting of bainitic ferrite (BF) and martensite-austenite (M-A) constituent. The change of matrix component from pearlite to duplex BF/M-A structure led to drops of ultimate tensile strengths and elongation values but small effects on yield strengths and hardness values. No benefits of tensile properties were gained from the duplex structure due to coarse BF/M-A size.

Keywords: Sintered Fe-Mo-Si-C alloys, Copper addition, Phase transformation, Mechanical properties

1. Introduction
Silicon carbide (SiC) powder can react with iron (Fe) or Fe-base powders at temperatures close to normal sintering temperatures for such Fe or Fe-base powder compacts [1, 2]. Sintering of Fe + 5wt.% SiC powder compacts at 1200°C resulted in the microstructure consisting of nodular graphite-like particles surrounded with ferrite and a pearlite structure. This microstructural feature was designated as ductile cast iron-like microstructure [1]. Similar microstructures were also reported in other systems [3, 4].
Copper (Cu) is a common additive powder mixed with Fe powder to produce sintered Fe-base materials. The addition of Cu in Fe-0.85Mo + 0.6 wt.% graphite powder mixtures resulted in mechanical property modification. The Cu additions with contents of 0.07 to 0.85 wt.% to 0.90 carbon rail steels resulted in small pearlite transformation delay but appreciable pearlite interlamellar spacing refinement [5]. The copper addition to 0.15C-1.5Mn-1.5Si TRIP-aided multiphase cold-rolled steel sheets resulted in the increase of retained austenite volume fraction, although it did not affect the stability [6]. Similarly, the study on Cu addition in a hot rolled ferrite-based lightweight steel revealed that Cu addition delayed bainitic transformation, resulting in higher volume fraction of retained austenite with lower stability in the steel [7]. In ductile cast irons added with 0.2 to 2.0 wt.% Cu, the graphite nodules are not influenced by Cu but the pearlite fraction increases with increasing added Cu contents in the range of 0.2-0.8 wt. %, and it maintains at roughly constant with further increase of Cu [8].

Due to the effects of Cu on phase transformation behaviours in sintered and wrought steels given above, it is interesting to explore how Cu addition affect the matrices of sintered Fe-Mo-Si-C alloys produced under slow cooling rate.

2. Materials and methods
Sintered Fe-Mo-Si-C alloys without and with Cu addition were prepared by sintering powder mixture compacts of pre-alloyed Fe-0.85Mo powder, fixed 4wt. % silicon carbide powder and varied graphite powder contents. The nominal compositions of sintered alloys are given in Table 1. The powder mixtures were compacted into tensile test bars with green density of 6.5 g/cm³. The green compacts were sintered at 1,250 °C for 45 min in a vacuum furnace. After sintering, sintered specimens were cooled in the sintering furnace with cooling rate of 0.1 °C/s. Microstructures were investigated by using optical microscopy (OM) and scanning electron microscopy (SEM). Phase identification was conducted by using X-ray diffraction (XRD) technique. Mechanical properties of the sintered materials, such as tensile and hardness, were tested by a tensile testing machine (Instron model 8801) and hardness tester (Rockwell scale B), respectively.

| Alloy | SiC (wt. %) | Graphite (wt.%) | Copper (wt. %) | Nominal composition (wt. %) |
|-------|-------------|-----------------|----------------|-----------------------------|
|       |             |                 |                | C | Si | Mo | Cu | Fe |
| 0Cu00G | 4.0         | 0.0             | 0.0            | 1.2 | 2.8 | 0.82 | 0.0 | Bal. |
| 0Cu01G | 4.0         | 0.1             | 0.0            | 1.3 | 2.8 | 0.82 | 0.0 | Bal. |
| 0Cu02G | 4.0         | 0.2             | 0.0            | 1.4 | 2.8 | 0.81 | 0.0 | Bal. |
| 0Cu03G | 4.0         | 0.3             | 0.0            | 1.5 | 2.8 | 0.81 | 0.0 | Bal. |
| 0Cu04G | 4.0         | 0.4             | 0.0            | 1.6 | 2.8 | 0.81 | 0.0 | Bal. |
| 2Cu00G | 4.0         | 0.0             | 2.0            | 1.2 | 2.8 | 0.80 | 2.0 | Bal. |
| 2Cu01G | 4.0         | 0.1             | 2.0            | 1.3 | 2.8 | 0.80 | 2.0 | Bal. |
| 2Cu02G | 4.0         | 0.2             | 2.0            | 1.4 | 2.8 | 0.80 | 2.0 | Bal. |
| 2Cu03G | 4.0         | 0.3             | 2.0            | 1.5 | 2.8 | 0.80 | 2.0 | Bal. |
| 2Cu04G | 4.0         | 0.4             | 2.0            | 1.6 | 2.8 | 0.80 | 2.0 | Bal. |

3. Results and discussion

3.1 Microstructure
The sintered Cu-free alloys (Figure 1a-1e) showed common microstructural features consisting of a black particle surrounded with ferrite halo and pearlite. The SEM image showing the common microstructural feature is shown in Figure 2a. Pearlite structures consisting of ferrite and carbide lamellae are shown in Figure 2b. Black particle morphology changed from nodular to a vermicular shape when the added graphite content was increased. XRD patterns of the sintered Cu-free alloys (Figure 3a) show only body-centered cubic (bcc) crystal structure of α-ferrite. No peaks corresponding to face-
centered cubic (fcc) crystal structure of $\alpha$-ferrite indicate that there is a very small amount or no austenite remaining in the the sintered Cu-free alloys. The characteristics and formation mechanism of black particles were already given in [9]. The formation mechanisms for ferrite and pearlite in ductile cast irons given in [10] can be used for explaining ferrite and pearlite transformations in the sintered Cu-free alloys of this work. Thus, the explanation for ferrite and pearlite formations is not repeated here. The sintered Cu-containing alloys (Figure 1f-1j) also showed common microstructural feature similar to those of the sintered Cu-free alloys. The black particle and ferrite halo in the sintered Cu-containing alloys were not affected by Cu addition. However, the pearlite structure disappeared and was replaced by duplex structure in the sintered Cu-containing alloys. The SEM image showing the common microstructural feature in the sintered Cu-containing alloys is given in Figure 2c. The SEM image showing the duplex structure is given in Figure 2d. XRD patterns of the sintered Cu-containing alloys (Figure 3b) show both bcc and fcc crystal structures. This indicates that there are both ferrite and austenite in the sintered Cu-containing alloys. According to the SEM image given in Figure, 2d and XRD patterns given in Figure 3b, the duplex structure is characterized by alternating bainitic ferrite (BF) plates and martensite-austenite (M-A) islands. The size and shape of both BF plates with M-A islands are roughly similar and equal. There are all microstructural features classified according to [11], but no carbide particles are observed in the duplex BF/M-A structure.

The duplex BF/M-A structure given in Figure 2d is similar to microstructures of steels transformed at low temperatures [11-13]. This implies that the duplex BF/M-A structure is the result of phase transformation from parent austenite phase to duplex structure at a low temperature. Since the cooling rate employed in this work is quite low (0.1°C/s), the parent austenite must have stability sufficient to reach a low temperature phase transformation field. Due to no carbide precipitation in the duplex BF/M-A structure, this microstructure type may be classified as one of carbide-free bainite structures.
Figure 1. OM images of sintered Cu-free and Cu-containing alloys.
Figure 2. SEM micrographs of sintered Fe-Mo-Si-C-(Cu) alloys: (a) overall microstructure of sintered Fe-Mo-Si-0.3C alloy, (b) Pearlite structure of sintered Fe-Mo-Si-0.3C alloy, (c) overall microstructure of sintered Fe-Mo-Si-0.3C-2Cu alloy, and (d) duplex BF/M-A structure of sintered Fe-Mo-Si-0.3C-2Cu alloy.

Figure 3. XRD patterns of sintered Fe-Mo-Si-C alloys with varied graphite contents; (a) without Cu addition, and (b) with 2 wt.% Cu addition.

3.2 Mechanical properties
With increasing carbon content, tensile strengths (ultimate tensile strength (UTS) and yield strength or (YS)) of experimental sintered alloys increased to optimum values and then slightly dropped as shown in Figure 4. Elongation followed similar trend of the tensile strength. Both strength and ductility of the sintered Cu-containing alloys were inferior to the sintered Cu-free ones. The existence of strength and elongation optimal values is attributed to composite microstructure consisting of black particle, ferrite and pearlite or duplex structure. The optimum strength or elongation value is resulted from the contributions of these microstructural components. The inferior strength in the sintered Cu-containing alloys is attributed to coarser scales of duplex BF/M-A structure, compared to finer scales of ferrite and cementite lamellae in pearlite of the sintered Cu-free alloys. The superior strength of superbainitic steels depends strongly on very fine slender microstructural components [14, 15].
Figure 4. Mechanical properties of sintered Fe-Mo-Si-C alloys without and with Cu modification; (a) UTS, (b) Yield strength, (c) Elongation and (d) Hardness.

Although, the sintered Cu-containing alloys have a detectable amount of retained austenite (Figure 3b), they do not gain the benefit of transformation-induced plasticity (TRIP) effect, which is depending on the transformation of austenite to martensite during deformation [16, 17]. The inferior ductility of the sintered Cu-containing alloys may be related to retained austenite characters. Optimum retained austenite characters (volume fraction, morphology, and stability) are required for ductility enhancement [18-21]. In general, compared to block retained austenite, the thin film one is more stable and has higher C concentration. According to SEM image given in Figure 2d, the inferior ductility of the sintered Cu-containing alloys is related to retained austenite with a blocky shape. Regarding hardness, Figure 4d indicates that Cu addition does not significantly affect hardness values.

4. Conclusion
The Cu addition to sintered Fe-Mo-Si-C alloys led to changes of microstructures and tensile properties as summarized below.

1. The Cu addition led to change of pearlite to duplex BF/M-A structure but little changes of black particle and ferrite halo.
2. The coarser scales of BF/M-A components led to inferior tensile strength in the sintered Cu-containing alloys.
3. The inferior ductility in the sintered Cu-containing alloys may be attributed to retained austenite characters in duplex BF/M-A structure.
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