The effect of molybdenum on the microstructure and mechanical behaviour of the sintered Fe-Mo-Mn-Si-C composite

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Abstract
Experimental sintered Fe-Mo-Mn-Si-C composites were prepared from 3 different pre-alloyed Fe-Mo-Mn powders, namely Fe-0.50Mo-0.15Mn, Fe-0.85Mo-0.15Mn and Fe-1.50Mo-0.15Mn, mixed with fixed 4 wt.% silicon carbide powder. Sintered Fe-SiC composite was also prepared, as a reference material, from pure Fe powder mixed with fixed 4 wt.% silicon carbide powder. All specimens were processed by using the ‘press and sinter’ method. Sintering was performed in a vacuum furnace at 1250°C for 45 minutes and slow cooling in the furnace. The microstructures of most sintered alloys showed a common feature consisting of a black particle enveloped with ferrite and pearlite. Sintered composites produced from high-molybdenum powders showed different matrices, in which some pearlite regions were replaced by BF/M-A structures. The Tensile and hardness test showed that the sintered alloys exhibited an increase of tensile strength, yield strength, and hardness with increasing molybdenum content. The pearlite + BF/M-A fractions of sintered composites played important roles in material strengthening. In the sintered composites produced from high-molybdenum powders, the carbide-free BF/M-A structure showed a promising strengthening effect.

Keywords: Sintering, Fe-Mo-Mn-Si-C, Pearlite, Carbide-free bainite, Mechanical property.

1. Introduction
The traditional process of ‘press and sinter’ is commonly used for producing particulate-reinforcement composites. The early attempts to produce silicon carbide (SiC)-reinforced metal matrix composites (MMCs) revealed that interfacial reaction between SiC and iron-base matrix occurred during heating and sintering [1-3]. In 316L/SiC system [1], interfacial reaction resulted in intergranular liquid phase formation. In Fe/SiC system [2, 3], SiC residual particle was enveloped with ferrite-pearlite matrix. Later, pre-alloyed powders, such as Fe-Mo [4] and Fe-Cr-Mo [5] powders, and diffusion bonded
powders [6], were employed as matrices. The final microstructures of sintered composites strongly depended on pre-alloyed powder composition. In the Fe-Mo/SiC systems [4], ductile iron-like microstructure consisting of black (graphite-containing) particle surrounded with ferrite-pearlite matrix was a common microstructural feature. In the Fe-Cr-Mo/SiC systems [5], pearlitic ductile iron-like microstructure was obtained. In the diffusion bonded powders added with SiC systems [6], the matrices surrounding black particles contained bainite instead of pearlite.

These sintered composites based on pre-alloyed powders [4-5] showed promising tensile properties and had graphite-containing particles embedded in their matrices. The formation of graphite-containing particles is attributed to SiC decomposition, interfacial reaction, melting and re-solidification in SiC site vicinities. The interactions between SiC and iron-base powder particles was given by experimental evidence [7]. These interactions were also considered by thermodynamic models as given in [8, 9].

The materials consisting of graphite-containing particles embedded in iron base matrices are classified as self-lubricating composites due to lubricity of graphite [10-12]. The self-lubricating composites containing graphite particles are commonly applied as train brake linings [13,14]. Definitively, tribological properties of self-lubricating composites or brakes pads depend on lubricant characteristics [15, 16]. However, according to the recent study [17], the matrix of train brake linings plays an important role on braking performance, such as stable coefficient of friction (COF) and wear rate. To have such good braking performance, the brake matrix should have mechanical properties as good as tribological properties.

Thus, the sintered composites, having graphite-containing particles embedded in iron-based matrices, have potential for applications as train brake linings. This present work focuses on the influence of molybdenum content in pre-alloyed powders, used for making composite matrices, on mechanical properties of sintered composites. Pure iron powder was also used for producing a sintered composite as the reference material.

2. Materials and Methods

2.1 Specimen Preparation
Sintered composites were prepared from 4 different metal powders, including pure iron (Fe) and 3 pre-alloyed Fe-Mo powders, mixed with fixed 4 wt.% silicon carbide powder and 1 wt.% zinc stearate as a lubricant. The nominal compositions of experimental sintered composites are given in Table 1. Specimen preparation procedure included cold pressing and the sintering of powder mixture compacts. Green specimens were produced by compacting powder mixtures into standard tensile test bars (MPIF standard 10) with green density of 6.50 ± 0.01 g/cm³. Green compacts were sintered at 1250°C for 45 minutes in a vacuum atmosphere. After sintering, the specimens were slowly cooled in the sintering furnace.

2.2 Hardness and tensile tests
Rockwell scale B (HRB) hardness test, with ball diameter of 1/16 inch and 100 kgf load, was used to measure the hardness of each specimen. This test was carried out on un-etched surface of a specimen. Five indentations on each sintered composite were pressed for obtaining a mean hardness value. For tensile test, sintered composites were tensioned at room temperature by using Instron 8801 Universal Instrument with load cell of 100kN and speed of 1 mm/min. Three specimens of sintered composite were tested for obtaining average the tensile properties.

2.3 Microstructure Observation
Microstructures of sintered composites were observed by optical microscopy (OM) and scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS). A surface of a specimen was abraded on silicon carbide grit papers to number 4000 and then polished with 6, 3, and 1 µm diamond pastes. The polished samples were etched with 2% Nital and cleaned by ethanol. The SEM was operated at 20 kV to observe the details of microstructure. Phase identification was carried out by using X-ray diffraction (XRD) technique.
Table 1. Nominal composition of experimental sintered composites

| Composite | Metal powder | SiC (wt. %) | Composite nominal composition (wt. %) |
|-----------|--------------|-------------|--------------------------------------|
|           |              | C | Si | Mo | Mn | Fe    |
| 0.00Mo    | Fe           | 1.20 | 2.80 | 0.00 | 0.00 | Bal. |
| 0.50Mo    | Fe-0.5Mo-0.15Mn | 1.20 | 2.80 | 0.48 | 0.14 | Bal. |
| 0.85Mo    | Fe-0.85Mo-0.15Mn | 1.20 | 2.80 | 0.82 | 0.14 | Bal. |
| 1.50Mo    | Fe-1.5Mo-0.15Mn | 1.20 | 2.80 | 1.44 | 0.14 | Bal. |

3. Results and Discussion

3.1 Microstructure

All experimental sintered composites exhibited common microstructural features consisting of black particle(s) surrounded with white and dark areas (Figure 1). The black particles had different shapes from irregular to spherical ones. They were identified as graphite-containing particles. The white area contained polygonal ferrite grains the forms of halos around black particles. The dark area was revealed by SEM (Figure 2) to contain a pearlite structure and bainitic ferrite (BF) and martensite-austenite (MA) constituent. The BF/MA structure with no carbide precipitation was observed in sintered composites with high molybdenum contents (sintered 0.85Mo and 1.50Mo composites). Area fractions of microstructural components in sintered composites were measured and presented in Table 2.

The microstructural features as shown in Figure 1 resemble those of sintered composites [3,4, 10-12] and of ferritic-pearlitic ductile irons [17, 18]. The formation of ductile iron-like microstructure was briefly explained in [4]. The conditions, under which ferrite and pearlite transformations occur in ductile irons, are also explained in [19]. Discussion on such issues is not repeated here but the attention is focused on the molybdenum effect on the sintered composite matrix feature.

Pearlite structures are found in all experimental sintered composites produced under slow continuous cooling. The existence of a pearlite structure indicates that cementite (Fe₃C) precipitation does form at high temperatures, under which substitutional alloying elements (silicon and molybdenum) are possible to undergo partitioning. XRD patterns given in Figure 3 show strong peaks corresponding to α-iron or ferrite (labelled) and weak peaks corresponding to cementite (not labelled). Other alloy carbides are not detected by XRD. This suggests that the partitioning of silicon from cementite to ferrite occurs to favor cementite precipitation and hence pearlite transformation. It is well-known that silicon retards the precipitation of cementite from different parent materials or phases, such as cast ions, martensite and austenite [20]. This is due to the fact that silicon has low solubility in cementite (Fe₃C), i.e., up to 4.5 at. % Si [21]. Theoretical study suggests that the formation of (FeSi)₃C carbide is associated with high formation energy [22], which is not thermodynamically favored.

In the sintered composites with high molybdenum contents, such as sintered 0.85Mo and 1.50Mo composites, the BF/MA structure forms at low temperatures. The BF/MA formation is strongly under the influence of molybdenum. Under continuous cooling, molybdenum additionally retards ferrite and pearlite transformations by shifting the corresponding transformation fields to lower cooling rates [23, 24]. The delay of high-temperature transformations opens up the window for low-temperature transformations even under a slow cooling. The BF/MA constituent contains no carbide particles. This indicates that carbide precipitation retardation occurs at low temperatures in such sintered composites.
Figure 1. Optical micrograph of sintered composites (a) 0.00Mo composite, (b) 0.50Mo composite, (c) 0.85Mo composite, and (d) 1.50Mo composite.

Figure 2. SEM micrographs of sintered composites (a) 0.00Mo composite, (b) 0.50Mo composite, (c) 0.85Mo composite, and (d) 1.50Mo composite.
Table 2. Total area of each phase of sintered materials.

| Composite | Black particle | Ferrite | Pearlite + BF/M-A |
|-----------|----------------|---------|-------------------|
| 0.00Mo    | 3.8            | 66.2    | 30.0              |
| 0.50Mo    | 8.5            | 36.1    | 55.4              |
| 0.85Mo    | 19.0           | 23.2    | 57.8              |
| 1.50Mo    | 19.0           | 8.5     | 72.5              |

Figure 3. XRD patterns of the sintered composites.

3.2 Mechanical property

The Tensile strength and hardness of sintered composites increased with increasing molybdenum content while the values of elongation at break were in the range of 2.5-4.0 % (Figure 4). The strength and hardness of sintered composites depends strongly on pearlite + BF/M-A fractions, which are promoted by high molybdenum content. The fraction of soft phase or ferrite is supposed to dictate ductility of sintered composites, but experimental results do not give any evidences to support such a concept.

Figure 4. Mechanical properties of the sintered composites; (a) hardness, (b) ultimate tensile strength, (c) yield strength, (d) elongation at break.
4. Conclusion
The influences of molybdenum on microstructure and mechanical property of sintered composites were investigated and the conclusions were drawn as given below.
1) General microstructures of sintered composites resembled those of ferrite-pearlite ductile irons.
2) Molybdenum retards ferrite and pearlite transformations and promotes BF/M-A formation.
3) Strength and hardness of sintered composites are influenced by pearlite + BF/M-A fraction.

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