Effect of Sintering Temperature and Cooling Rate on the Microstructure and Hardness of Fe-Cr-Mo-V-W-C Sintered Steel added with MoS2

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Abstract. In this work, the Fe-Cr-Mo-V-W-C sintered steels added with MoS2 (1, 3 and 5 wt.%) were produced by powder metallurgy process. The specimens were prepared by mixing, compacting and sintering at temperatures of 1150, 1200 and 1250°C for 45 min in vacuum furnace. After sintering, the specimens were cooled down with N2 at the different cooling rate (0.1 and 5.2°C/s). The density, hardness and microstructure of the sintered Fe-Cr-Mo-V-W-C steels were investigated. The experimental results indicated that the density and hardness of sintered steel could be improved by increase MoS2 addition, cooling rate and sintering temperature. The sintering mechanism was varied from solid state sintering to liquid phase sintering depend on sintering temperatures and MoS2 content. The presence of liquid phases and the increasing of cooling rate resulted in the amount of carbide precipitated decreased in the steel grain but increased precipitation at grain boundaries. The solidified of liquid and eutectic phases were found rising by increased cooling rate. Carbide precipitation in steel grain could be improved by added MoS2 and sintered at low temperature. From the results, it was indicated that the addition of MoS2, increase sintering temperature and cooling rate resulted in the precipitation of carbide, solidified liquid and eutectic phases, and grain growth in the sintered Fe-Cr-Mo-V-W-C steel.

Keywords: MoS2, carbide, sintering, liquid phase, cooling rate

1. Introduction

The Fe-Cr-Mo-V-W-C powder is used to produce the sintered parts that using in the wear resistance and high temperature applications [1]. This steel powder was developed for using in the conventional compaction process. However, it is lower compressibility than tool steel and high speed steel powder [2]. For the sintered parts, the mechanical properties and wear resistance are influenced by the variation of density and porosity. Therefore, the addition of additive powders for improved mechanical properties and wear resistance were found in many previous works [3-5]. MoS2 powder is used as additive powder...
in the sintering of high speed steel [4, 6, 7] and stainless steel [8, 9]. MoS$_2$ reacted to the steel matrix and produced the liquid phases at high temperature. The sintered density and porosity can be improved by MoS$_2$ addition. However, the performance of MoS$_2$ on the sintering of Fe-Cr-Mo-V-W-C in vacuum is interesting. Effects of MoS$_2$ addition on sintering temperature and cooling rate and other parameters also need explication. Therefore, in this work, the effect of MoS$_2$ content, sintering temperature and cooling rate on the microstructure and hardness of Fe-Cr-Mo-V-W sintered steel were studied.

2. Experimental Procedure
Specimens in this work were prepared by powder metallurgy process. Fe-Cr-Mo-V-W-C powder was added with various amount of MoS$_2$ powder (0, 3 and 5 wt.%) and zinc stearate (1 wt.%). The chemical composition of Fe-Cr-Mo-V-W-C powder is shown in Table 1. The mixtures were mixed thoroughly in the tumbling mixer for 1 hr. at the speed of 34 rpm. The mixed powders were compacted into the uniaxial die to produce the specimen of Ø 25 mm with 4 mm in thickness. At the compression pressure of 700 MPa, average green density of specimens was about 6.3 g/cm$^3$ by the Archimedes water immersion method. The compacted specimens were sintered in the vacuum furnace at 1150, 1200 and 1250$^\circ$C for 45 min. Subsequently, specimens were cooled down in different cooling rate of 0.1 and 5.2$^\circ$C/s with N$_2$. The sintered density was compared with the green density. The sintered specimens were cut, ground, polished and etched with Murakami etchant for microstructure examination. The microstructure of sintered specimens in the different cooling rate were examined under optical microscope and scanning electron microscope with electron dispersive spectroscopy (EDS) for element analysis. Rockwell scale A was used to evaluate the macro-hardness of sintered specimens.

| Table 1  | Chemical composition of Fe-Cr-Mo-V-W-C powder |
|----------|---------------------------------------------|
| Element  | C   | Si   | Cr  | V   | W   | Mo  | Fe  |
| Content  | (wt.%) | 1.50 | 0.50 | 16.00 | 1.50 | 1.50 | 1.50 | Bal. |

3. Results and Discussion

3.1 Sintered Density
Density of Fe-Cr-Mo-V-W-C steel added with MoS$_2$ sintered at 1150, 1200 and 1250$^\circ$C with different cooling rate of 0.1 and 5.2$^\circ$C/s is shown in Figure 1. Sintered density was improved by increase sintering temperature and cooling rate. Sintered density of specimens without MoS$_2$ added was in the range 6.33-6.37 g/cm$^3$ at cooling rate of 0.1$^\circ$C/s and 6.58-7.77 g/cm$^3$ at cooling rate of 5.2$^\circ$C/s. In addition, sintered density of Fe-Cr-Mo-V-W-C steel was improved by MoS$_2$ added, especially at cooling rate of 0.1$^\circ$C/s. However, the high sintering temperature resulted in the aggressive sintering and densification on Fe-Cr-Mo-V-W-C steel both with and without MoS$_2$ added. It is indicated that the density of specimen was highly increased after sintered at 1250$^\circ$C especially at cooling rate of 5.2$^\circ$C/s. Figure 2 shows shape of sintered specimens at 1150$^\circ$C and 1250$^\circ$C. Effect of sintering temperature and cooling rate on porosity of sintered specimens is shown in Figure 3. The great reduction of porosity was found in the specimens at cooling rate of 5.2$^\circ$C/s. Therefore, the increasing of sinter density resulted in the decreasing of porosity in sintered specimens.

3.2 Hardness of sintered specimens
Hardness of sintered specimens is shown in Figure 4. The hardness of sintered Fe-Cr-Mo-V-W-C steel added with MoS$_2$ was improved by increased sintering temperature and amount of MoS$_2$. Hardness of specimen was greater improved by sintered at 1250$^\circ$C. However, the increasing of cooling rate from 0.1 to 5.2$^\circ$C/s seemed less effect on increasing of hardness of sintered steels.
Figure 1. Sintered density of Fe-Cr-Mo-V-W-C steel added with MoS$_2$ under different sintering temperature and cooling rate.

Figure 2. Specimens after sintered at (a) 1150°C and (b) 1250°C.

Figure 3. Effect of sintering temperature and cooling rate on porosity of sintered Fe-Cr-Mo-V-W-C steel added with MoS$_2$. 
3.3.1 Cooling rate at 0.1 °C/s

Microstructures of sintered Fe-Cr-Mo-V-W-C steel from cooling rate of 0.1°C/s are shown in Figure 5. Microstructure of Fe-Cr-Mo-V-W-C steel sintered at 1150°C showed distribution of small carbide particles in the microstructure with the good bonding and rounded pores in solid state sintering as shown in Figure 5(a). The bonding of steel matrix was improved and porosity decreased after sintered at 1200°C as shown in Figure 5(b). However, the evidence of liquid phase sintering was found in the microstructure after sintered at 1250°C. The rounded solid grain with solidified liquid at grain boundary was found in the microstructure. It was found that small carbide particles precipitated in the center of grain and at grain boundaries as shown in Figure 5(c). In high chromium-carbon steel system, small liquid fraction can be formed in the microstructure at temperature below 1250°C [10-12]. The liquid phases in the sintered of Fe-Cr-Mo-V-W-C steel at 1250°C resulted in the density and hardness improvement as shown in Figure 1 and Figure 4, respectively. In this system, M7C3 and M23C6 chromium base carbide were expected to precipitate in the steel matrix [1].

3.3 Microstructures

Microstructures of sintered Fe-Cr-Mo-V-W-C steel from cooling rate of 0.1°C/s are shown in Figure 5. Microstructure of Fe-Cr-Mo-V-W-C steel sintered at 1150°C showed distribution of small carbide particles in the microstructure with the good bonding and rounded pores in solid state sintering as shown in Figure 5(a). The bonding of steel matrix was improved and porosity decreased after sintered at 1200°C as shown in Figure 5(b). However, the evidence of liquid phase sintering was found in the microstructure after sintered at 1250°C. The rounded solid grain with solidified liquid at grain boundary was found in the microstructure. It was found that small carbide particles precipitated in the center of grain and at grain boundaries as shown in Figure 5(c). In high chromium-carbon steel system, small liquid fraction can be formed in the microstructure at temperature below 1250°C [10-12]. The liquid phases in the sintered of Fe-Cr-Mo-V-W-C steel at 1250°C resulted in the density and hardness improvement as shown in Figure 1 and Figure 4, respectively. In this system, M7C3 and M23C6 chromium base carbide were expected to precipitate in the steel matrix [1].
Original particle boundaries in microstructure reduced after sintered at 1200°C. It was exhibited that better bonding particles in the microstructure as revealed by rounded pore, prior to particle boundaries and porosity reduction as shown in Figure 6(b). Small carbide particles were found in microstructures. Typical SEM images in Figure 7(a) and (b) showed amount of carbide increased by added MoS2. The addition of MoS2 resulted in improve densification of sintered high speed steel by acting as sinterability enhancer in the sintering process [4]. Therefore, sintered density of MoS2 added specimens in this work was improved as shown in Figure 1. In addition, the addition of MoS2 resulted in increasing of liquid phase during sintering at 1250°C, as indicated by increasing of solidified liquid phase and eutectic phase at grain boundary as shown in Figure 6(c). This is due to the reaction of MoS2 and steel matrix to produce the liquid phase at high sintering temperature [3]. The appearance of liquid phase resulted in density, porosity and hardness of specimens improved as shown in Figure 1, 3 and 4, respectively. The increasing of MoS2 amount and sintered at lower temperature (1150°C) demonstrated that the increasing of porosity and prior particle boundaries as shown in Figure 6(d). However, when increased sintering temperature the densification of sintered steel was improved and carbide particles were found in microstructure. At 1250°C, the eutectic phase and solidified of liquid phases was found at grain boundaries as shown in Figure 6(e). The dark phases and eutectic phases in microstructure of sintered specimens were found similar in the literatures [3, 4]. In this system, MoS2 reacts to the steel matrix and alloy elements. Therefore the mix M6C carbides were expected to form in the steel matrix [4]. This type of carbide is hard and thermally stability [1].

Figure 6. Microstructure of Fe-Cr-Mo-V-W-C steel added MoS2 sintered in different temperatures and cooling rate at 0.1°C/s; (a) MoS2 1 wt.% sintered at 1150°C, (b) MoS2 1 wt.% sintered at 1200°C, (c) MoS2 1 wt.% sintered at 1250°C, (d) MoS2 5 wt.% sintered at 1150°C and (e) MoS2 5 wt.% sintered at 1250°C
3.3.2 Cooling rate at 5.2 °C/s

Figure 8 shows microstructures of sintered Fe-Cr-Mo-V-W-C steel from cooling rate at 5.2°C/s. Small carbide particle precipitated homogeneously in microstructure after sintered at 1150°C. The microstructure showed good bonding and less outline of prior particle boundaries as shown in Figure 8(a). The outline of prior particle and porosity were reduced by increased sintering temperature up to 1200°C as shown in Figure 8(b). The fine carbide particles were found in the microstructures. However, it can be seen that amount of carbide precipitated less than that of lower cooling rate (0.1°C/s). Because of short time for carbide precipitated during cool down at high cooling rate. Effect of cooling rate on carbide precipitation was discussed in previous works [2, 13, 14]. The sintering process changed from solid stage sintering to liquid phase sintering stage when increased sintering temperature to 1250°C. The solidified of liquid phase was found in microstructure as shown in Figure 8(c). The microstructure indicated grain coarsening with rounded grain boundaries and eutectic phases along grain boundaries. It was seen that the eutectic phase fraction was more than that of slow cooling rate. In addition, formation of liquid phases resulted in decreasing of carbide precipitation in the area close to the grain boundaries as shown in Figure 8(c).

Microstructures of Fe-Cr-Mo-V-W-C added with MoS₂ sintered in various temperature and subsequent cooled down at 5.2°C/s are shown in Figure 9. In this cooling rate, the bonding of particles and porosity was improved due to increase sintering temperature as shown in Figure 9(a) and (b), respectively. Whereas the microstructure showed the solidified of liquid phases and eutectic phase at grain boundaries after sintered at 1250°C as shown in Figure 9(c). The influence of higher cooling rate (5.2°C/s) showed precipitation of carbide in microstructures was less than that found from cooling rate of 0.1°C/s. Whereas the eutectic phase fraction from high cooling rate was more than that of low cooling rate. The increasing of MoS₂ in the sintered steel showed the increasing of carbide precipitation in microstructure as shown in Figure 9(d). When increased sintering temperature, the precipitation of carbide inside the grain was reduced whereas the precipitation of carbide at grain boundaries was increased as shown in...
Figure 9(e). Specimens were sintered under liquid phase sintering process after sinter at 1250°C. The eutectic phase, solidified of liquid and coarse grain size with rounded boundaries effected from liquid phase sintering as shown in Figure 9(f). From these results, it is indicated that the variation of MoS₂ content, sintering temperature and cooling rate resulted in the precipitation of carbide and the fraction of solidified liquid and eutectic phases in the microstructure of sintered Fe-Cr-Mo-V-W-C steel. However, the characterization of carbide types, crystallography of matrix, effect of tempering time and temperatures, etc. are need to further study.

Figure 9. Microstructure of Fe-Cr-Mo-V-W-C steel added MoS₂ sintered in different temperatures and cooling rate at 5.2°C/s; (a) MoS₂ 1 wt.% sintered at 1150°C, (b) MoS₂ 1 wt.% sintered at 1200°C, (c) MoS₂ 1 wt.% sintered at 1250°C, (d) MoS₂ 5 wt.% sintered at 1150°C, (e) MoS₂ 5 wt.% sintered at 1200°C and (f) MoS₂ 5 wt.% sintered at 1250°C

4. Conclusion
In this study, the effect of MoS₂ content, sintering temperatures and cooling rate in the sintering of Fe-Cr-Mo-V-W-C steels were investigated. The results indicated that the sintered density and hardness of sintered steels were improved by increase sintering temperature. The sintering mechanism was varied from solid state sintering (1150 and 1200°C) to liquid phase sintering (1250°C). The presence of liquid phase resulted in the decrease of carbide precipitation inside the grains but increase the carbide precipitation at grain boundaries. In addition, the increasing of cool rate showed the decreasing of carbide precipitation in the microstructures. However, the high cooling rate resulted in the increasing of liquid and eutectic phases in the sintered steel. The increasing of MoS₂ in the sintered steel showed the increasing of carbide precipitation in microstructure at low temperature whereas MoS₂ influenced on the precipitation of carbides at grain boundaries when sintered at higher temperature.

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