Manufacture of powder metallurgy molybdenum-rich steels with good wear-resisting property

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ABSTRACT

The powder metallurgy molybdenum-rich steels, used in a new friction system, were prepared. Effect of carbide types on wear-resisting property of the steels was studied. The wear behavior of the steels and the couple part were also studied. M\textsubscript{2}C carbides and M\textsubscript{6}C carbides exit in the steels. The friction pair materials enter steady working condition within 50 seconds and have good match capability. On dry friction test, crisp M\textsubscript{2}C carbides, which are distributed along crystal border, dissever the matrix and decrease wear-resisting property of the steels obviously. Goblet carbides consist of many fine grainy M\textsubscript{6}C carbides. This kind of carbide has high bond strength with the matrix and is useful to good wear-resisting property of the steels.

INTRODUCTION

Wear occurs in a wide variety of items and results in severe economic loss. On the other hand, with the rapid development of the society, the requests for more excellent property materials, for use in demanding environments (e.g. high temperature, badly lubricant condition), are ever increasing\textsuperscript{[1,2]}. Therefore attention to high wear resistant materials is one important aim of materials designers\textsuperscript{[3,4]}. The powder metallurgy (PM) manufacturing process, which is experiencing growth because of its high material utilization and designed flexibility, is one way to obtain the PM multi-components steels with both high wear resistance and good mechanical properties\textsuperscript{[5,6]}. Addition of strong carbide-forming element, e.g. molybdenum, chromium, vanadium and titanium by powder metallurgy (P/M) process techniques is one way to obtain the multi-components iron-based materials with both high wear resistance and good mechanical properties\textsuperscript{[3,4]}. These elements have a great affinity for carbon and form very hard wear-resistant metallic carbides. Then the microstructure in these materials is very complex\textsuperscript{[5-7]}. It consists of a tempered martensitic matrix and various types of hard carbides, including block (primary) carbides and fine secondary carbides. The hardness and strength of the carbides are higher than those of the matrix. In cases of wear the carbides protrude above the nominal surface of the materials to support mostly loading, and thereby protect the matrix from further wear, which is beneficial for the wear resistance of the material. On the other hand, the matrix absorbs the energy, which fixes the carbides...
and prevents them from breaking or detaching from the matrix, thereby eliminating the presence of abrasive particles detrimental to the wear rate. Although the existence of the hard carbides is beneficial to the improvement of the materials properties, it is reported that the nucleation, propagation and interaction of micro cracks in multi-components iron-based materials occur preferentially in the grain boundaries of coarse and hard carbides\[8-10\]. In this sense, carbide volume fraction, type, morphology and distribution of primary and eutectic carbides play an important role on the properties and, as a consequence, in the tribological behavior of these materials\[11-15\].

It is worth mentioning that wear resistance, which is just a single parameter in a specific frictional system, is not an inherent property of the materials. A P/M steel with high molybdenum element content (8.0~10.0% Mo) is examined in this paper. These types of steels are used as spacing adjustment pieces in a new friction system with a high power engine. The couple part in this friction system is a cast iron (international standards). The high degree of match of these friction part materials can prolong the service life of the materials, and thereby increases the engine efficiency. The aim of this paper is to evaluate the effect of the molybdenum-rich carbides type, morphology and distribution on the wear behavior of the P/M steels. Special emphasis is given to the wear mechanisms of the friction pair materials in the friction system.

**EXPERIMENTAL PROCEDURE**

The studied materials in this paper consisted of two series of the P/M steels (8.0~10.0wt% Mo, 1.3~1.4wt% C and balance Fe) and the cast irons (international standard, 0.90~1.20wt% Cr, 0.15~0.25wt% Mo, 0.17~0.37wt% Si, 0.50~0.80wt% Mn). The P/M steels contained a strong carbide-forming element, which allowed them to form the molybdenum-rich carbides for a good wear-resisting property. Natural graphite was also present in the P/M steels. The mixed powders were cold pressed at 600MPa with a single action die and sintered at 1270°C for 120 minutes and annealed at 1100°C for 6 hours in a vacuum atmosphere. Then the P/M steels were quenched at 900°C for 30 minutes and tempered at 280°C for 60 minutes. The cast irons were quenched at 880°C for 30 minutes and tempered at 180°C for 60 minutes. The properties of two series of materials were shown in TABLE 1.

<table>
<thead>
<tr>
<th>Table 1: Properties of the friction pair materials</th>
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<tbody>
<tr>
<td>Properties</td>
</tr>
<tr>
<td>Hardness (HRC)</td>
</tr>
<tr>
<td>Flexural Strength (MPa)</td>
</tr>
<tr>
<td>Impact Toughness (J·cm²)</td>
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</table>

The P/M steels were ground, polished and etched with the 2% nitric acid solution. The wear tests were carried out on a standard ball-on-flat sliding wear test machine (UMT-3). The friction system includes a stationary cylindrical materials (the cast irons) and to-and-fro movement flat materials (the P/M steels). All tests were carried out at a constant load of 4 N, a sliding speed of 1000 revolutions per minute without a lubricant. The tests were interrupted after running for different sliding time (30 minutes, 60 minutes and 120 minutes).

The microstructures of the P/M steels and the wear surface microstructures of all the materials were examined by optical microscopy (F1-M3), scanning electron microscopy (SEM, SIRION 200) and energy dispersive spectroscopy (EDS). The phase identification and the phase composition of the P/M steels were determined by X-ray diffraction and energy dispersive spectroscopy (EDS) analysis respectively.

Wear ratio ($W_s$) of each series materials was calculated, using Eq.(1).

$$W_s = \frac{v}{pI}$$  
(1)

Where $v$ is the wear volume loss of the material; $p$ is the constant load; $I$ is the movement distance of the material.

**RESULTS AND DISCUSSION**

**Wear curve graph**

Figure 1 presents the wear curve graph of the P/M steels from the ball-on-flat sliding wear test.

The abrasion factor of the P/M steels changes distinctly in the initial wear stage. At the beginning of the wear test, there are a lot of protruding parts in the rough
original surfaces of the friction pair materials. The protruding parts squeeze each other and result in an abrasion factor that is low, but changes distinctly. After the protruding parts are rubbed out, the contact area of the friction pair materials remains constant, and therefore the abrasion factor becomes roughly constant. The friction system enters steady working condition. In this paper, the time to reach the steady-state regime is shorter than 50 seconds.

**Wear resistance**

TABLE 2 shows the wear ratio with the different wear test time. The wear ratio is low and increases very slowly within the steady-state regime. Moreover, the two friction pair materials in the friction system have a quite similar wear ratio, showing that these two materials have high wear-resistance and good matching ability.

TABLE 2 : Wear ratio of the materials

<table>
<thead>
<tr>
<th>Wear test time (minutes)</th>
<th>wear ratio (10^{-15}kg \cdot m^{-1} \cdot N^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P/M steel cast iron</td>
</tr>
<tr>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td>60</td>
<td>1.996 1.988</td>
</tr>
<tr>
<td>120</td>
<td>2.013 2.009</td>
</tr>
</tbody>
</table>

**Microstructure of the original surfaces**

Figure 2 and Figure 3 are the XRD patterns and the microstructure of the P/M steel before wear test.

Two carbide types, i.e. M\textsubscript{2}C carbides and M\textsubscript{6}C carbides are present in the material, Figure 2. This multi-components iron-based P/M material, Figure 3, indicates a microstructure typical of tempered martensite and different carbide types. These carbides, the shapes of which are needle, block and fine granular, are dispersed heterogeneously in the microstructure. Noteworthy is that the alloying elements promote a decrease of density, which results in a number of near round pores.

Figure 2 : XRD patterns of the P/M steel before wear test

Figure 3 : SEM image of the P/M steel before wear test

Figure 4 displays the microstructure of the cast iron before wear test. This material has very high density and a uniform, even microstructure.

Figure 4 : SEM image of the cast iron before wear test
Microstructures of the worn surfaces

Figure 5 denotes typical aspects of the worn surface microstructures and illustrates wear mechanisms of the two friction pair materials with the different wear test time, respectively.

The dominant wear mechanism acting in the two friction pair materials is abrasion with the wear test of 30 minutes and of 60 minutes. But the morphology of the worn surfaces is distinctly different between the two friction pair materials. The dimensions of the grooves present in the P/M steels, Figure 5(a) and Figure 5(c), seem to be wider and deeper than those present in the cast irons, Figure 5(b) and Figure 5(d). In addition, the grooves present in the P/M steels, which are often stopped and deviated by the carbides, Figure 5(a) and Figure 5(c), are irregular. However, the grooves present in the cast irons, Figure 5(b) and Figure 5(d), are clearly homogeneous and unidirectional.

Figure 5 : Worn surfaces of the two friction pair materials
The dominant wear mechanism acting in the two friction pair materials changes with the wear test of 120 minutes. The dominant wear mechanism acting in the P/M steels changes from abrasion to adhesion, Figure 5(e), whereas that acting in the cast irons is still abrasion, Figure 5(f). The hardness of the cast irons is higher than that of the P/M steels, which results in the cast irons having a lower wear degree.

Figure 6 indicates SEM images of the worn surfaces in the P/M steels with the wear test of 60 minutes, respectively.

The degree of pores in the worn surface is higher than that of the surface before wear test. Moreover, a lot of white needle carbides and white block carbides are present in the worn surfaces, Figure 6(a). It is worth noting that the carbides protrude above the worn surface due to preferential wear of the matrix, and support mostly loading. Under these circumstances the carbides wear behavior markedly influences the materials wear-resistance. In this paper, different carbides types are shown to possess differing wear behaviors.

As shown in Figure 6(b), a higher-magnification SEM image of the area A of Figure 6(a), the white block carbides are surrounded by a lot of fine granular carbides. These carbides are neither cracked nor broken up even in the exposed part, so there is a high bonding strength between the carbides and the matrix. This type of carbide protects the matrix from further wear, and is useful to the wear-resistance of the materials. On the other hand, because of the high bonding strength, the matrix firmly fixes the carbides and prevents them from breaking or detaching from the matrix. Otherwise the separated carbides will form abrasive particle and decrease the wear rate.

As shown in Figure 6(c), a higher-magnification SEM image of the area B of Figure 6(a). The white needle carbides distribute along crystal borders. These carbides are easy to separate from the matrix, thus lose their protective effect and leave many cracks in the worn surfaces. Therefore, the matrix, which is isolated by the needle carbides, peels off from the worn surfaces and leaves a big pore. In this wear process, large pores will result in higher plastic strains in the matrix, which in turn lead to a higher probability of crack formation, and consequently a higher tendency of wear. The white needle carbides, which distribute along crystal borders, decrease the wear-resistance of the materials.
Figures in the P/M steels with the wear test of 60 minutes, respectively.

**TABLE 3 : EDS results of the P/M steels worn surfaces with the wear test of 60 minutes**

<table>
<thead>
<tr>
<th>Point</th>
<th>Type</th>
<th>Element content (at %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 6(b), a</td>
<td>M₆C</td>
<td>53.69 35.84 10.47</td>
</tr>
<tr>
<td>Figure 6(c), b</td>
<td>M₃C</td>
<td>77.52 13.65 8.83</td>
</tr>
<tr>
<td>Figure 6(c), c</td>
<td>Matrix</td>
<td>4.09 88.57 7.34</td>
</tr>
</tbody>
</table>

According to EDS results, high molybdenum contents of white block carbides, point a of Figure 6(b), and of white needle carbides, point b of Figure 6(c), are observed at 53.69at% and 77.52at% respectively. However, iron content (35.84at%) of white block carbides are obviously different from those of white needle carbides (13.65at%). According to the XRD pattern and EDS results, the carbide types can be identified that white needle carbides are M₃C carbides and white block carbides are M₆C carbides. Molybdenum element diffuses in the matrix, point c of Figure 6(c).

**Figure 7 : SEM images of the P/M steels worn surfaces with the wear test of 120 minutes**

**TABLE 4 : EDS results of the P/M steels worn surfaces with the wear test of 120 minutes**

<table>
<thead>
<tr>
<th>Point</th>
<th>Type</th>
<th>Element content (at %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 7(b), a</td>
<td>M₆C</td>
<td>54.28 36.55 9.17</td>
</tr>
<tr>
<td>Figure 7(c), b</td>
<td>M₃C</td>
<td>73.92 16.33 9.75</td>
</tr>
<tr>
<td>Figure 7(c), c</td>
<td>Matrix</td>
<td>2.51 91.89 5.60</td>
</tr>
</tbody>
</table>

Figure 7 and TABLE 4 indicate SEM images and EDS results of the worn surfaces in the P/M steels with the wear test of 120 minutes, respectively.

The degree of pores in the worn surface is not significantly changed with the prolonging wear test time. But, some big pores appear in the worn surfaces, Figure 7(a). Figure 7(b) is a higher-magnification SEM image of the area A of Figure 7(a). With a longer wear time, a lot of fine granular M₆C carbides (point a of Figure 7(b), TABLE 4) still remain in the matrix. However, as shown in Figure 7(c), a higher-magnification SEM image of the area B of Figure 7(a), almost all of the white needle M₃C carbides (point b of Figure 7(c), TABLE 4) have separated from the matrix. Therefore, the matrix (point c of Figure 7(c), TABLE 4, which is isolated by the needle carbides, peels off the worn surfaces and leaves pore. In this type of wear process, large pores will result in higher plastic strains in the matrix, which in turn lead to a higher probability of crack formation, and consequently to a higher tendency of wear.

Figure 8 displays SEM images of the worn surfaces in the cast irons with the different wear test time, respectively.

There are clearly homogeneous and unidirectional grooves, parallel appearing in the surface. The microstructure is uniform and even, so no phase makes major influence on the wear behavior of the cast irons. With the
prolonging wear test time, the dimensions of the grooves present in the cast irons seem to be wider and deeper.

The dominant wear mechanism acting in the two friction pair materials changes as a function of increasing wear test time. The dominant wear mechanism acting in the P/M steel changes from abrasion to adhesion whereas that acting in the cast iron is always abrasion.

The different types of carbides play significant various roles on the wear-resisting property of the P/M steels. The white block carbides (M₆C) are useful to the wear-resistance of the materials. The white needle carbides (M₆C) decrease the wear-resistance of the materials.

The microstructure of the cast iron is uniform and even, so no phase makes major influence on the wear behavior of the material.

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