Microstructure and Properties of Boronizing Layer of Fe-based Powder Metallurgy Compacts Prepared by Boronizing and Sintering Simultaneously

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Abstract:
In this study, the boronized layers were formed on the surfaces of specimens with a composition of Fe-2 wt. % Cu-0.4 wt. % C by sintering and boronizing simultaneously, using a pack boronizing method. The processes were performed in the temperature range of 1050 - 1150 °C at a holding time of 4 hours in 97 % N₂ and 3 % H₂ atmosphere. Scanning electron microscopy examinations showed that the boronized layers formed on the surface of boronized and sintered specimens have a denticular morphology. The thicknesses of the boronized layers varied from 63 to 208 μm depending on the processing temperature. The structures of the boronized layers were Fe₂B and FeB confirmed by X-ray diffraction analysis. The microhardness values of boronized layers ranged from 1360 to 2066 HVₐ₃ much higher than that of substrate hardness which was about 186 HVₐ₃. Wear testing results showed that the wear resistance of the boronized and sintered specimens was significantly improved, resulting from increased surface microhardness.

Keywords: Powder metallurgy; Pack boronizing; Microstructure; Microhardness; Wear.

Introduction

Manufacturing of many mechanical components [1-3] by powder metallurgy (P/M) technology has been frequently used in manufacturing industry owing to their low energy consumption, high materials utilization and low production cost resulting from the near net shape process [4-6]. Therefore, some P/M structural parts with high sintered density as well as high wear resistance have been widely used in automotive systems, such as cam lobes, gears and valve seats etc. [3]. The surface hardening was usually carried out for these components to obtain a harder layer on surfaces and tough core in the center, which exhibited both high wear resistance and strength. In the past few years, surface hardening processes such as gas nitriding [1, 7, 8], plasma nitriding [5, 9], glow-discharge treatment [10], nitriding and nitrocarburizing [11], as well as surface carburizing [12, 13] treatments have been widely used for surface hardening treatments of P/M parts.

Boronizing is a thermochemical surface-hardening process that enriches the material surface by diffusing boron atoms into the surface at high temperatures. This process is similar in its physical and chemical characteristics to other surface hardening treatments, such as carburization and nitriding. It has been successfully applied to all ferrous materials, nickel
alloys, titanium alloys, and sintered carbides [14, 15]. Generally, the process temperature of thermal diffusion treatments of boronizing compounds should be between 973 and 1273 K. This process can be performed in solid, liquid or gaseous medium. The most frequently utilized method is pack boronizing which is a process similar to pack carburizing process. Especially, powder-pack boronizing has the advantage of simplicity and cost-effectiveness in comparison with other boronizing processes [16-19]. Boron atoms, owing to their relatively small size and high mobility at process temperature can diffuse into ferrous metals, resulting in the formation of both single Fe<sub>2</sub>B and FeB-based polyphases coatings which is mainly used to improve wear resistance of the components for tribological applications. The thickness and proportion of each boride depend on chemical composition of workpiece, boronizing medium, process temperature and duration of treatment [16, 20-22].

In the present study, boronizing of P/M parts can be referred to as a one-step process in which boronizing and sintering are fulfilled simultaneously. Its obvious merit is to simplify the traditional boronizing process and decrease production costs. The purpose of this paper is to provide an available boronizing-sintering process for the production of P/M materials with boride in their surface. It is also expected that this study could help to develop the fabrication of special P/M materials with good properties of a surface layer containing boride.

2. Experimental procedures
2.1 Materials and sintering process

The water atomized iron powder (Höganäs AHC100.29), together with 2 wt. % copper and 0.4 wt. % natural graphite with purity higher than 99 %, were used to fabricate compacts. The average diameters of different particles for iron, copper and graphite were 45-125 μm, 37 μm and 60 μm, respectively. Mineral oil (0.3 ml/kg) and zinc stearate (5 g/kg) were added to the mixture as lubricant. After being blended with a blender running at a rate of 33 rpm for 60 min, the powder mixture was uniaxially cold pressed to a green density of 7.0 g/cm³. The size of the compacts was Ø 13 mm × 10.6 mm. The compacts were enveloped by boronizing medium which contains 5 wt. % B<sub>4</sub>C as donor, 5 wt. % KBF<sub>4</sub> as an activity and 90 wt. % SiC as diluent. Subsequently, they were packed in a boronizing box made of special steel. The box was then placed into an electrical resistance furnace for boronizing. The compact specimens were boronized at different temperatures (1050, 1100, 1120 and 1150 °C) for 4 hours in a 90 % N<sub>2</sub> - 3 % H<sub>2</sub> atmosphere. The specimens were taken out from the box by removing the used boronizing mixture when the box was gradually cooled to room temperature.

2.2 Characterization of boronized specimens

After the surfaces of the boronized specimens were ground, polished and etched with a 4% Nital solution, their microstructures were observed by SEM (Model JSM-5310, Japan). The average thickness of the boronized layers was measured in the microscope.

The presence of borides formed on specimen surfaces was checked by a Rigaku X-ray diffractometer (D/Max 2500PC) with a Cu Kα radiation source of a wavelength of 1.541 Å over a 2θ range from 20 ° to 90 °.

The Vickers microhardness measurements were carried out from the surface to the substrate along the cross-section using a HXD-1000 microhardness tester with a load of 300 g and indentation time of 15 s. The final values quoted for the microhardness were the averages of 10 measurements.

Wear testing was conducted with a pin on disc type machine. All wear tests were carried out under dry sliding conditions at room temperature of 25 °C. Specimens 6 mm in
diameter and 10 mm in height were machined from the boronized specimens and the only sintered specimens for comparison. Specimen surfaces were thoroughly degreased by acetone and dried before wear testing. The tests were carried out with different applied loads (40, 70, 100, 130 and 160 N) at a sliding speed of 0.785 m/s. Specimens were weighed on an electrical balance with an accuracy of 0.1 mg before and after wear testing. The weight losses calculated by worn volume before and after wear testing were given by the averages of three specimens after sliding distance of 376.8 m. The 70 mm-diameter disc made of high carbon chromium steel was hardened to a hardness of 57 HRC, and the bearing surface of the disc was grounded to a constant surface roughness of ~0.4 μm Ra. The worn surfaces of the wear pins were examined by SEM.

3. Results and Discussions
3.1 X-ray diffraction analysis

Fig. 1 shows the XRD patterns for the boronized specimens at different temperatures for 4 hrs and un-boronized specimens sintered at 1120 °C for 4 hrs. It can be seen that the surface of the un-boronized specimen is mainly α-Fe shown in Fig. 1(a). After boronizing treatment at 1050, 1120, 1150 °C for 4 hrs, the XRD patterns as shown in Fig. 1(b), (c), (d), reveal that the boronized layers mainly consist of Fe₂B, and only a small amount of FeB was detected.

![Fig.1 X-ray diffraction patterns of (a) un-boronized specimen sintered at 1120 °C for 4 hrs and boronized specimens at different temperature: (b) 1050 °C, (c) 1120 °C, (d) 1150 °C for 4 hrs, respectively.](image-url)
Furthermore, the intensity of the Fe$_2$B (002), (022) and (330) peaks become more intensive as boronizing temperature increases, indicating that these Fe$_2$B orientation were becoming dominant for higher boronizing temperature.

3.2 Microstructures

The cross-sectional microstructures of the boronized layer for different specimens are shown in Fig. 2. It can be seen that the surfaces of the boronized specimens are composed of three distinct regions, i.e.: (i) a surface layer, primarily consisting of Fe$_2$B and FeB phases; (ii) a transition zone, being rich in boron and (iii) matrix, which is not affected by boronizing process.

The prominent phase formed in the boronized layer is Fe$_2$B while a small amount of FeB is detected by XRD analysis (Fig.1). As the boronized temperature increases, the boronized layer becomes thicker.

The thicknesses of the boronized layer corresponding to the sintering temperature are listed in Tab. I.

**Tab. I** Case depth of boronized specimens at different temperature for 4 hrs.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>The depth of boride layer (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1050</td>
<td>63</td>
</tr>
<tr>
<td>1100</td>
<td>121</td>
</tr>
<tr>
<td>1120</td>
<td>179</td>
</tr>
<tr>
<td>1150</td>
<td>208</td>
</tr>
</tbody>
</table>

Fig. 2 The microstructure in a cross-section of a boronized layer of specimens boronized at: (a) 1050 °C, (b) 1100 °C (c) 1120 °C, (d) 1150°C for 4 hrs, respectively.
3.3 Microhardness and wear behavior

3.3.1 Microhardness

The microhardness of the boronized layer, transition zone and matrix were measured along the cross-section of specimens, as shown in Fig. 4. The microhardness in the outer part of the boronized layer is relatively lower resulting from the crystallographic disorder and friability, which is in agreement with the results in Ref. [23]. It can be seen that the microhardness is higher in the subsurface of boronized layer. And the microhardness values of specimens boronized at different temperatures are in the range of 1487-1545 (1050 °C), 1354-1887 (1100 °C), 1331-1882 (1120 °C) and 1360-2066 (1150 °C) HV_{0.3}, respectively. It can be found from Fig. 4 that the microhardness values of all these boronized layers are much higher than that of the substrate, i.e. 186 HV_{0.3}. The transitional regions have an intermediate microhardness of about 855 HV_{0.3}, which is also higher than that of the substrate.

![Fig. 3 Microhardness profiles in cross section of boronized layers formed on the surface of specimens boronized at different temperature for 4 hrs.](image-url)

Then, the microhardness gradually decreases along the cross-section until reaching the substrate at ~250 μm. The enhancement in the microhardness on the surface is due to the presence of harder phases Fe_{2}B and FeB (see Fig. 2). It can be seen from Fig. 3 that the microhardness values of the boronized layer is related to the temperature which is in accordance with the tendency that the thickness of the layer increases with increasing temperature as shown in Fig. 2.

3.3.2 Wear behavior

The variations in friction coefficient and wear rate to load for boronized specimens at various temperatures are shown in Figs. 4 and 5, respectively. In order to find the differences in friction coefficients and wear behaviour through their different wear mechanisms, the un-boronized specimen sintered at 1120 °C was also examined. The friction coefficient had been calculated from friction force using Coulomb’s law of friction (μ = F/N). It can be seen that
the friction coefficients have a highest value at 40 N and gradually decrease and finally
decrease to the lowest level at high load with the loads increases. For the boronized
specimens, the changing trend of the friction coefficient with load is similar to that of the as-
sintered specimen. It is obvious that the friction coefficient of the boronized specimens is
much higher than that of the as-sintered specimens under the same applied load. It is probably
due to a large amount of worn debris are produced in the sliding and reached steady-state. The
debris compositions may significantly affect the friction behavior, e.g. softer debris usually
produces lower friction [24].

![Graph showing variation of friction coefficient to loads for the boronized and un-boronized specimens.](image)

**Fig. 4** Variation of friction coefficient to loads for the boronized and un-boronized specimens.

![Graph showing variation of wear rate to loads for boronized and un-boronized specimens.](image)

**Fig. 5** Variation of wear rate to loads for boronized and un-boronized specimens.

Besides the increase of sliding friction coefficients, the wear rates of the boronized
specimens were much lower compared with those of the as-sintered specimen under the
employed loads (Fig. 5). Moreover, the wear resistance of the boronized layer increases with
the increase of boronizing temperature from 1050 to 1150°C. Under the present loading
conditions, it is obvious that the wear resistance increases with the increase of the surface microhardness and the layer thickness. It can be clearly seen from the inset shown in Fig. 5, at 1050°C, the wear rate increases rapidly as the applied load beyond 100 N, which is ascribed to the thinner boronized layer compared to that boronized at the higher temperatures.

Fig. 6 SEM micrographs of worn surfaces of (a) un-boronized specimen sintered at 1120°C for 4 hrs and boronized specimens at different temperatures: (b) 1050 °C, (c) 1120°C, (d) 1150°C for 4 hrs, respectively.

Fig. 6 shows the micrographs of the worn surfaces of both boronized and un-boronized specimens at the moderate load 100 N. The characterization of the worn surfaces reveals quite different wear behaviour between boronized and un-boronized specimens. From Fig. 6(a), it is seen that abrasive grooves and adhesion wear appear in the worn surface of the un-boronized specimen. The un-boronized specimens are mainly characterized by adhesion, scratch and serious plastic deformation. On the contrast, the boronized specimens are mainly characterized by scuffing and brittle micro-fracture (Fig. 6(b)-(d)). It can be seen that the abrasive wear with a few shallower and narrower grooves are exhibited, and the delaminated debris can be observed.

4. Conclusions

1. It is shown that the powder metallurgy compacts can be boronized in a mixture of SiC-5 wt.% B₄C-5 wt.% KBF₄ at 1100-1150°C for 4 hrs. The XRD studies reveal that dominant phase is Fe₂B except a little FeB in the boronized layers.

2. The microhardness distribution of the boronized layer presents a gradient change and a hardness range of 1360-2066 HV₀.₃ is obtained. Experimental results reveal that higher boronizing temperature will result in thicker boronized layers.
3. The wear resistance of the boronized specimens is higher than that un-boronized ones under dry sliding conditions.

Acknowledgements

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References

у звисности од температуре обраде. Структуре боронизираних слојева су биле Fe₂B и FeB што је потврђено анализом рентгенске дифракције. Вредности микротврдоће боронизираних слојева су биле од 1360 до 2066 HV 0,3 што је много више од тврдоће субстрата која је била око 186 HV 0,3. Резултати испитивања хабања су показали да је отпорност на хабање знатно побољшана за боронизирани и синтерована узорке као резултат повећања површинске микротврдоће.

Кључне речи: Металургија праха, пакетна боронизација, микроструктура, микротврдоћа, хабање..