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Boride layer growth kinetics during boriding of molybdenum by the Spark Plasma Sintering (SPS) technology

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ABSTRACT

Molybdenum borides have potential industrial applications as abrasive, corrosion-resistant and electrode materials due to their high hardness values, chemical inertness, and electronic conductivity. In this work, boride layers are formed on the surface of Mo samples using a pack boriding method with the assistance of the spark plasma sintering technique. The process was performed in the temperature range 1000 ~ 1400°C with a holding time of 30 minutes. The microstructure, microhardness and fracture toughness of the molybdenum boride layer are investigated by optical microscopy, X-ray diffraction and microhardness indentations. Results showed that the boride layer mainly composed of MoB, have thickness in the range ~6 – 155 μm . The boriding kinetics is studied by connecting the boride layer thickness with the boriding temperature. The activation energy and pre-exponential constant are estimated from the experimental results, and are 218.8 KJ/mol and 1.41 cm^2/s respectively. The MoB layers are found to have a preferred orientation in the (002) direction, which is reflected by a distinct columnar growth observed in the optical micrographs of polished cross-sections of SPS samples.

Keywords: Molybdenum boride, spark plasma sintering boriding, layer thickness, growth kinetics, XRD

1. Introduction

Boronizing (also called boriding) is a reliable and functional surface-hardening process which is widely used in industry to produce extremely hard and wear-resistant surfaces [1, 2]. The process involves the heating of the well-cleaned material at a certain temperature range, in contact with boronaceous solid powder, paste, liquid, or gaseous medium [3-9]. During boriding, the diffusion and subsequent reaction of boron atoms with metallic substrate forms interstitial boron compounds. The resulting layer may consist of either a single-phase boride or a polyphase boride layer. The type of metal under treatment, the boronizing method and composition of boronizing media, temperature and time of treatment, play important roles in deciding the quality and disposition of obtained boride layers. In general, the thickness of boride layer increases with the increase of boriding temperature and time, but varies for different materials under the same boridation conditions [10]. Among all different kinds of boriding methods, only pack boriding has been widely used on a commercial basis. Yet the pack boriding process has the disadvantages of relatively high processing temperature and long process duration for getting an effective boride layer thickness. Spark plasma sintering (SPS) boriding is thus introduced to activate the pack boriding medium as well as the workpiece with a high current discharge [4, 11, 12].

Most researches on boriding deal with the boriding of ferrous materials and some of them with titanium alloys [1]. Yet, nonferrous materials such as nickel- [13-15] and cobalt-based [15] alloys, as well as refractory metals and alloys [11, 16, 17] can be borided. Molybdenum (Mo) has a wide range of industrial applications due to its unique combination of physical, chemical and mechanical properties [18]. Molybdenum borides have attracted considerable interest for technical applications because of their high melting point, chemical stability, extremely high hardness, high strength and excellent resistance against mechanical and corrosive wear [19-22]. Molybdenum borides are very hard but also brittle. This limitation may be partially circumvented if they are used as coatings over less brittle metallic molybdenum substrates. But there are very few investigations dealing with the boriding of molybdenum [16, 23].

In this study, the boriding of Mo is carried out by spark plasma sintering boriding process using boride carbide (B_4C) based powder pack. Boriding was performed in

vacuum between 1000 to 1400°C for a period of 30 minutes each. The microstructure and mechanical properties of the molybdenum samples after SPS boriding is investigated by optical microscope, X-ray diffraction and microhardness indentation.

2 Experimental Procedure

Commercial molybdenum rod (Goodfellow, Cambridge, UK, 99.95% purity) with a diameter of 10 mm was used as the testing sample in the boriding experiment. The molybdenum rod was cut into discs with a thickness of 5 mm, polished at both sides and degreased by acetone before boriding. A pack boriding powder mixture (ARCI, India) composed of B₄C with SiC as a diluent was used as the boriding media in this experiment. The sample disc was imbedded in the boriding media, packed in a Ø20 mm graphite die set and placed into the spark plasma sintering equipment (Sumitomo Coal and Mining, Japan, Model: Dr. Sinter 1050). The boriding parameters are listed in Table 1. A relatively short boriding duration is chosen in this study to highlight the ability of SPS, as it is expected that SPS boriding can get an effective boride layer within a short period as compared to most conventional pack boriding process that requires over 2 hours.

Table I. SPS boriding parameter for Moly samples

Sample Code	Boride Treatment
M1	1000°C for 30 mins
M2	1100°C for 30 mins
M3	1200°C for 30 mins
M4	1300°C for 30 mins
M5	1400°C for 30 mins

After boriding, the samples were degreased with acetone in an ultrasonic cleaner. X-Ray diffraction analysis was carried out on a Philips MPD 1880 XRD system to

investigate the phase composition of the boride layer. Subsequently, the sample was sectioned, mounted and polished for microstructure inspection and indentation test.

Vicker's indentation is used to obtain the microhardness on the surface and cross-section of the borided samples. In order to obtain an optimal result, each average microhardness value is an average of 20 points with the same load for each specimen.

Vicker's indentation was also applied to measure the toughness of the boride layer the measurement of crack length initiated by indentation. Having obtained the crack length and hardness, the fracture toughness of each coating was calculated. The indentating load is set at 2000 mN.

The fracture toughness was calculated from the following:

$$K_{IC} = 0.016(E/H)^{1/2}(P/C^{3/2}) \quad (1)$$

Where K_{IC} is the fracture toughness, $\text{MPa}\sqrt{\text{m}}$; P is the indentator load, kgf; E is the Young's modulus, GPa; H is the hardness, GPa; and C is the crack length (mm).

3. Results and Discussion

3.1 Microstructure

The cross-sectional microstructure of molybdenum boride layer of samples borided at different temperatures is shown in Figure 1. At 1000°C , the molybdenum boride layer starts to nucleate, and the grains are equi-axial and randomly distributed. At 1100°C , the molybdenum boride layer displays a mixture of the random grain and columnar structure. Further growth of the grains leads to the formation of columnar structure. From 1200°C , the borided Mo layer displayed a full columnar structure. The orientation of the columnar structure is more intensified as temperature increases. The boride layer was quite brittle since cracks can be observed for temperature 1100 and 1200°C . The formation of cracks occurs parallel to the surface.

The measurement of boride layer thickness (case depth) is exceedingly crucial for the study of boride layer growth kinetics. Yet, since the borided case depth is not evenly distributed along the surface of the base metal, the definition of case depth is not immediately obvious. In our previous study [12], we have developed a simple picture-

processing program to calculate the case depth, d , from the cross-sectional boride layer area, A , divided by the cross-sectional boride layer length, l , as depicted in Figure 1(f):

$$d = \frac{A}{l} \quad (2)$$

The case depth corresponding to the SPS boriding temperature is listed in Table II. By increasing the temperature from 1000 to 1400°C, the boride layer increases from 14 μm to 150 μm in thickness respectively. Increasing temperature from 1100 to 1200°C or 1200 to 1300°C offers an additional thickness of 50 μm as compared to other temperature differences. It is observed that, for the Mo samples borided at temperature 1300 and 1400°C, a thin layer appears in the interface between the MoB layer and the substrate.

Table II. Case Depth and Mechanical Properties of SPS Borided Mo Samples

Sample	Case Depth (μm)	Cross-Sectional Hardness (HV)	Surface Hardness (HV)	Young's Modulus E (Gpa)	Fracture Toughness ($\text{MPa} \sqrt{\text{m}}$)
M1	14 $\pm$ 5	1770 $\pm$ 150	3417 $\pm$ 400	-	-
M2	32 $\pm$ 5	1598 $\pm$ 120	3005 $\pm$ 290	-	-
M3	87 $\pm$ 5	1615 $\pm$ 140	2535 $\pm$ 410	148 $\pm$ 6	2.71
M4	135 $\pm$ 5	1735 $\pm$ 140	-	188 $\pm$ 8	3.68
M5	150 $\pm$ 5	1810 $\pm$ 130	-	229 $\pm$ 4	5.64

Figure 2 shows the X-ray diffraction (XRD) patterns of the borided Mo layer as the treatment temperature increases. MoB was detected for all temperatures. As temperature increases, Molybdenum Carbide (MoC) and Silicon Carbide (SiC) were detected, due to the diffusion of carbon and impurities were deposited on the borided surface. The intensity of the phase MoB (008) has the highest peak for all treatment temperature except 1200°C, where all peaks of MoB were intensified, with the intensity at (105) to be higher than (008). It is interesting to note that full columnar growth occurs at 1200°C, MoB shows a preferred orientation that causes an influence of the intensity distribution of the XRD patterns.

Two of the Mo samples borided at 1300°C and 1400°C were sent for annealing in vacuum to observe any phase or metallurgic changes. The annealing is done at a

temperature of 1000°C for 30 mins. Figures 3 and 4 show the XRD patterns of the annealed borided Mo. There is no significant change in the intensity ratio in the XRD pattern for the samples before and after annealing. As shown in shown in Table III, the cross sectional micro-hardness values also show no variation after annealing, which implies that the annealing cannot cause the stress relief in the boride layer, and the hardness of molybdenum boride can be maintained at high temperature.

Table III Cross-sectional micro-hardness of boride layer before and after annealing

	Cross Sectional Vicker Hardness (HV)	
	Before Heat treatment	After Heat treatment
Borided Mo at 1300°C	1735±140	1739±140
Borided Mo at 1400°C	1810±130	1840±130

In order to investigate the phase change along the depth of the sample, layer removal was conducted by polishing the borided surface and XRD was carried out after each removal of 20 µm of borided layer to investigate the area of interest. Figure 5 shows the X-Ray pattern of borided Mo for each polish removal. Gradual removal of boride layers removed the SiC and MoC and there was a distinctive preferred orientation at (200) plane for MoB after the 1st polish. The substrate peaks were observed from the 3rd polish. Consequent polishing intensifies the substrate peaks.

3.2 Mechanical Properties

3.2.1 Microhardness

The average surface and cross-sectional hardness is also shown in Table II. The surface indentation for 1300 and 1400°C is not possible, since the surface roughness was high. The surface hardness of the boride layer achieved a hardness of 3000 HV. The average cross-sectional microhardness shows no significant difference among different boride samples, which is around 1600 to 1800 HV for all samples. The cross-sectional Vicker's hardness distribution is shown in Figure 6.

3.2.2 Fracture Toughness

The crack length propagates longer at a lower boriding temperature as shown in Figure 1. This indicates that thin boride layer appears to be more brittle. The fracture toughness result confirms this tendency, as shown in Table II. Fracture toughness is improved at higher temperature. As cracks are easily form at lower temperature of 1100 and 1200°C, the borided Mo layer appears to be more brittle at thickness less than the thickness attained at 1300°C. As a result, a thicker boride layer will provide a greater resistance to impact.

3.3 Boriding kinetics

Assuming unidirectional boron diffusion and parabolic growth, the variation of boride layer thickness with time can be described by [24]:

$$d^2 = Dt \quad (3)$$

where d is the boride layer thickness (cm), t is the time (s) and D is the growth rate constant. The diffusion of boron in the boride layer is the main factor affecting the layer growth. The relationship between the growth rate constant, D , activation energy, Q , and the temperature in Kelvin, T , can be expressed as an Arrhenius equation [25]:

$$D = D_0 \exp(-Q/RT) \quad (4)$$

where D_0 is the pre-exponential constant and R is the gas constant. By plotting $\ln D$ vs. $1/T$, the Q and D_0 values can be determined. Fig. 7 gives the plot of $\ln D$ vs. $1/T$ for SPS borided molybdenum specimens with the data shown in Table II. The activation energy, Q , and the pre-exponential constant, D_0 , can be deduced from Figure 7, and these are 218.8 kJ/mol and 1.41 cm²/s respectively.

4. Conclusion Remarks

SPS boriding of refractory metal molybdenum has been carried out in the temperature range 1000–1400 °C with a holding time of 30 min. The boride layer consisted mainly of MoB for most of the SPS boriding samples. The microstructure, mechanical properties

and boriding kinetics of SPS borided Mo samples are investigated. The following conclusions can be deduced from the study:

- 1) Boride layer mainly consists of columnar-structured MoB layer. The MoB layer has a strong (200) preferred crystallographic orientation after the top layer has been removed. The boride layer thickness increases with increasing SPS boriding temperature at the rate of $\sim 50 \mu\text{m}$ for every 100°C increment in the range $1100 - 1300^\circ\text{C}$ and 30 min of SPS treatment.
- 2) Annealing the boride layer at the temperature of 1000°C for 30 mins has no significant impact on the microstructure and microhardness of the boride layer. This suggests that the phase formed in the borided layer is stable.
- 3) The boride layer had high Vicker's hardness values up to $1810 \pm 130 H_v$. The presence of microcracks on the boride layer may account for the brittleness of MoB. A thicker molybdenum boride layer will improve fracture toughness.
- 4) The SPS boriding of molybdenum has an activation energy of 218.8 kJ/mol and a pre-exponential constant of $1.41 \text{ cm}^2/\text{s}$ respectively.

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(a) M1 (1000°C)

(b) M2 (1100°C)

(c) M3 (1200°C)

(d) M4 (1300°C)

(e) M5 (1400°C)

(f) Boride layer thickness estimation

Figure 1 Cross sectional optical microstructure of molybdenum samples borided at different temperatures for 30 minutes

Figure 2 XRD patterns of Borided Mo with Increasing Temperature.

Figure 3 Comparison of XRD patterns of (a) Mo Borided at 1300°C and (b) after annealed.

Figure 4 Comparison of XRD patterns of (a) Mo Borided at 1400°C and (b) after annealed.

Figure 5 XRD patterns on the Effect of Polishing 20μm/step on Borided Mo.

Figure 6 MicroHardness Profile of Borided Mo.

Fig. 7. $\ln D$ vs. $1/T$ for SPS boriding mild steel specimens with a soak time of 30 min.