Properties of Multi-Component CrBMoS Coatings by Pulsed Magnetron Sputtering from Powder Targets

Y.W. Zhou¹, ²*, Z. Zhao¹, C.Y. Zheng, P.J. Kelly²

¹School of Materials Science and Engineering, University of Science and Technology of Liaoning, No.185 Qianshan Rd., Hi-tech Zone, Anshan, Liaoning, China 114004
²Surface Engineering Group, Dalton Research Institute, Manchester Metropolitan University, Manchester, M1 5GD, UK

Abstract

CrB2 and MoS2 multi-component coatings were prepared by pulsed magnetron sputtering from loosely packed powder targets, with the mixture powder of CrB2 and MoS2 at the atomic ratio 1:1. These three materials are known as good corrosion resistance, high hardness and good wear, respectively. Molybdenum disulfide is recognized as a solid lubricant material by virtue of its low friction characteristics. The structures and compositions of the coatings were examined by SEM, XRD and WDX. The study of deposition rate shows that the thicknesses of the coatings strongly depend on the pulsed on factor. The mechanical and tribological properties of the coatings were investigated by adjusting the deposition parameters, which the hardness and friction coefficient of the coatings can be as high as 16GPa and as low as 0.02, respectively. The results show that the coatings prepared from CrB2 and MoS2 targets have reasonable hardness and very good wear-resistant property.

Key words: Pulsed magnetron sputtering; Tribology; Solid lubricant; Powder targets

1. Introduction

There is no doubt that the properties of coatings depend on their compositions, structure and therefore the techniques used to prepare them. Chromium, boron and sulfur have attracted increased interest due to the useful properties of their compounds, including high hardness, low coefficient of friction and the ability to act as a solid lubricant [1-5]. These properties can only be achieved if the films are correctly prepared. Pulsed magnetron sputtering in a closed unbalanced magnetic field is considered as one of the most effective techniques for preparing dense, defect-free coatings, due to its many advantages, such as high ionization rate, dense and high energy plasma etc. [6-8]. Loosely packed powder mixtures as sputtering targets have also been proved to be one of the most effective and economic methods to produce the multi-component coatings [2-4, 9-12].

In this study, multi-component coatings were therefore deposited by pulsed magnetron sputtering from mixed CrB2 and MoS2 powders. The characteristics of the coatings, in terms of their structure, compositions, and mechanical and tribological properties are presented in this paper. The results demonstrate the potential of these multi-component materials as hard solid lubricant coatings.

2. Experimental

The coatings were deposited in a special designed powder rig [9-12]. The target to substrate separation was 150 mm. CrB2, and MoS2 powders were mixed, according to atomic ratio 1:1, and the powders were blended in a rotary drum for several hours to obtain a uniform mixture. The powder mixture was then spread across a recessed magnetron backing plate and lightly tamped to form a target with a uniform thickness.

Silicon wafers and stainless steel discs were used as substrates to suit specific analytical techniques. The substrates were cleaned, first externally by isopropanol, and then internally by RF at 150W power for 10min in an Ar atmosphere.
Films were then deposited using a 10kW Advanced Energy Industries Pinnacle Plus pulsed DC magnetron driver in its power regulation mode at 400 W, 80% duty for 4 hours, at various frequencies (50, 100, 175, 250 and 350 kHz). Also, to compensate for the losses of B during deposition, chunks of boron (approximately 1 cm³) were placed in the racetrack region on the target and the coatings with additional B were prepared in the same manner as mentioned above.

The structures and compositions of the coatings were examined by scanning electron microscopy (SEM), X-ray diffraction (XRD) and electron probe micro-analyser (EPMA) in energy dispersive X-ray (EDX) techniques. Mechanical properties of the films deposited on silicon wafers were evaluated by nano-indentation using a Nanotest 500 (Micromaterials Ltd., UK). A Berkovich pyramid diamond indenter was used to make 16 indentations per sample. The tribological properties of the coatings were also investigated by thrust washer wear tests. The washer wear tests were performed using a dry WC washer at 30 rpm rotary speed under applied loads of 15 kg. The results presented in this paper are the average of the friction coefficient of each coating.

Coatings were also analysed via scratch testing, employing a CSR – 01 scratch tester. Coating failure was in this case taken to be at the appearance of flaking of the coating, which can also be described as the limit of the load bearing capacity.

3. Result and discussion

3.1. Structures

The SEM micrograph of the fracture section of a typical CrB₂MoS₂ coating is shown in Figure 1. As can be seen, the coating appears to have a dense, defect-free structure, presumably benefiting from the high ion energy flux to the substrate when operating in the pulsed unbalanced magnetron sputtering mode [6-8]. Similar results have been obtained for other materials produced by this deposition technique [2-5, 9-12]. Some effect of target conditioning on the crystalline structure of the films was observed, as shown in Figures 2 and Figures 3. The diffraction peaks of the coating when the target was first used (run 1) are shown in Figure 2. The peak at d=1.35699 is clearly observed, which may include unresolved contributions from the MoS₂ (200) (d=1.3688), CrB₂ (111) (d=1.336) and silicon substrate (400) (d=1.357) peaks. The high intensity of the peak is typical of silicon substrates, but the broadening of the lower part of the peak may be due to the contributions from CrB₂ and MoS₂. The diffraction peaks of the coating deposited after the target had been running for 20 hours (run 5) is shown in Figure 3, in which diffractions from the Cr (200) and Mo (200) peaks become obvious. This may indicate the loss of light elements of sulfur and especially boron. The EDX analysis do show significant loss of boron, although there is not a great difference in the boron content between the coatings from run 1 and run 5. Also, the losses of sulfur in the examined coatings are not significant. The EDX, which can be referred as semi-quantity results, are listed in Table 1.

Table 1
Compositions of the coatings (CrB₂:MoS₂ =1:1) of run 1 and run 5 by EDX analysis

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Cr</th>
<th>B</th>
<th>Mo</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29.79</td>
<td>6.16</td>
<td>19.67</td>
<td>41.7</td>
</tr>
<tr>
<td>5</td>
<td>27.78</td>
<td>5.61</td>
<td>20.26</td>
<td>43.91</td>
</tr>
</tbody>
</table>
contribute to the low coefficient of friction in solid lubricant materials [4-5]. Therefore, the losses of sulfur during the deposition may not be significant in these cases, which are consistent with the results of EDX analysis.

![Figure 4. Friction response of coating (CrB_2:MoS_2 =1:1) during dry thrust washer test against a WC counterface for 10 hours](image)

### 3.3. Hardness-test

The results from the nanotester show that the hardness values of the coatings are around 12-16GPa (Table 2), which are not as hard as CrB_2 (39GPa[2]), because of the losses of element of boron and the mixture of the soft material of MoS_2 [2-4]. Therefore, the hardness of the coatings might be expected to be lower than would normally be obtained for a stoichiometric CrB_2 coating.

### 3.4. Scratch-test

The results of the scratch tests can be seen in Table 2. The failure loads of the CrB_2MoS_2 coatings are above 25N, except the result of the coating from the very first run, which could be caused by the slightly contaminations on the surface of the target. The study in reference 4 proved that the content of oxygen between the interface of the coating material and the substrate could cause the deterioration of the adhesion. The surfaces of the powder from the first run were normally surrounded by air, and difficult to remove the air off completely.
Table 2
Properties of the multi-component coatings via various deposition conditions

<table>
<thead>
<tr>
<th>run No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulse factor(μs)</td>
<td>16</td>
<td>8</td>
<td>4.6</td>
<td>3.2</td>
<td>2.3</td>
</tr>
<tr>
<td>Deposition rate(nm/min)</td>
<td>13.6</td>
<td>5.5</td>
<td>3.6</td>
<td>1.7</td>
<td>1.6</td>
</tr>
<tr>
<td>Hardness (GPa)</td>
<td>Cr:B:Mo:S 1:2:1:2(atomic) Above composition + B</td>
<td>15.7</td>
<td>16</td>
<td>14</td>
<td>14</td>
</tr>
<tr>
<td>Failure Load (N)</td>
<td>Cr:B:Mo:S 1:2:1:2(atomic) Above composition + B</td>
<td>18</td>
<td>34</td>
<td>30</td>
<td>25</td>
</tr>
</tbody>
</table>

3.5. Pulse factor via the properties of the coatings

The term of pulse factor has been introduced, which is found by multiplying the reciprocal of pulse frequency by the duty factor, and therefore represents the length of the pulse on period per cycle in microseconds. Figure 7 shows the variation in deposition rate with pulse factors for these conditions. Also, the deposition rates, properties of the coatings via the pulse factors are listed in Table 2. It can be seen the deposition rate increased as the increases of the pulse factor, i.e. the decreases of pulse frequency. The mechanical and tribological properties do not show much effect on the pulse factors.

3.6. Coatings with additional boron

Chunks of boron were placed along the erosion track of the target to supplement for the losses of boron during deposition. The coatings were again deposited under the conditions: varied frequency, duty 80%, power 400W, for 2 hours. The crystallinity of the coatings is shown in Figure 5. Once again a single broad peak was observed at approximately 69° in 2 theta mode. The width of the peak is greater than that observed for the earlier coatings, which may imply that there is a greater contribution from the CrB₂ peak, considering the position of the peak of CrB₂ is 1.336, further away from the peak position 1.3599 than MoS₂ 1.3688 and Si 1.357. The hardness of the coating is 16GPa (Table 2), which is slightly higher than the coatings without additional boron, although the adhesion of the coatings is slightly lower, see Table 2. The most significant result comes from the thrust washer wear tests. The friction coefficient for this coating decreased to 0.02 after an initial conditioning period; see Figure 6. This result is much lower than published results for CrBMoSmulti-component coatings from other sources [4-5].
\[ \lambda = \frac{RT}{\sqrt{2 \pi d^2 N_A^2}} \]  

in which \( d \), the diameter of gas molecules and \( \lambda \), the free path length, \( \lambda \) will be much longer when \( d \) decreases at the same conditions. Therefore, the \( \lambda \) of boron gas atoms is longer due to their smaller diameter than those of Chromium, Molybdenum atoms, which means the boron atoms are more moveable and easier losses from the plasma.

Boron and Molybdenum disulfide are well known as hard and solid lubricant materials respectively. The dense nanostructure [2] of the mixed compound coatings also contribute the high hardness and low friction coefficient, because nanostructure provides boundary nets and the sediment of MoS\(_2\) are very fine.

4. Conclusion

1. The method of deposition of multi-component coatings from mixed CrB\(_2\) and MoS\(_2\) powder targets, by pulsed DC magnetron sputtering can produce dense, defect free thin films.
2. However, light elements, especially boron, can be lost during the deposition.
3. The tribological and mechanical properties of the multi-component CrB\(_2\) and MoS\(_2\) coatings show potential for future applications. The friction coefficient can be as low as 0.02, whilst the hardness of the coatings is in the range 14-16 GPa.
4. The pulse factor only affects on the deposition rate of the coatings, and shows no much difference on the mechanical and tribological properties.
5. Additional chunks of boron can supply for the losses of boron element during deposition processes, and the hardness of the coatings with additional B increases slightly.

Acknowledgement

The authors would like to take this chance to thank Geoff France and Zhibin Liu for their help in the SEM analysis and wear testing.

This work is supported by the National Natural Science Foundation of China in No. 50872048.
References


