Tribological and Corrosion Properties of Cr-Zr-N Coatings

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In this work, ternary Cr-Zr-N coatings with not only much improved mechanical properties but also a very low surface roughness were synthesized by closed field unbalanced magnetron sputtering with vertical magnetron sources and their tribological properties under various relative humidity (RH) conditions were investigated. Especially, in the case of the Cr$_{1-x}$Zr$_x$N coating with $x = 0.34$, its friction coefficient obtained under a 90 % RH environment was compared with that of DLC (diamond like carbon) films measured under the same conditions. In addition, to evaluate the corrosion behavior of the coatings, we carried out potentiodynamic polarization tests in a deaerated 3.5 wt.% NaCl solution at 40 °C and we compared the results with those obtained from CrN films. The tribological behaviors of the Cr-Zr-N coatings did not seem to be significantly affected by the humidity of the air. Under a 90 % RH environment, the average friction coefficient of the Cr$_{1-x}$Zr$_x$N coating with $x = 0.34$ against a steel ball was approximately 0.17 and this value was lower than those of the CrN (0.49) and DLC (0.2) films. In the potentiodynamic polarization test results, we found that the corrosion resistance of the Cr-Zr-N coatings was significantly improved in comparison with that of CrN and that their corrosion current density ($i_{corr}$) and corrosion rate decreased with increasing Zr content ($x$ value).

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Keywords: Cr-Zr-N coatings, Surface roughness, Friction coefficient, Corrosion resistance, Humidity

I. INTRODUCTION

For many years, chromium nitrides have been extensively used as a protective hard coating in various industries due to their high thermal stability and good wear resistance, as well as their superior corrosion resistance [1-3]. However, in spite of their excellent properties, the CrN films still show inadequate properties for some specific applications, such as high speed machining and high temperature and severely corrosive conditions, because of the limitations of binary systems. Recently, in order to improve the mechanical and the chemical properties of the CrN, Cr-based ternary nitride coatings, such as Cr-Ti-N [4], Cr-Al-N [5], Cr-W-N [6], Cr-Si-N [7] and Cr-Zr-N [8-10], have been developed and their excellent properties have been reported in many papers. Especially, in our previous study [9], the Cr-Zr-N coatings synthesized by a closed field unbalanced magnetron sputtering with vertical magnetron sources showed quite unique characteristics in that, compared with CrN, they had not only much improved mechanical properties, but also a very low surface roughness and their surface became smoother with increasing Zr content in the films.

In this work, the tribological properties of the Cr-Zr-N coatings under various relative humidity (RH) conditions were investigated and, in case of the Cr$_{1-x}$Zr$_x$N coating with $x = 0.34$, its friction coefficient under a 90 % RH environment was compared with that of DLC films measured under the same conditions. In addition, to evaluate their corrosion behavior, we carried out potentiodynamic polarization tests in a deaerated 3.5 wt.% NaCl solution at 40 °C and we compared the results with those obtained from CrN films.

II. EXPERIMENTS

The Cr$_{1-x}$Zr$_x$N coatings with various Zr contents ($x = Zr/(Cr + Zr)$) were deposited on silicon (100) wafers and AISI H13 tool steel by closed field unbalanced magnetron sputtering with vertical magnetron sources Cr and Zr targets (99.99 % purity) installed, respectively. Deposition was performed at a total working pressure...
of the Zr content were analyzed using an EG&G PAR model 263A galvanostat/potentiostat system. A three electrode electrochemical cell was used with high purity carbon rod counter electrode and an Ag/AgCl electrode as the reference electrode. The specimen to be tested was the working electrode. The specimen was loaded in a Teflon sample holder and the surface area exposed to the corrosive medium was approximately 1.0 cm². The test solution was 3.5 wt. % NaCl, which was deaerated with pure N₂ gas for 1 h before testing to remove the dissolved oxygen. All tests were performed at 40 °C under open-air conditions. The specimen was cleaned in distilled water before loading in the Teflon sample holder. The specimen was placed in such a way that the Luggin capillary of the reference electrode was close to the working electrode and this distance was maintained for all the tests. The sample was kept in the solution for 60 min prior to the potentiodynamic polarization study in order to establish the open-circuit potential (E_{OCP}) or the steady state. The polarization curves were measured at a scan rate of 0.166 mV/s, starting from an initial potential of −250 mV vs. the open circuit potential of the tested sample. The Tafel plot was obtained after the electrochemical measurements. The corrosion potential (E_{corr}) and the corrosion current density (i_{corr}) were deduced from the Tafel plot (that is, log i vs. E plot).

III. RESULTS AND DISCUSSION

The characteristics of the CrN and the Cr_{1-x}ZrₓN coatings deposited on the Si wafer substrate are summarized in Table 1. The Cr_{1-x}ZrₓN coating with x = 0.34 had the higher hardness value (33 GPa), a lower surface roughness (R_ms = 0.82 nm) and a much denser microstructure compared with CrN, as shown in Table 1. The details for the characteristics of the coatings are described in our previous publication [9].

From the wear test against the AISI 52100 steel ball without lubricant in air, the average friction coefficients of the coatings as a function of RH are shown in Figure 2. In the case of the CrN films, the friction coefficient showed a tendency to decrease slightly from 0.56 down to 0.49 with increasing RH from 0 to 90 %. However, the Cr_{1-x}ZrₓN coatings with x = 0.15, 0.25 and 0.34 did not seem to be affected by the humidity environment because their friction coefficients remained constant without regard to change in RH. In addition, the friction coefficient of the Cr_{1-x}ZrₓN coatings decreased with increasing Zr content (x value) in the films. Figure 3 shows the friction coefficients of the Cr_{1-x}ZrₓN (x = 0.34) and the DLC [11] coatings obtained from wear tests under a 90 % RH environment. As shown in this figure, the friction coefficient of DLC gradually increased with increasing wear cycle and its value was investigated to become higher than that of the Cr_{1-x}ZrₓN coating with
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Table 1. Characteristics of the coatings examined in this work.

<table>
<thead>
<tr>
<th>Properties</th>
<th>CrN</th>
<th>Cr(_{1-x})Zr(_x)N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x = 0.15</td>
<td>x = 0.25</td>
</tr>
<tr>
<td>Hardness (GPa)</td>
<td>22</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>x = 0.25</td>
<td>34</td>
</tr>
<tr>
<td>Elastic Modulus (GPa)</td>
<td>353</td>
<td>382</td>
</tr>
<tr>
<td>Roughness (R(_{rms})) (nm)</td>
<td>5.19</td>
<td>2.37</td>
</tr>
<tr>
<td></td>
<td>x = 0.34</td>
<td>1.17</td>
</tr>
</tbody>
</table>

Fig. 2. Average friction coefficients of the CrN and the Cr\(_{1-x}\)Zr\(_x\)N coatings with x = 0.15, 0.25 and 0.34 under various RH conditions.

Fig. 3. Friction coefficients of the Cr\(_{1-x}\)Zr\(_x\)N (x = 0.34) and the DLC coatings under a 90 % RH condition.

x = 0.34 from approximately 20,000 cycles. The average friction coefficient of the Cr\(_{1-x}\)Zr\(_x\)N coating with x = 0.34 under a 90 % RH condition was measured to be approximately 0.17 and this value is lower than those of the CrN (approximately 0.17) and the DLC (approximately 0.2) films. The tribological behavior of the DLC films against a steel ball was reported to strongly depend upon the relative humidity, in that the friction coefficients increased as the relative humidity increased. This increase in the friction coefficients was attributed to the formation of Fe rich debris on the surface of the DLC films, which was accelerated by a high relative humidity [11]. However, in case of the Cr-Zr-N coating with x = 0.34, although the relative humidity increased, no apparent variation in the wear track morphology (refer to Figure 4) and the friction coefficient against a steel ball was observed and excellent tribological properties were preserved regardless of the RH variation. These results suggest the possibility that the Cr\(_{1-x}\)Zr\(_x\)N coating with x = 0.34 could be substituted for the DLC films used under wear conditions against steel counterparts in a high relative humidity environment, as well as in applications that require very good wear resistance, such as water-based hydraulic pumps and their parts.

Figure 4 illustrates the wear track formed in the coatings after wear tests. The CrN coating shows a much wider wear track than the Cr\(_{1-x}\)Zr\(_x\)N coatings under both relative humidity conditions, suggesting that more extensive wear occurred in the CrN coating. In addition, an adhesive type wear behavior resulting from the wear debris of the coating and the steel ball was observed and a decolorization of the surface wear track was clearly
Fig. 4. Wear track images of the CrN and the Cr$_{1-x}$Zr$_x$N coatings with $x = 0.25$ and 0.34 under 50 and 90 % RH conditions.

Fig. 5. Potentiodynamic polarization curves of the coatings and the AISI H13 steel substrate in a 3.5 % NaCl solution.

identified under optical microscopy. However, from the wear tracks of the Cr$_{1-x}$Zr$_x$N coatings with $x = 0.25$ and 0.34, smooth and abrasive type wear without any sign of debris adhesion was observed. Especially, compared to other coatings, the Cr$_{1-x}$Zr$_x$N coating with $x = 0.34$ showed very limited signs of wear tracks under both relative humidity conditions. Also, its wear volume and wear rate were too negligible to be measured under the test conditions used in this work. This enhancement of the tribological properties of the Cr$_{1-x}$Zr$_x$N coating with $x = 0.34$ could be attributed to its very low surface roughness and high hardness, as shown in Table 1.

Potentiodynamic polarization curves for the coatings (thickness: approximately 2.5 µm) deposited on the AISI H13 steel substrate measured in 3.5 wt.% NaCl solution at 40 °C are presented in Figure 5. The polarization curve of the uncoated substrate is also presented as a reference. As shown in Figure 5, the anodic polarization curves of the CrN and the Cr$_{1-x}$Zr$_x$N ($x = 0.15$ and 0.34) coatings showed relative positive corrosion potential and lower current density than those of the substrate. This means that the coatings act as a protective barrier against the reaction of the substrate. Table 2 summarizes the corrosion parameters of all specimens obtained from the polarization curves. The corrosion current density ($i_{corr}$) is an important parameter to assess the kinetics of the corrosion reaction and it is normally proportional to the corrosion rate. In the case of the substrate, the corrosion current density is about 86.8 µA/cm$^2$, which significantly decreased to approximately 35.4 µA/cm$^2$ for the CrN coating. Also, the Cr$_{1-x}$Zr$_x$N coatings exhibited much lower corrosion current densities than the CrN coating did. The Cr$_{1-x}$Zr$_x$N coating with $x = 0.34$ exhibited the lowest corrosion current density ($i_{corr} = 6.3$ µA/cm$^2$) and the lowest corrosion rate (3.2 mils/year: mp/y). The results indicate that the addition of Zr to the CrN coatings improves the chemical inertness in an aggressive aqueous environment. From polarization test results, the protective efficiency, $P_r$ (%), of the coatings can be calculated by using

$$P_r(\%) = \left[1 - \left(\frac{i_{corr}}{i_{0,corr}}\right)^n\right] \times 100,$$

where $i_{corr}$ and $i_{0,corr}$ indicate the corrosion current densities of the coating and the substrate, respectively [12]. The calculated protective efficiencies for all tested coatings are presented in Table 2. The protective ability
Table 2. Potentiodynamic polarization data of the coatings and the substrate in 3.5 % NaCl solution.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Substrate (AISI H13)</th>
<th>CrN</th>
<th>Cr₁₋ₓZrₓN</th>
</tr>
</thead>
<tbody>
<tr>
<td>E&lt;sub&gt;corr&lt;/sub&gt; (mV)</td>
<td>—568.9</td>
<td>—495.4</td>
<td>—437.1</td>
</tr>
<tr>
<td>i&lt;sub&gt;corr&lt;/sub&gt; (μA/cm²)</td>
<td>86.8</td>
<td>35.4</td>
<td>7.9</td>
</tr>
<tr>
<td>Protective Efficiency (%)</td>
<td>—</td>
<td>59</td>
<td>91</td>
</tr>
<tr>
<td>Corrosion Rate (mpy)</td>
<td>80.1</td>
<td>70.1</td>
<td>30.9</td>
</tr>
</tbody>
</table>

of the Cr₁₋ₓZrₓN coatings increased with increasing x value and the Cr₁₋ₓZrₓN coating with x = 0.34 showed the highest protective efficiency of approximately 93 % caused by the lowest corrosion current density of 6.3 μA/cm². The superior corrosion resistance property of the Cr₁₋ₓZrₓN coating with x = 0.34 could be mainly due to the formation of a much denser microstructure in comparison with other coatings, which limit the defects in the coating layer and block the direct path for the corrosion between a corrosive environment and the substrate [13-16].

IV. CONCLUSIONS

The Cr-Zr-N coatings synthesized in this work, compared with CrN, have not only much improved mechanical properties but also a very lower surface roughness with increasing Zr content. In the case of CrN, its average friction coefficient against a steel ball showed a tendency to decrease slightly from 0.56 down to 0.49 with increasing relative humidity (RH) from 0 to 90 %. However, the friction coefficients of the Cr₁₋ₓZrₓN coatings remained constant without regard to change in the RH. Especially, the Cr₁₋ₓZrₓN coating with x = 0.34 had an average friction coefficient of approximately 0.17 under a 90 % RH. In addition, its wear volume and wear rate were too negligible to be measured. The potentiodynamic test results showed that the corrosion resistance of the Cr₁₋ₓZrₓN coatings was significantly improved in comparison with CrN and that their corrosion current density (i<sub>corr</sub>) and corrosion rate decreased with increasing Zr content (x value). The highest protective efficiency, approximately 93 %, was exhibited in the Cr₁₋ₓZrₓN coating with x = 0.34.

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REFERENCES