Tribological properties of TiN and TiC films in vacuum at high temperature

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Abstract

TiN and TiC films were deposited by activated reactive evaporation using a hollow cathode discharge. Their tribological properties were studied by the ring-on-disc tribotester. The rubbed surface of the disc samples was observed by scanning electron microscopy, and their roughness profile was measured by the SOLANDEKTAK II roughness tester. The friction coefficient was about 0.14 for the wear couple of the TiN-coated ring against the TiC-coated disc in air at room temperature, and the wear couple also showed excellent wear resistance. The friction coefficient decreased with the increase of temperature for the wear couple of the TiN-coated ring against the TiC-coated disc in a vacuum of pressure $2.6 \times 10^{-3} \text{ Pa}$ at temperatures up to 623 K, and the wear trace of the disc samples was very light for 10 min at 673 K after the friction surface of the wear couple was ground in for 5 min at 473 K and for 5 min at 623 K, in a vacuum of pressure $2.6 \times 10^{-3} \text{ Pa}$.

Keywords: Tin; Tribology

1. Introduction

It is well known that there are three main types of lubricants, e.g. fluid, gaseous and solid lubricants which may be used to minimize wear and to ensure accurate operation of mechanical components in triboccontact in a variety of environments including space. However, the normal lubricant is not suitable for space technology. Therefore, it is necessary to study and develop the most suitable lubricant for every desired space application. The solid lubricants can be applied as thin films on the mechanical components. These solid lubricants may be either organic or inorganic. Among the inorganic lubricants, there are metallic lubricants (such as Pb, Au, Ag) and non-metallic lubricants. The latter may further be divided into soft non-metallic lubricants such as MoS$_2$ and BN and hard non-metallic lubricants such as TiN, TiC and c-BN [1–12]. A TiC film with high hardness and low friction against steel is a good candidate for providing the necessary tribological properties for extreme environments. A TiN film with high hardness and excellent wear resistance is widely used in industry [13–18]. It is well known that the friction coefficient and wear resistance of the wear couple have a close relation to the partners of the wear couple and also the application environments [3]. In the present study, the tribological performances of the TiC and TiN films have been studied and the films were deposited by the reactive ion-plating method. In order to improve the adhesion of the film to a substrate, a thin Ti interlayer was inserted between the film and the substrate while the TiN and TiC films are expected to be solid lubricants for space technology. Their tribological tests were made in air at room temperature, and in vacuum environments both at room temperature and elevated temperatures. The results are summarized in this paper.

2. Sample preparation

The form and size of the ring sample made of JIS SUS 304 stainless steel are shown in Fig. 1. There are two kinds of ring samples: (a) the friction surface of the ring abraded with 400 grade emery paper; and (b) abraded with 1200 grade emery paper, and then the
two series of samples were coated with the TiN film or TiC film to a thickness of about 3 μm by activated reactive evaporation using a hollow cathode discharge (HCD-ARE).

The disc samples are divided into two kinds according to their shape. One was square (30 x 30 mm²) with a thickness of 5 mm. These disc samples were prepared by JIS SUS 304 stainless steel with three different surface conditions: (a) abraded with 400 grade emery paper; (b) abraded with emery paper of 1200 grade and then coated with a TiN film of about 3 μm; and (c) the commercial steel plate, its surface kept as received without any mechanical preparation before deposition, coated with a TiC film of 4–10 μm. The films were deposited by the HCD-ARE method. All the substrates were first ultrasonically cleaned for 10 min in an acetone bath, and then were further bombardied by argon ion at a pressure of 2.7 Pa and a substrate bias voltage of -5 kV for 10 min before deposition of the film. In order to enhance the adhesion of the films to the steel substrate, a very thin Ti layer was pre-deposited on the substrate [19–24].

The characteristics of the TiN and TiC films are summarized in Table 1.

The other kind of disc samples was made of circular (φ, 50 x 1 mm²) silicon wafers, on which a c-BN film of about 0.4 μm was deposited by modified ARE accompanied by a gas activation nozzle using two electron-beam evaporation sources, i.e. a hollow-cathode discharge gun and a conventional electron-beam gun. The adhesion of the c-BN film to the substrate was improved by inserting a silicon nitride interlayer, the silicon content of which had to be gradually decreased to zero from the substrate [2, 16].

### 3. Experimental procedure

#### 3.1. Experimental equipment

Fig. 2 shows the schematic diagram of the ring-on-disc tribotester, which can be used in a vacuum with a residual pressure of 1 x 10⁻³ Pa at temperatures up to 873 K. The load is supplied through a linear head (8). The torque is measured by the load cell (4). The friction coefficient is given by $u = [(F_1/A)/(F_2/A)] = (F_1/F_2)$, where $F_1$ is the friction force, $F_2$ is the load and $A$ is the contact dimensions of the ring and the disc. The temperatures were measured by a thermocouple set at a distance 1 mm from the friction surface of the disc sample. The rotation speed was 50 rpm for

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**Table 1**

<table>
<thead>
<tr>
<th>Property</th>
<th>TiN</th>
<th>TiC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microhardness (N mm⁻²)</td>
<td>21000</td>
<td>32000</td>
</tr>
<tr>
<td>Thermal expansion coefficient (K⁻¹)</td>
<td>9.3 x 10⁻⁶</td>
<td>7.7 x 10⁻⁶</td>
</tr>
<tr>
<td>Young's modulus (MPa)</td>
<td>260 x 10³</td>
<td>500 x 10³</td>
</tr>
<tr>
<td>Density (g cm⁻³)</td>
<td>5.2</td>
<td>4.9</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>2950</td>
<td>3150</td>
</tr>
<tr>
<td>Thermal conduct rate (cal cm⁻¹ s⁻¹ °C⁻¹)</td>
<td>0.07</td>
<td>0.041–0.06</td>
</tr>
<tr>
<td>Resistivity (μΩ cm)</td>
<td>22–130</td>
<td>70–173</td>
</tr>
</tbody>
</table>
all the tests. Before the tribo-tests, the samples were cleaned for 3 min in acetone.

3.2. Assessment of tribological properties in air at room temperature

For comparison, the friction coefficients of different weak couples in air at room temperature were first tested. These wear couples and sliding time are described in Table 2. The relation between the friction coefficient of the different wear couples and sliding time was studied. Such wear couples are summarized in Table 3. The changes of the friction coefficient with the preparation methods of the substrate was also analyzed. The pre-treatment methods before TiN deposition were: (1) the surface was simply polished, and (2) the polished surface was further etched by an alcohol solution of 4% nitric acid.

Table 2
Wear couples for the friction coefficients in air

<table>
<thead>
<tr>
<th>Ring</th>
<th>Disc</th>
<th>Sliding time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN on SUS 304</td>
<td>TiN on SUS 304</td>
<td>6</td>
</tr>
<tr>
<td>TiN on SUS 304</td>
<td>TiC on SUS 304</td>
<td>10</td>
</tr>
<tr>
<td>TiN on SUS 304</td>
<td>SUS 304</td>
<td>10</td>
</tr>
<tr>
<td>TiN on SUS 304</td>
<td>Aluminium</td>
<td>10</td>
</tr>
<tr>
<td>SUS 304</td>
<td>TiN on SUS 304</td>
<td>10</td>
</tr>
<tr>
<td>SUS 304</td>
<td>TiC on SUS 304</td>
<td>20</td>
</tr>
<tr>
<td>SUS 304</td>
<td>Aluminium</td>
<td>10</td>
</tr>
<tr>
<td>SUS 304</td>
<td>SUS 304</td>
<td>10</td>
</tr>
</tbody>
</table>

Load was 9.8 N for all wear couples

Table 3
Wear couples for the relation between friction coefficient and sliding time

<table>
<thead>
<tr>
<th>Ring</th>
<th>TiN on SUS 304</th>
<th>SUS 304</th>
<th>TiN on SUS 304</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disc</td>
<td>TiN on SUS 304</td>
<td>TiC on SUS 304</td>
<td>TiC on SUS 304</td>
</tr>
</tbody>
</table>

Table 4
The wear couples and test conditions for the tribological properties in vacuum

<table>
<thead>
<tr>
<th>Ring</th>
<th>SUS 304</th>
<th>TiC on SUS 304</th>
<th>TiN on SUS 304</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disc</td>
<td>TiN on SUS 304</td>
<td>c-BN on Si wafer</td>
<td>TiC on SUS 304</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Test pressures</th>
<th>Point 1</th>
<th>Point 2</th>
<th>Point 3</th>
<th>Point 4</th>
<th>Point 5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Atmosphere</td>
<td>13 Pa</td>
<td>1.3 Pa</td>
<td>1.3 × 10⁻¹ Pa</td>
<td>1.3 × 10⁻² Pa</td>
</tr>
<tr>
<td></td>
<td>1.3 Pa</td>
<td>1.3 Pa</td>
<td>1.3 × 10⁻¹ Pa</td>
<td>1.3 × 10⁻² Pa</td>
<td>1.3 × 10⁻³ Pa</td>
</tr>
<tr>
<td></td>
<td>1.3 × 10⁻¹ Pa</td>
<td>1.3 × 10⁻² Pa</td>
<td>1.3 × 10⁻³ Pa</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Load | 9.8 N |
Sliding time | 5 min |

3.3. Assessment of tribological properties in vacuum environments

3.3.1. At room temperature

Assessment of the tribological properties of the TiN and TiC films in vacuum environments at room temperature was performed. The wear couples and test conditions are detailed in Table 4.

3.3.2. At elevated temperatures

Firstly, the influence of temperatures on the friction coefficient in vacuum was studied for the wear couple of the TiN-coated ring against the TiC-coated disc. When the chamber pressure was decreased from atmospheric to 2.6 × 10⁻³ Pa, the friction coefficient of the wear couple was measured at room temperature. Then the sample was successfully heated to 473 K, 623 K and 673 K at which the friction coefficients of the same wear couple were measured. Maintenance of the chamber pressure 2.6 × 10⁻³ Pa during the whole test period was realized by introducing argon into the vacuum chamber. The sliding time was 5 min for the each point. Then, similar samples were divided into three groups, and the wear resistances of the TiN film against the TiC film were analyzed under three conditions: (1) a sliding time of 10 min in a vacuum of pressure 3.5 × 10⁻¹ Pa at 673 K; (2) a sliding time of 10 min in a vacuum of pressure 1 × 10⁻² Pa at 673 K; and (3) a sliding time of 5 min at 473 K, a sliding time of 5 min at 623 K and a sliding time of 10 min at 673 K in a vacuum of pressure 2.6 × 10⁻³ Pa.

3.4. Post observations

The rubbed surface of the disc samples was observed by scanning electron microscopy (SEM) and the roughness profile of the rubbed surface of the disc samples were measured by the SOLANTEKTAK II roughness tester.
4. Results and discussion

4.1. Tribological properties in air at room temperature

The final steady values of the friction coefficients of different wear couples are given in Table 5. Table 5 shows that the friction coefficients of the TiN or TiC films vary with the weak partners. Therefore, in order to optimize a wear couple, besides the materials of which the couple and its coating are made optimal matching of the wear partners is one important factor for the design of the couple [1, 3, 8]. Table 5 also shows that among the tested couples the TiN/TiC couple shows the lowest friction coefficient, and it was confirmed by SEM observation that their wear resistance was also the best. Generally, it is believed that a good wear couple has one member of the couple harder than the other [1]. Although both the TiN film and TiC film are hard films, the hardness (HV32000 N mm\(^{-2}\)) of the TiC film is higher than HV21000 N mm\(^{-2}\) of the TiN film. Therefore, the wear couple of the TiN film against the TiC film meets a good matching [5, 12]. In Table 5, the friction coefficient of the TiN-coated ring against the TiC-coated disc is the same as that of the wear couple of the stainless steel ring against the TiN-coated disc. This value is much higher than the value reported in Ref. [5], and may result from the fact that the hardness (HV3600 N mm\(^{-2}\)) of the SUS 304 stainless steel substrate used in this study is much lower than HV8500 N mm\(^{-2}\) of the HSS substrate used in Ref. [5], so the thin TiN film may be crushed under high stress and then the TiN film is in contact with the steel substrate. This was confirmed through observation of the worn surface of the disc samples by SEM. Some small plow grooves existed in the worn surface. The view mentioned above may be further confirmed from Fig. 3, e.g. the friction coefficient of the wear couple of the TiN-coated ring/TiC-coated disc rapidly decreased to a steady minimum of 0.2 with sliding time, and then gradually increased to a maximum of about 0.65 after 2 min sliding.

It can be considered that the fast decrease of the friction coefficient of the wear couple during the initial sliding stage may result from the evaporation of the adsorbates on the sample surfaces by frictional heating so that a direct contact of the two fresh TiN surfaces may form. The increase of the friction coefficient may be due to the TiN film being gradually crushed under high stress, and final emergence of the maximum friction coefficient may result from the direct contact of the TiN film with the stainless steel substrate [3]. Fig. 4 shows the influence of sliding time on the friction coefficient for the wear couple of a JIS SUS 304 stainless steel ring against the TiC-coated disc. The friction coefficient initially increased to a maximum, and then gradually decreased to a minimum of 0.34 after 15 min sliding. As in the above case, the initial increase of the friction coefficient may also be due to the evaporation of the adsorbates on the sample surfaces by frictional heating, and then the decrease of the friction coefficient results from the generation of an oxide film on the surface of the stainless steel substrate by frictional heating [3]. Fig. 5 shows that the relation between the friction coefficient and sliding time for the wear couple of the TiN-coated ring against the TiC-coated disc. The shape of the curve is similar to that in Fig. 4, however the sliding time by which the friction coefficient decreased to the steady value is shorter than that in Fig. 4. It can be

<table>
<thead>
<tr>
<th>Disc</th>
<th>SUS304</th>
<th>TiN/SUS304</th>
<th>TiC/SUS304</th>
<th>AL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ring</td>
<td>0.56–0.66</td>
<td>0.59–0.98</td>
<td>0.30–0.37</td>
<td>0.40–0.59</td>
</tr>
<tr>
<td>SUS304</td>
<td>0.59–0.98</td>
<td>0.59–0.98</td>
<td>0.13–0.16</td>
<td>0.49–0.69</td>
</tr>
</tbody>
</table>

Fig. 3. Relation between the friction coefficient and sliding time (TiN film–TiN film) in air.

Fig. 4. Relation between the friction coefficient and sliding time (SUS 304–TiC film) in air.
considered that the TiN and TiC films are very hard with good adhesive wear performance so that the films can maintain their completeness, and frictional heating exists on the surface of the films during the experiment. Therefore, the oxide film can rapidly form on the surface of the TiN film [3, 5]. In comparison with Fig. 3, only one steady value of the friction coefficient exists in Fig. 5. It can be considered that the TiC film coated on the disc sample was thicker and harder than the TiN film coated on the disc sample in Fig. 3, so that the TiC film may not be crushed under the present experimental conditions. The experimental results of the different pre-treatment of the samples showed that the friction coefficient (0.43) of pre-treatment method (1) was higher than the 0.22 of method (2). It may be due to the difference in roughness of the sample surface prepared by the different methods.

4.2. The tribological properties in vacuum

Fig. 6 shows the influence of vacuum pressures on the friction coefficient for the wear couple of the TiC-coated ring against the c-BN-coated disc. The friction coefficient of the wear couple changes clearly with the vacuum pressure. At first, the friction coefficient gradually decreased to a minimum of 0.06 with decreasing vacuum pressures from 13 Pa down to $1.3 \times 10^{-1}$ Pa, and then increased a little to about 0.07 with a further decrease of the vacuum pressures. The initial decrease of the friction coefficient with the decrease of vacuum pressures is thought to be due to the gradual evaporation of the adsorbates on the sample surfaces by frictional heating in vacuum. In a vacuum of pressure $1.3 \times 10^{-1}$ Pa, the evaporation of the adsorbates may reach the limit under the present experimental conditions so that the friction coefficient of the wear couple decreased to the minimum. Then, the friction surfaces of the wear couple were further ground in and their friction coefficient reached the final steady value [3]. Fig. 7 shows the relation between the friction coefficient and the vacuum pressures for the wear couple of the stainless steel ring against the TiN-coated disc. The reason of the change of the friction coefficient with residual pressures may be similar to that for the wear couple of the TiC-coated ring against the c-BN-coated disc. Fig. 8 shows the influence of vacuum pressures on the friction coefficient for the wear couple of the TiN-coated ring against the TiC-coated disc. The friction coefficient of the wear couple gradually increased from 0.22 to about 0.6 with the decrease of vacuum pressures from 1 atm to $1.3 \times 10^{-3}$ Pa. The increase of the friction coefficient of the wear couple may be expected.
4.3. Tribological properties in vacuum at high temperature

Fig. 9 shows the influence of temperature on the friction coefficient in a vacuum of $2.6 \times 10^{-3}$ Pa for the wear couple of the TiN-coated ring against the TiC-coated disc. The friction coefficient of the wear couple gradually decreased to a minimum of 0.2 with the rise in temperature below 623 K, and then the friction coefficient increased to 0.38 at 673 K. It is well known that the TiN film begins to be oxidized from 623 K in air. Therefore, it can be considered that a steady oxide film may form on the surface of the TiN film at 623 K by frictional heating at a residual pressure of $2.6 \times 10^{-3}$ Pa, which may lead to lowering of the friction coefficient to a minimum. The increase of the friction coefficient at 673 K, may be induced by deterioration of the oxide film on the TiN film [3]. At 673 K, the friction coefficient of the wear couple was about 0.78 in a vacuum of $3.4 \times 10^{-1}$ Pa and was about 0.59 in a vacuum of $1 \times 10^{-3}$ Pa. Fig. 10 shows the wear traces on the rubbed surface of the disc samples under different conditions. Making a comparison between
Figs. 10(a) and 10(b), it can be seen that the section area of the wear trace in Fig. 10(a) is larger (D, 16 × 10^{-3} mm × W, 0.58 mm = 9.28 × 10^{-3} mm^{-2}) than that (D, 24 × 10^{-3} mm × W, 0.3 mm = 7.2 × 10^{-3} mm^{-2}) in Fig. 10(b). Therefore, the wear of the couple increased with the increase of vacuum pressures at 673 K. The depths of the wear traces in Figs. 10(a) and 10(b) have exceeded the thickness of the TiC film. This is one reason why the friction coefficients were as high as mentioned above for the wear couple of the TiN film/TiC film at 673 K in vacuums of 3.4 × 10^{-1} Pa and 1 × 10^{-3} Pa. In Fig. 10(c), the wear trace of the rubbed surface of the disc sample is very light, which may result from the fact that the friction coefficient of the wear couple became lower with the formation of the protection film on the friction surface after the friction surfaces of the couple were ground in for 5 min at 473 K and 623 K at a pressure of 2.6 × 10^{-3} Pa. This result shows that the wear-in situations are also important for the performance of the wear couples [3].

5. Conclusions

1. The friction coefficient of the TiN film against the TiC film was about 0.14 in air at room temperature, and the wear couple also possessed excellent wear resistance.

2. The friction coefficient gradually decreased with the decreasing vacuum pressures from atmospheric pressure down to 1.3 × 10^{-1} Pa, and then increased a little with a further decrease of the pressures, for the wear couples of the TiC film against the c-BN film and the stainless steel film against the TiN film. The friction coefficient increased with the decrease of vacuum pressures for the wear couple of the TiN film/TiC film.

3. The friction coefficient gradually decreased with increasing temperatures to 623 K for the wear couple of the TiN film against the TiC film in a vacuum of pressure 2.6 × 10^{-3} Pa, and its wear trace was also very light. It is promising that TiN and TiC films may be good solid lubricants for space applications.

References