Original Article

Design and high-temperature tribological properties of CoCrW with rare earth fluoride composites

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1. Introduction

With the development of aero-engine and braking systems of train, the wear of sleeves and brake disc is becoming more and more serious under unlubricated condition. Especially, the high-temperature wear is one of the main factors influencing the working life of mechanical parts. Thus, wear resistant materials should be developed in order to improve the efficiency and service life of mechanical parts [1–3]. In recent years, many types of self-lubricating composites were fabricated to meet the need of high-temperature tribological design of equipment, including metal matrix composites and ceramic matrix composites [4–6]. The addition of solid lubricants is the common method to improve high-temperature tribological properties of materials. And therefore, iron matrix, nickel matrix and ceramic matrix composites with solid lubricants were widely reported [1,7–9]. The investigations indicated that composites showed desirable results at elevated temperatures. However, these composites also had their own shortcomings. Large amount of solid lubricants destroyed the continuity of matrix due to the poor wettability, resulting in a considerable decrease in the hardness of composites [10]. It is hard to achieve a balance between tribological and mechani-
2. **Experimental procedure**

2.1. **Specimens preparation**

The commercial Co powder with a size of 64 μm, Cr with a size of about 53 μm, W with a size of 70 μm, Mo with a size of 70 μm, LaF₃ with a size of about 30 μm, and silver with a size of 60 μm were used as the raw materials in this study. All powders were analytical pure. Table 1 gives the compositions of composites. The prepared composites were denoted as CW, CL, CM and CA. The powders were thoroughly mixed by using a high-energy ball mill for 6 h. The milling speed was 200 rpm. Ratio of ball to mixed powder was 10:1. Four specimens were sintered by using a high-temperature sintering furnace. A graphite die was used in this study. When the temperature reached up to 1100 °C, the mixtures were pressed with a pressure of 32 MPa for 30 min under vacuum condition (10⁻² Pa), and then the specimen was cooled down naturally in furnace.

### Table 1 – Compositions of Co matrix composites (wt.%).

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Co</th>
<th>Cr</th>
<th>W</th>
<th>LaF₃</th>
<th>Mo</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>CW</td>
<td>78</td>
<td>15</td>
<td>7</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CL</td>
<td>68</td>
<td>15</td>
<td>7</td>
<td>10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CM</td>
<td>60</td>
<td>15</td>
<td>7</td>
<td>10</td>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>CA</td>
<td>51</td>
<td>15</td>
<td>7</td>
<td>10</td>
<td>8</td>
<td>9</td>
</tr>
</tbody>
</table>

The tribological performance was evaluated by using a ball-on-disk tribo-tester from RT to 1000 °C in air (see Fig. 1). The upper ball was fixed, and the disk rotated. The ball was the Si₃N₄ ceramic ball (diameter: 6 mm, hardness: 15 GPa) as the tribo-couple. The sliding radius of test was 5 mm. The sintered specimens were the disk with a dimension of \( \Phi \times 4 \text{ mm} \), which were polished to a surface roughness of 0.3 μm (Ra) before each test. The testing surfaces were ultrasonically cleaned. The load and sliding speed was 10 N and 0.20 m/s, respectively. Testing temperatures were room temperature (24 °C)-1000 °C, and temperature interval was 200 °C. The testing duration was 20 min. Cross profile of wear tracks was tested by a contact surface profiler in order to calculate the wear volume. The wear rates, \( W = V/LF \), were calculated according to a function that takes three parameters: wear volume, sliding distance and load. The unit of wear rate of specimens was mm³/m.N. The friction coefficient of composites was automatically recorded by computer. Each testing point was repeated three times.

The worn morphologies and microstructures of composites were analyzed by SEM (IT-300) equipped with EDS (X-MAX-50). The Vickers-hardness (Hv) of specimens was tested by a Vickers-hardness instrument (MH-5) with a load of 200 g and a dwell time of 10 s. The sintered density was tested according to the Archimedes’ principle. Phases of specimens were examined by using X-ray Diffraction (DIFFRACTOMETER-6000).

3. **Results and discussion**

3.1. **Microstructure and physical properties**

Fig. 2 gives the XRD patterns of different cobalt matrix composites. At elevated temperatures, W and Cr elements have high solid solubility in the crystal lattice of Co according to their phase diagram [23]. Co reacts with Cr and W due to the high-temperature solid solution reaction, and forms high-temperature \( \gamma \) phase with face centered cubic during solidification. With the decreasing of temperature, part of \( \gamma \) (fcc) transforms into \( \varepsilon \) (hcp) because of the martensitic phase.
and porosity. The hardness transformation, resulting in the ε (hcp) and γ (fcc) of two allotropes in matrix [24]. When Mo element diffuses into the crystal structure of solid solutions of Co alloys, which further leads to a slight increase in lattice parameters of cobalt due to the big radius of Mo element. Herein, the angle of diffraction peaks of ε (hcp) and γ (fcc) for specimen CM slightly decreases according to the Bragg equation. In this case, the position of diffraction peaks moves to the low angle area. The diffraction peaks of LaF₃ and silver are obvious in the figure, and no peak of corresponding compound is detected. It indicates that LaF₃ and silver do not form other compound at high temperature. For CA, it is confirmed that the main phases consist of ε (hcp), γ (fcc), LaF₃ and silver.

The back scattering electron image and element distribution maps of CA are shown in Fig. 3. The microstructure of composite is compacted, and no hole is noted. The distribution of each ingredient is uniform in matrix according to EDS analysis (see Fig. 3b–h). Different compositions keep a good interface bonding. It is beneficial for mechanical and tribological properties of composites. The continuous dark grey area is the Co-Cr-W-Mo solid solution phases which correspond to the ε (hcp) and γ (fcc) phase. The bright area of nearly round is the W-rich area, and the irregular shape is the silver phase. LaF₃ phase is located in the fine and dispersed light grey area according to the distribution of La and F elements.

Table 2 shows the Vickers-hardness, sintered density and porosity of obtained composites. It is clear that Vickers-hardness of composites decreases with the addition of LaF₃ and silver. One reason is that the poor sinterability of solid lubricants obviously influences the formation of sintering neck of alloy particles and destroy the continuity of matrix [25,26]. Another reason is that solid lubricants have low hardness. The silver has excellent toughness and compatibility with metal. Thus, during sintering, the silver can fill some fine holes in matrix, resulting in a good compactness. However, Mo element shows a solid solution strengthening effect because of the formation of compounds. And therefore, the hardness of specimen CM increases. Generally speaking, CM has the highest hardness in comparison with CW, CL and CA. Additionally, the sintering density of specimens varies with the addition of different compositions. The low density composition reduces the sintered density, and the high density composition increases the sintered density.

### 3.2. High-temperature tribological properties

Fig. 4 gives the friction coefficient traces of CA for three experiments at room temperature. The process of friction of CA includes two stages: running-in and steady wear stages. The running-in stage is short and less 4 min. The friction coefficient of CA is determined according to the steady wear stage. At other testing temperatures, similar trend is found on the time-friction relationship of other specimens.

The friction coefficients of obtained specimens with temperature sliding against Si₃N₄ ceramic ball at 10 N and 0.20 m/s are given in Fig. 5. The friction coefficients of specimens generally decrease with increasing of temperatures from 24 °C to 1000 °C. The trend of friction coefficients is dependent on the variation of temperature [21]. CL has higher friction coefficient than that of CW when the testing temperature is <600 °C. While testing temperature is >600 °C, the friction coefficient of CL decreases. Friction coefficient of CM increases due to the addition of molybdenum. However, CL and CA keep the low friction coefficients as compared with that of CW above.

![Fig. 1 – Configuration of high-temperature tribo-tester.](image1)

![Fig. 2 – XRD patterns of different specimens.](image2)

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Vickers hardness (HV)</th>
<th>Density (g/cm³)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CW</td>
<td>486</td>
<td>8.89</td>
<td>0.3%</td>
</tr>
<tr>
<td>CL</td>
<td>431</td>
<td>8.45</td>
<td>0.6%</td>
</tr>
<tr>
<td>CM</td>
<td>512</td>
<td>8.53</td>
<td>0.5%</td>
</tr>
<tr>
<td>CA</td>
<td>457</td>
<td>8.67</td>
<td>0.3%</td>
</tr>
</tbody>
</table>
Fig. 3 – Microstructure and element distribution maps of CA.

Fig. 4 – Typical curves of friction coefficient of CA with time at RT.

Fig. 5 – Friction coefficients of obtained composites with temperature at 10 N and 0.20 m/s.

800 °C. CA has the most stable friction coefficients from 24 °C to 1000 °C.

Fig. 6 illustrates the wear rates of composites with temperature at 0.20 m/s and 10 N. The wear rate of CW increases, and the value reaches a maximum at 600 °C. Subsequently, the wear rate decreases as temperature rises. Other specimens show the similar trend from 24 °C to 1000 °C. Below 400 °C, the wear rates of CL and CM are higher than that of CW. Above 400 °C, the specimens shows good wear resistance. It means that LaF₃ degrades the low-temperature wear resistance of composites. Mo obviously changes the wear behaviors of specimen CM, especially, at high temperature. In general, CA shows the best wear resistance at all testing temperatures, and the wear rates is about 1.2–3.6 × 10⁻⁵ mm³/N.m. According to the
results, the wear rates of prepared Co matrix self-lubricating composites was about 10 times lower than those of Ni matrix and ZrO₂ matrix composites from 24 °C to 1000 °C that were previously reported by other researchers [27,28]. The corresponding wear mechanisms will be discussed below.

The tribological behaviors of composites greatly depend on compositions and temperature. At lower temperature, ingredients and wear debris are oxidized due to the friction heat and external temperature, and form oxides on the contact surfaces [18]. However, the speed of oxides removal is > that of oxidation. At this point, little oxides cannot form an obvious and stable oxides film on the wear tracks (see Fig. 7a). Meanwhile, the oxidation-oxides removal-oxidation is accelerated, resulting in high friction coefficient and wear rates. With increasing of temperature, oxidation predominates in the oxidation-oxides removal-oxidation in order that large amount of oxides and complex compounds increases on the worn tracks (see Fig. 8). These compounds form a stable oxides film containing oxides, silver, chrome, molybdate and fluoride on the wear tracks of composites (see Fig. 7b) [1,15,28]. The oxidation-oxides removal-oxidation is restricted. Not only does the intact oxides film reduce the oxidation of materials, it also strengthens tribological properties of composites. Herein, the friction and wear rate of composites decrease when temperature rises. LaF₃ and Mo do not possess lubricating effect at low temperature. Furthermore, LaF₃ destroy the continuity of matrix. And therefore, CL and CM show high friction coefficients and wear rates. Above 600 °C, LaF₃ melts and forms compounds in order to provide lubricating effect. When Mo changes into MoO₃, Co₃Mo₂O₈ and Ag₂MoO₄, Mo shows lubricating effect during sliding. Therefore, CM, CL and CA show self-lubricating property from 600 °C to 1000 °C. The hardness of materials is the most important parameter for the wear resistance of materials [29]. The hardness of composites decreases with increasing of temperature. Additionally, the phase transformation of ε → γ leads to the a decrease in hardness [30]. In this case, the wear rate of composites increases at low temperature. CM has higher hardness than that of CL, so CM has a good wear resistance. The silver is a low-temperature solid lubricant because of its toughness. During sliding, the silver can smear on the surfaces of wear tracks and form an Ag-rich lubricating film. At high temperature, the silver reacts with other ingredients, and forms AgF₃ and Ag₂MoO₄ that are high-temperature solid lubricants [27,31]. Due to the synergistic effect of silver, LaCrO₃, Ag₂MoO₄, AgF₃, metal oxides and LaF₃ (see Fig. 8), the CA shows the most excellent tribological performance than those of other specimens from 24 °C to 1000 °C.

### 3.3 Analysis of worn surfaces

SEM images of wear tracks of obtained composites sliding against Si₃N₄ ball at room temperature are given in Fig. 9. The

![Fig. 6 – Wear rates of obtained composites with temperature at 10 N and 0.20 m/s.](image)

![Fig. 7 – Cross-sectional morphologies of CA at (a) 400 °C and (b) 1000 °C.](image)

![Fig. 8 – XRD patterns of worn surfaces of CA.](image)
plastic deformation, wear debris and grooves are noted on the worn surfaces of CW and CL (see Fig. 9a and b), suggesting that the wear mechanism is plastic deformation and abrasive wear at RT. The worn surface of specimen CM has a low surface roughness, and slight plastic deformation and micro-grooves are noted on the worn surfaces (see Fig. 9c). Plastic deformation resistance of matrix is reinforced because of the solid solution strengthening effect of Mo. High hardness can cause the increase of sliding resistance of asperities. Hence, the friction coefficients of CM is high. It also means that CM shows slight abrasive wear. CA shows the distinct worn morphology as compared with other specimens at room temperature (see Fig. 9d). A dense and continuous lubricating film covers the surface of wear track. The lubricating film is the silver-rich phase according to the analysis of EDS (see Fig. 10). The soft silver smears on the worn track under the reciprocating effect of tribo-couple, and separates tribo-couples [25,28]. The silver lubricating film greatly improve the tribological behaviors as is evident from the Figs. 5 and 6, especially, at low temperature. The wear mechanism of CA is characterized by abrasive wear.

Fig. 11 depicts the SEM images of worn tracks of different specimens at 600 °C. The wear track of CW is covered by much wear debris. Due to the decrease of hardness, the material peels off from the worn surfaces and becomes wear debris. It corresponds to the high wear. Plastic deformation and grooves are obvious on the worn track, suggesting that the wear mechanism of CW is mainly abrasive wear. However, a discontinuous lubricating film is found on the worn surfaces of CL, CM and CA (see Fig. 11b, c and d). It means that the solid lubricants start to provide a lubricating effect.

Obviously, the coverage of lubricating film of CA is higher than those of CL and CM, thereby keeping the lowest friction coefficients and wear rates. The wear is accompanied by grooves and plastic deformation. By comprehensive consideration, CL, CM and CA suffer from slight oxidative wear and abrasive wear at 600 °C. The worn surfaces of composites at 1000 °C are shown in Fig. 12. At high temperature, metal oxides and compounds form a stable oxides film on the surfaces of wear tracks, and the continuous oxides film covers the whole worn surfaces of specimens at 1000 °C. This oxides film maintains the low friction and wear of composites at higher temperature [22,24]. Additionally, the specimens show the characteristic of grooves. The dominant wear mechanism of composites is oxidative wear and slight abrasive wear.
Fig. 11 – Worn surface morphologies of four composites at 600 °C: (a) CW, (b) CL, (c) CM and (d) CA.

Fig. 12 – Worn surface morphologies of four composites at 1000 °C: (a) CW, (b) CL, (c) CM and (d) CA.
Fig. 13 – SEM images of worn scars of Si$_3$N$_4$ ceramic balls rubbing against CA at different temperatures: (a) RT, (b) 600 °C, (c) 1000 °C and (d) EDS analysis in c.

Fig. 14 – Illustration of the transformation of wear process.
**Fig. 13** shows wear scars of Si$_3$N$_4$ ball sliding against CA at different temperatures. The significant transferred layer is visible on the worn surfaces. The transferred layer becomes more and more compacted and continuous when temperature increases. According to the EDS (see **Fig. 13d**), the ingredient of oxides film is similar with that of transferred layer, indicating that the transferred layer has lubricating effect. Because of the presence of lubricating film, it changes the wear model between specimen and ball. Because of the formation of oxides film, the wear of tribo-couples turns into the wear of film-to-film (see **Fig. 14**) [32].

### 4. Conclusions

(1) The microstructure of Co matrix self-lubricating composites was compacted, the distribution of ingredients was uniform in matrix. LaF$_3$ and Ag degraded the hardness of materials, whereas Mo reinforced the hardness of materials due to the solid solutions strengthening effect. The target composites consisted of e, γ, LaF$_3$ and silver.

(2) At low temperature, LaF$_3$ and Mo destroyed the lubricating properties and wear resistance of alloys. Composites showed high friction coefficients and wear rates. At high temperature, LaF$_3$ and Mo obviously improved the tribological properties. Cobalt matrix composites had a continuous self-lubricating properties due to the addition of silver from RT to 1000°C. It was attributed to the lubricating effect of chromates, molybdates, silver, metal oxides and LaF$_3$. LaF$_3$ only showed lubrication above 600°C. When Mo formed compounds, Mo possessed lubricating effect. The silver formed silver-rich lubricating film which improved low-temperature tribological properties.

(3) Co-15Cr-7W-10LaF$_3$-8Mo-9Ag showed the most excellent tribological performance from RT to 1000°C, and the wear rate was about 1.2–3.6 × 10$^{-5}$ mm$^3$/N.m. The presence of oxides film changed the wear model. The wear mechanisms of composites were mainly abrasive wear and oxidative wear.

**Conflict of interest**

The authors declare no conflicts of interest.

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**Appendix A. Supplementary data**

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jmrt.2019.12.072.

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