High temperature oxidation and wear behaviour of powder metallurgically
developed Ni-Cr-W-Al-Ti-MoS$_2$ composite

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Nickel-chromium matrix composites reinforced with tungsten, aluminum, titanium and molybdenum disulfides are
developed by a powder metallurgy method. The high temperature oxidation properties, the friction and wear behaviour of
the composites under dry sliding condition are investigated using the pin-on-disc. The oxidation behaviour of composite is
studied by scanning electron microscopy (SEM), the worn surfaces and worn chips are observed by X-ray diffraction (XRD)
and optical microscope. The results show that the kinetic curves of oxidation for composite obey the parabolic law, the
oxide scales consist of Cr$_2$O$_3$ and NiCr$_2$O$_4$. Both the friction coefficient and wear rate of composites decrease with the
increase of temperature before 400°C, but the wear rate is the highest at 600°C. The oxidative wear is the main wear
mechanism for the composites.

Keywords: Molybdenum disulfides, Ni-Cr matrix composite, Oxidation, Wear behaviour

With the development of aerospace technology, turbine engines used in aviation make demands of lubricants with temperature capability of over a wide range of temperature, the conventional grease lubrication systems no longer meet the ever-rising requirements$^1$. It is an urgent need to develop advanced materials that work with excellent self-lubrication within a wide temperature range. The combination of different materials could produce the improved mechanical, chemical, and tribological properties depending upon the distribution of phases and the composition of basic phase in the composite. Ni-Cr composite is one leading candidate for high temperature structural applications due to its excellent high-temperature performance$^{2-4}$.

However, it is disadvantageous to the use of strengthening and lubricating phases in Ni-Cr composites for high temperature application because of their susceptibility to oxidation in air at high temperature.

To access the performance of Ni-Cr-W-Al-MoS$_2$ composite, the present work is to investigate the oxidation and wear behaviour of Ni-Cr-W-Al-MoS$_2$ composite at high temperature in air. Strengthening phases Mo, Al, Ti, and lubricant phase MoS$_2$ reinforced Ni-Cr matrix composites were developed by a powder metallurgy method, which are recommended to be used for high temperature applications.

Experimental Procedure

Preparation of composites
The Ni-20Cr powder (purity of 98.0%, grain size of 60 µm) and 15 wt.% tungsten (20 µm), 3.8 wt.% aluminum (80 µm), 5.5 wt.% titanium (80 µm), and 6 wt.% MoS$_2$ (30 µm) were mechanically mixed together. The mixture was pressed in graphite dies under a pressure of 16 MPa by FVPHP-R-10 vacuum-hot-pressing furnace. The furnace was drawn to a vacuum of 10$^{-5}$ Pa and protected by nitrogen gas, which was heated to 1240°C at a rate of 20°C/min. The specimens were hot pressed for 15 min in a pure nitrogen atmosphere, and then one disk in size of Φ45 × 5 mm was developed.

Oxidation kinetics
The composites were sliced into 10 mm × 4 mm × 4 mm blocks, ground down to 600 emery paper, washed in water, alcohol and then dried immediately. The isothermal oxidation was performed in a chamber furnace at 800°C and 900°C for 100 h in air, and the weight changes were measured after 1, 3, 5, 10, 25, 50, 75 and 100 h using DT2100 analytical balance with an accuracy of 0.1 mg. The oxidized samples

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were examined using scanning electron microscopy (SEM) and X-ray diffraction (XRD).

**Friction and wear tests**

The friction coefficient of the composites was measured using a MG-2000 high-temperature pin-on-disk apparatus under dry condition. The upper samples of flat-ended composite pins \((d_5 \text{ mm} \times 15 \text{ mm})\) were kept still, while counterface disks were rotated. The mating material was alumina ceramic disk \((d_{52} \text{ mm} \times 8 \text{ mm}, \text{ hardness HRC 70, roughness 1.5 } \mu\text{m})\). The experiments were operated with a load of 100 N at a sliding velocity of 0.8 m/s at the room temperature, 200°C, 400°C and 600°C. The sliding distance was 1500 m and the average wear track with a diameter of \(d_{31} \text{ mm}\). The frictional moment was recorded by a computer consistently. After cleaning by ethanol, the wear mass losses of pins were weighed by an analytical balance with accuracy of 0.1 mg. The ratio of mass loss to sliding distance was taken as the wear rate to evaluate wear resistance of the composites. The phases and morphologies of the worn surfaces were analyzed by XRD and optical microscope.

**Results and Discussion**

Figure 1 shows the morphologies of composite surface after vacuum hot pressing. There are three phases: the hoar phase, the gray phase and the dark one. The hoar phase is the metallic matrix which contains Ni, Cr, Mo and slight amount of Si. The dark phase is mainly SiO\(_2\) that is commonly included in the MoS\(_2\) raw material. The gray phase contains Ni, Cr and S\(^{5,6}\), which is a eutectic which contains Cr\(_x\)Sy and Ni(Cr) alloy. Therefore, the alloy material is mainly composed of the metallic matrix and the eutectic\(^7\).

![Fig. 1—Optical morphologies of Ni-Cr-W-Al-Ti-MoS\(_2\) composite](image)

**Oxidation dynamic curve**

The oxidation rates were determined by calculating the mass gain per square centimeter of composites. The kinetics curves of Ni-Cr-W-Al-Ti-MoS\(_2\) oxidized at 800°C and 900°C are shown in Fig. 2. The mass gain of the composites increases continuously with time. At 800°C after 100 h, a mass gain of 0.86 mg/cm\(^2\) is observed, while at 900°C, a mass gain of 2.26 mg/cm\(^2\) is obtained. In addition, the relationship between the mass gain and time is nearly parabolic law.

In preliminary period of 10 h, oxidation speeds up with the nucleation of oxides on the crystal interfaces, which is the formation period of oxide film. Then, the velocity slows down and enters into the growth period, which lasts for 20 h. During the oxidation process, surface inborn reaction turns into diffusion gradually, along with the time, the oxidation speed slows down gradually.

The (weight gain/unit area)\(^2\) versus time at different temperature is shown in Fig. 3 indicating that the oxidation process has nearly followed the parabolic rate law for all the composites. The values of parabolic rate constants \((Kp)\) have been calculated for all the investigated cases, which are based on the parabolic rate equation for the high temperature oxidation process\(^8,9\).

![Fig. 2—Oxidation kinetics curves of Ni-based composite at 800°C and 900°C](image)

![Fig. 3—Dependence of the square root of the mass gain of Ni-based composite on oxidation time at 800°C and 900°C](image)
\[ x^2 = K_p t + C \]

Where \( x \) is the weight change per unit surface area, \( t \) is the time and \( K_p \) is the parabolic growth rate constant. There are two parabolic rate constants \((K_{p1} \text{ and } K_{p2})\) during oxidation period, indicating that oxidation mechanism is changed, as shown in Table 1, change time is 17 h at 800°C and 12 h at 900°C.

The \( K_p \) values for the Ni-Cr-W-Al-Ti-MoS\(_2\) composite was found to be \( 2.74 \times 10^{-3} \text{ mg}^2 \cdot \text{cm}^{-4} \cdot \text{h}^{-1} \) before 17 h, then changed to a value of \( 0.59 \times 10^{-3} \text{ mg}^2 \cdot \text{cm}^{-4} \cdot \text{h}^{-1} \) for the range 17-100 h at 800°C. Similarly the various values of \( K_p \) for the composites at 900°C were found to be \( 92.31 \times 10^{-3} \text{ mg}^2 \cdot \text{cm}^{-4} \cdot \text{h}^{-1} \) for 0-12 h range and \( 40.91 \times 10^{-3} \text{ mg}^2 \cdot \text{cm}^{-4} \cdot \text{h}^{-1} \) for the rest of the exposure period.

It was proved that the oxidation mechanism from surface reaction into the diffusion control, high temperature is disadvantage to Cr\(^{3+}\) diffusion speed in oxidation layer\(^{10}\).

**Constitution of oxidation film**

Figure 4 shows the surface morphologies of Ni-Cr-W-Al-Ti-MoS\(_2\) composite after oxidation at 800°C and 900°C for 100 h. It can be seen that the scale is rather non-uniform, there are only a few acicular oxides on the surface at 800°C instead of continuous oxide films. A continuous scale was formed on the surface of the composite at 900°C. After 100 h oxidation at high temperature, the oxides on the surface consist of Cr\(_2O_3\) as well as NiCr\(_2O_4\) spinelle and TiO-TiO\(_2\) phase\(^{10,11}\). The oxidation films on the matrix firmly prevent the composite from oxidizing further. The content of Cr\(_2O_3\) has an increasing tendency with oxidation time. After 12 h, the main featured peaks of Cr\(_2O_3\) form, which shows that the oxidation film forms basically, consistent with the results from oxidation dynamic tests. In the later stage, oxidation process is mainly affected by Cr\(^{3+}\) diffusion. Though the dimension and magnitude of NiCr\(_2O_4\) spinelle increase with oxidation time, the continuous films cannot form, which has no control effect on oxidation velocity.

**Friction and wear behaviour**

The friction coefficient of the Ni-Cr-W-Al-Ti-MoS\(_2\) composite tested against the alumina ceramic disk counterbody, with 100 N load and 0.8 m/s velocity is shown in Fig. 5. It can be seen that the friction coefficient decreases at elevated temperature. At 200°C after an obvious slightly longe running-in stage, the coefficient of friction became stable and stayed at approximately 0.5. The friction coefficient was less stable at a level of approximately 0.3 when environment temperature was 400°C. The friction coefficient at 600°C was stable and lower than 0.2.

**Table 1— Parabolic reaction rate constants \( K_p \) and change time at different temperatures of Ni-based composite**

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>( K_{p1} \times 10^{-3} \text{ (mg}^2 \cdot \text{cm}^{-4} \cdot \text{h}^{-1}) )</th>
<th>( K_{p2} \times 10^{-3} \text{ (mg}^2 \cdot \text{cm}^{-4} \cdot \text{h}^{-1}) )</th>
<th>Change time/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>2.74</td>
<td>0.59</td>
<td>17</td>
</tr>
<tr>
<td>900</td>
<td>92.31</td>
<td>40.91</td>
<td>12</td>
</tr>
</tbody>
</table>

**Fig. 4—**SEM observation on the surface of Ni-based composite oxidized for 100 h at different temperatures.
The dynamic change regularity of friction coefficient versus sliding distance was different at 200°C, 400°C and 600°C, indicating that the composite has different wear mechanism at different temperatures.

Figure 6 shows the effects of temperature on the wear rates of the Ni-Cr-W-Al-Ti-MoS\(_2\) composites at a sliding speed of 0.8 m·s\(^{-1}\) under 100 N of load. The results show that the wear rate of the composite shows a steadily decreasing trend with an increase of temperature before 400°C, the corresponding value is the lowest, then 2.4 × 10\(^{-5}\) at 600°C, which is higher than that in room temperature.

**Sliding wear mechanism**

The characteristic of the composite and wear debris from the material rubbing against Al\(_2\)O\(_3\) at room temperature were measured using the XRD pattern. The result\(^{12}\) shows that the XRD spectrum of composite and wear debris is almost homologous, but the spectrum of nickel solution is widening, the diffraction peaks become broadened provide that Ni-based solid solutions has happened grain refinement and lattice distortion.

The grain refinement wear debris filled in uneven surface in the wear process, forming a dense protective film, separate direct contact of the friction surface\(^{12}\).

Figure 7 shows typical morphologies of worn surfaces of the composite pin and Al\(_2\)O\(_3\) ceramic disc under 100 N load at 600°C. The pin sample is oxford blue after friction, black substances are produced on the worn surface. In Fig. 7a, black sulfides form lubricating film on the worn surface at 600°C. There is an evidence of adhesion and ploughing on the worn surface, so the friction coefficient is low. It proved that the sulfides in Ni-Cr-based composites form eutectic substance\(^{13}\), which causes the melting point drop from about 1300°C to 600-900°C. It is plastic at high-temperature and easy to undergo deformation.
Archard et al.\textsuperscript{14} gave a flash point temperature formula:

\[
(\theta_\text{x})_{\text{max}} = 1.64 \theta_\text{m} \quad \ldots(1)
\]

Where \((\theta_\text{x})_{\text{max}}\) is the highest temperature on the friction surface, \(\theta_\text{m}\) is environment temperature. It can be concluded that with the 600°C environment temperature, the temperature on the friction surface is near 1000°C, this cause sulfides soften and melt and form lubricating films. Especially at higher temperature, \(\text{Cr}_{x}\text{S}_{y}\) transfers and clings to the counter surface, forming even and compact films between the worn surfaces\textsuperscript{15}. And the oxide NiO is also solid lubricant at high temperature, so the friction coefficient is lower than that of at 200°C.

Figure 8 shows that the wear debris after high temperature wear is consisted of NiO, MoO\(_3\), \(\text{Cr}_2\text{O}_3\), WO\(_3\) and NiWO\(_4\). At high temperature together with the heat produced by rubbing, NiO and WO\(_3\) are produced, and then NiWO\(_4\). According to Eq. (1), there are oxidative wear obviously. The produced oxides and tungstates make lubricating films on the worn surfaces and prevent the direct contacts between the pair surfaces, and the sulfides in the composite are solid lubricants too. Thus the friction coefficient is very low.

The hard phase \(\text{Cr}_2\text{O}_3\) in the wear debris has high hardness at high temperature. At high temperature, the matrix strength is dropped and introduced hard grain into friction surface, which makes the surface wear hardly and shows abrasive wear, addition with oxidative decomposition, so the wear rate is high.

**Conclusions**

The following conclusions may be drawn from this study:

(i) Nickel-based composites Ni-Cr-W-Al-Ti-MoS\(_2\) were developed by powder metallurgy (P/M). The kinetics curves is nearly followed the parabolic rate law at 800°C and 900°C, the oxides is mainly consist of \(\text{Cr}_2\text{O}_3\) and \(\text{NiCr}_2\text{O}_4\) spinelle.

(ii) The friction coefficient of the composite decreases with the increase of temperature at elevated temperature. The wear rate of the composite decreases before 400°C, then rises to \(2.4 \times 10^{-5}\) at 600°C.

(iii) The main wear mechanism is the oxidative wear at 600°C.

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**References**