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Tribological behavior of Ni-Cr-based composite at high temperatures

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Abstract: The wear behavior of Ni-Cr-based alloys was investigated at ambient and elevated temperatures. The wear samples were prepared by metallurgical hot pressing. Wear tests were carried out on a general purpose wear testing machine having a heating unit and pin-disc sample configuration. The counterface material was prepared from Al_2O_3 ceramics. The tests were carried out at room temperature (RT), 200 ℃ and 600 ℃. The effects of temperatures on the tribological properties were determined by using optical microscopy, and X-ray diffractometry. The results show that at room temperature the worn surfaces of the alloys are characterized by mild scuffing and micro cracks, the action of nano-crystal structural wear debris on the worn surfaces is responsible for the reduction of friction. At 200 ℃, the friction coefficient is the highest. The worn surfaces of the alloys are adhesive and oxidative. At 600 ℃, the friction coefficient is reduced due to the effect of the oxides, tungstates and sulfides residue on the worn surface.

Key words: Ni-based alloys; powder metallurgy; wear mechanism; tribological behavior; dry friction

1 Introduction

With the rapid development of modern science and technology, more and more mechanical devices work in widening temperature ranges, such as the turbine engines used in aviation and electrical industries. The conventional grease lubrication systems no longer meet the ever-rising requirements. It is urgent to develop materials that work with excellent self-lubrication within a wide temperature range. PETERSON et al studied the lubricative behaviors of oxides films and applied the antifriction principle of the autogenic oxides films to the development of high-temperature self-lubricating alloys[1−4]. Sulfides Cr_xS_y were found on the MoS_2-containing Ni-Cr-based alloys when rubbing against ceramics at high temperatures. The S-containing Ni-based alloys rubbing against ceramics with lubricative phases share self-lubricating properties in a wide temperature range[5−8], thus self-lubricating Ni-based alloy is used as the friction pair of ceramics and this is one of the leading approaches in solving the problem of ceramics lubrication at high temperatures[9−10]. In this paper, Ni-Cr-based alloys with lubricating MoS_2 or graphite were prepared by powder metallurgy with strengthening elements Mo, Al, Ti and W. The mechanical properties and tribological behaviors of the alloys as well as the wear mechanism at room temperature, 200 ℃ and 600 ℃ were studied.

2 Experimental

2.1 Material preparation

Ni-20Cr powder with 6%(mass fraction) MoS_2 or graphite powders were mixed with certain proportions of Mo, Al, Co, Ti and W powders. The fully mixed mixture was cold pressed into d45 mm×15 mm disks. The disks were then loaded into a graphite mould and separated from each other by graphite slices. The samples were prepared by vacuum hot pressing in an FVPHP-R-10 vacuum hot-presser. The conditions are as follows: operating temperature at 1 240 ℃, pressure at 16 MPa, and sintering time 15 min, nitrogen protection after degassing to 10^{-5} Pa.

2.2 Measurement of properties

Pin-on-disk approach was taken to measure the tribological properties of the alloys rubbing against Al_2O_3 ceramics. The instrument is an MG-2000 high-

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temperature tribometer, which runs from at room temperature(RT) up to 600 ℃. Pins were made from the samples, with a size of *d* 5 mm×15 mm each. Disks were of Al_2O_3 ceramics, with a size of *d* 52 mm×8 mm each. The pin was fixed and the disk was rotating against it. The disks wore a scar with a diameter of *d* 31 mm after rubbing. Prior to tests, pin and disk specimens were polished with 600# emery paper and were ultrasonically cleaned in an acetone bath. In tests, each applied normal load was 98 N, the sliding surface speed was 0.8 m/s, and the sliding distance under each temperature was 1.5 km. Every second the friction moment was recorded automatically. With the equation $\mu=F/N=M/(rN)$ (in which M is the friction moment, r is the circumgyrate radius, N is the load), the friction coefficient is to be calculated. An electronic balance with an accuracy of ±0.1 mg was used to weigh the worn mass loss. To study the wear mechanism, the structures of scar and debris were investigate through an X-ray diffractometer (XRD), and the morphologies of the worn scar were analysed through an optical microscope. Bending strength tests were taken on a CSS-44200 electron tester and hardness tests were carried out on an HB-3000 Sclerometer.

3 Results and discussion

3.1 Mechanical and tribological properties of alloys

The properties such as density, hardness and bending strength of Ni-Cr-based alloys with different compositions are depicted in Table 1. The density decreases with the addition of horniness reinforcement elements and soft lubricative phases, and the density of alloy with graphite is the lowest. The hardness increases significantly with the addition of horniness alloy phases and reaches about 1-2 times higher than that of the base alloy. The hardness with graphite is bigger than that with MoS_2. This is due to the carbides produced in hot pressing process. The bending strength is about half of the base alloy. This shows that the addition of alloy phases goes against material's bending property, again, the addition of graphite affects more than the addition of MoS_2.

Table 1 Effect of graphite and MoS_2 on physical-mechanical properties of Ni-Cr based alloys

Alloy composition	Density/ ($g\cdot cm^{-3}$)	Hardness, HB	Bending strength/MPa
Ni-Cr	8.9	220	780
Ni-Cr-W-Co-Al-Mo-Ti-Si-C	6.0	530	311
Ni-Cr-W-Co-Al-Mo-Ti-Si-MoS_2	7.5	496	400

The variations of the friction coefficient and wear rate of alloys rubbing against Al_2O_3 at different temperatures are presented in Table 2. With graphite addition, the average friction coefficient increases from 0.35 at room temperature(RT) to 0.78 at 200 ℃, then deceases to 0.18 at 600 ℃. The wear rate increases from $0.6\times10^{-14}(m^3\cdot N^{-1}\cdot m^{-1})$ at RT to $1.7\times10^{-14}(m^3\cdot N^{-1}\cdot m^{-1})$ at 200 ℃, then to $2.8\times10^{-14}(m^3\cdot N^{-1}\cdot m^{-1})$ at 600 ℃. With MoS_2 addition, the tendency to changes of friction coefficient and wear rate is of the same as with graphite addition. However the values are lower at high temperatures. Thus, at high-temperature, the tribological properties of alloys with MoS_2 content are more preferable than those with graphite content, although at room temperature the situation is different.

Table 2 Friction coefficient and wear rate of two samples at RT, 200 ℃ and 600 ℃

Sample	μ			Wear rate of pin/ [$10^{-14}(m^3\cdot N^{-1}\cdot m^{-1})$]		
	RT	200 ℃	600 ℃	RT	200 ℃	600℃
Ni-Cr-W-Co-Al-Mo-Ti-Si-C	0.35	0.78	0.18	0.6	1.7	2.8
Ni-Cr-W-Co-Al-Mo-Ti-Si-MoS_2	0.45	0.48	0.16	1.8	1.4	2.4

3.2 Wear mechanism

X-ray diffractions of the hot pressed material show that Ni (Cr，Mo ,Al , Ti) solid solutions, Cr_5S_6, Cr_6S_7, Cr_7S_8[11] and certain carbides are produced during the processes.

At room temperature, abrasive wear happens without obvious debris peeling off from the material with graphite addition, with clear wear tracks along the sliding direction, and the wear rate is relatively low. For the material with MoS_2 addition, the worn surfaces show less abrasive wear, but with more adhesive wear. That is to say, plastic deformation happens within the base material, while sulfides remain relatively stable. Thus, although sulfides self-lubricate, the ability to form lubricating films on the surface is limited. Due to the roughness of the worn surfaces and the looseness of the combination, wear debris falls from worn surfaces during rubbing against Al_2O_3, resulting in high wear rate of the material [12].

Fig.1 shows the XRD pattern of wear debris from the material rubbing against Al_2O_3 at room temperature. The half-high width B of the diffraction is taken from the figure. Under the Scherrer's equation $d=0.89\lambda/(B\cos\theta)$, the particle crystallite sizes of Ni based solid solution are calculated. The average value is 15.3 nm. It can be concluded that the plastic deformation rises up because the friction stress engenders the local high-temperature. During the continuous compression deformation process, the grains grow finer and the gain size achieves nanometer scale. Then some fall off from the wear surface and form the debris, which takes some effect of lubricant. To the alloy with graphite addition especially, the tungsten carbide produced during hot pressing is very hard, which acts as the 'ball bearing' during the rubbing. Thus the friction coefficient is low and the wear property is improved[13].

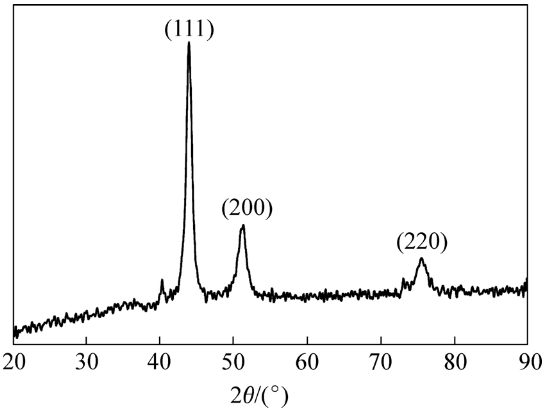

Fig.1 XRD pattern of wear debris products

Fig.2 shows some optical micrographs of the worn surfaces of the alloys at 200 ℃ and 600 ℃. As shown in Fig.2(a), the lubricant films are not formed on the worn surface of the material with graphite addition, and the celadon substance produced during the rubbing process daubs to the counter surface and is worn out easily. When the alloy rubs against the ceramic, the fallen substance aggravates the wear of the alloy, and the friction coefficient is high. At 200 ℃, graphite oxidization causes serious graphite content decrease at the surface area and cavity disfigurement appears. At 200 ℃, other alloy contents are not easily oxidized. This makes the wearing process worse and the friction coefficient and wear rate are both higher than that at room temperature. It is reported that the crystallization of microstructure on the alloy surfaces degrades at about 200 ℃. The alignment of the microcrystal structure is also harmed. The graphite is changed to the amorphous carbon structure. The degradation of structure weakens the lubricating properties of the alloy, results in higher friction coefficient and wear rate compared with that at room temperature [14]. At 600 ℃, as shown in Fig.2 (b), particles are observed and the worn surface is rough with plow traces and grain wear. The wear rate is high (Table 2). LU et al[15] reported that excellent mechanical properties still remained for Ni-based alloys at 500 ℃ and higher temperature. Nickel is easily oxidized at the surface and turned to NiO with excellent plasticity and glutinosity. NiO is a solid lubricant at high-temperature. So the friction coefficient should be lower than that at 200 ℃. However at this time, with the effect of ambient temperature and the heat produced by friction, oxidation occurs on the surface of alloy and the hardness is decreased. At the same time, WC granules that were produced during hot pressing make a difference coefficient of expansion between the oxide surface layer and the substrate, which contributes to the cracking and falling off of oxide layer from the worn surface. Thus causes the high wear rate.

In Figs.2(c) and (d), black substances are produced on the worn surface of the alloy with MoS_2 addition. In Fig.2(c), slight adhesive wear and plastic deformation are observed at 200 ℃ without the production of continuous lubricating films. The final result is that there is not remarkable change in the friction coefficient and wear rate compared with those at room temperature. In Fig.2(d), black sulfides form lubricating film on the worn surface at 600 ℃. So the friction coefficient is low. Former studies have also proved that the sulfides in Ni-Cr-based alloys form eutectic substance[5]. Thus causes the melting point drop from about 1 300 ℃ to 600−900 ℃. It is plastic at high-temperature and easy to undergo deformation. The lubricating mechanism is explained as follows: The black sulfides are eutectic material. Under local high-temperature caused by the friction, they soften and melt and form lubricating films. Especially at higher temperature, Cr_xS_y transfers and clings to the counter surface, forming even and compact films between the worn surfaces[16]. Thus the lubricating effect gets further improved.

The observed Cr_2O_3 phases in the debris and WC produced during hot pressing are both very hard even at high-temperature. At the same time the hardness of the substrate material drops at high-temperature. These hard granules then go easily into the counter surfaces, resulting in severe abrasion at the counter surfaces. Thus, the worn surfaces show abrasive wear at 600 ℃(Fig.2(d)) and the wear rate is high with the oxidative decomposition (Table 2).

Fig.3 shows the XRD analyses result of the wear debris produced during the rubbing process from the alloy with reinforcement phases and MoS_2 at 600 ℃. It is seen in Fig.3 that the wear debris is mainly composed of Ni solid solution and oxides produced during the wearing process, MoO_3, NiO, WO_3 and tungstates and so on.

The beginning temperature of oxidation for Ni is 395 ℃. Severe oxidation happens at 713 ℃. The beginning temperatures of oxidation for Co and WC are about 300 and 468 ℃ respectively. At high-temperature together with the heat produced by rubbing, CoO and WO_3 are produced. They combine and make $CoWO_4$. At such a stage it is obvious that oxidative wear is under way. Under rubbing, the produced oxides and tungstates make lubricating films on the worn surfaces. These films

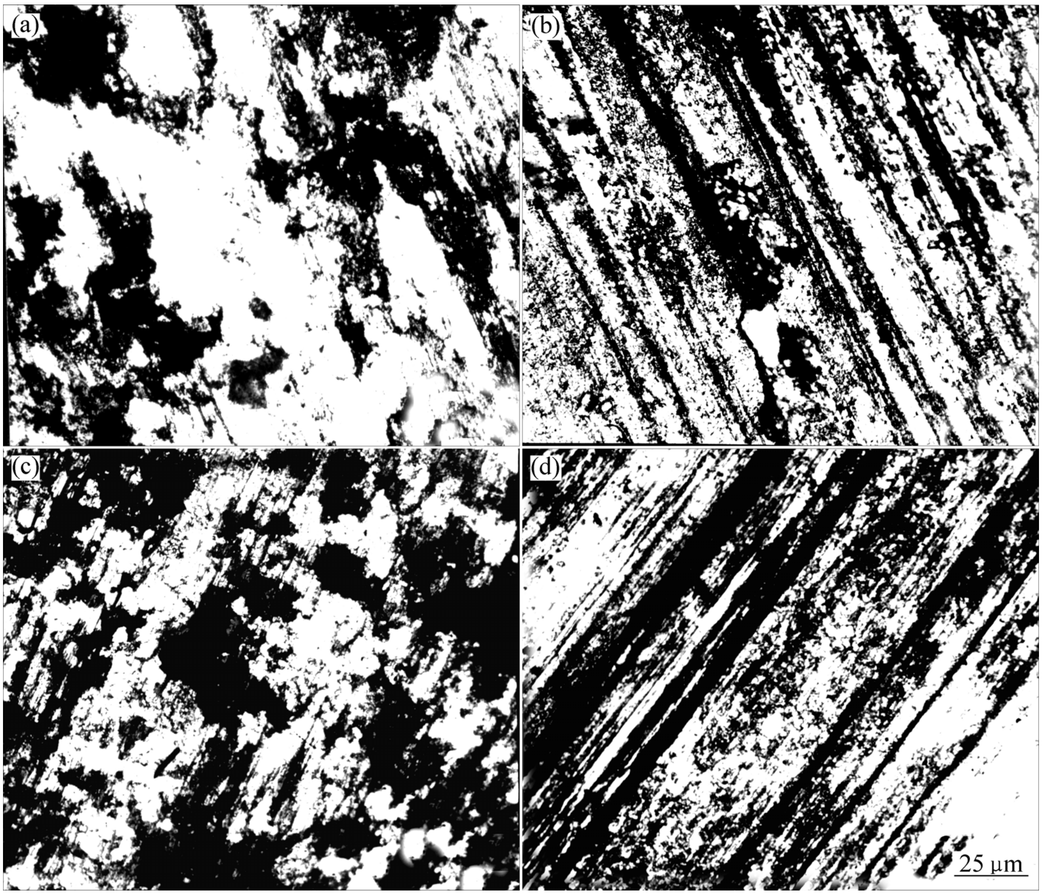

Fig.2 Optical micrographs of worn surfaces of alloys: (a) Ni-Cr-W-Al-Ti-6%C, 200 ℃, pin; (b) Ni-Cr-W-Al-Ti-6%C, 600 ℃, pin; (c) Ni-Cr-W-Al-Ti-6%MoS2, 200 ℃, pin; (d) Ni-Cr-W-Al-Ti-6% MoS2, 600 ℃, pin

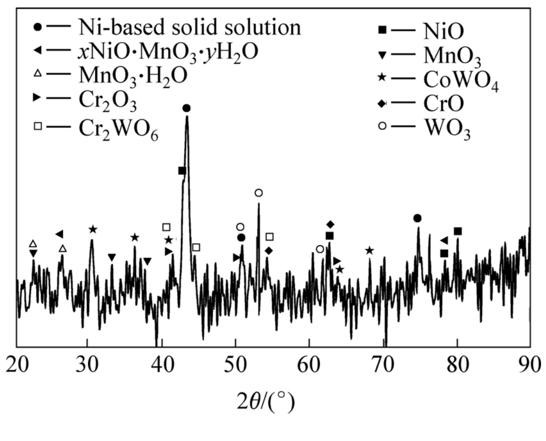

Fig.3 XRD pattern on wear debris of alloy with MoS_2 and reinforcement phase at 600 ℃

prevent the direct contacts between the pair surfaces at one hand, on the other hand they are solid lubricants, and the sulfides in the alloy are solid lubricants too. Thus the friction coefficient is very low.

When rubbing at 200 ℃, the oxidative lubrication does not happen. The high temperature only facilitates oxidation of the lubricative sulfides at the rubbing surfaces, and with the influences of the hard phases, the friction between the pin and disk is very severe and the friction coefficient is high.

4 Conclusions

1) Ni-Cr based self-lubricating alloys with reinforcements and 6% MoS_2 or graphite were prepared by P/M hot pressing. The alloys are mainly composed of Ni solid solution and sulfides eutectic. Carbides are found in the alloys with graphite addition.

2) Owing to the product of the solid solution and carbides, the hardness of the material improves significantly, while the bending strength deteriorates.

3) The nano crystal structured debris formed during the rubbing process at room temperature shows positive effect to tribological properties. At 200 ℃, there shows oxidative and adhesive wear due to the oxidation and high-temperature softening, while the insufficient ability to form the oxidative films results in total poor tribological properties. At 600 ℃, a high-temperature lubricating layer is formed by the alloy oxides and tungstates on the worn surface of the material. The final

result is the reduction of the friction coefficient.

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