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ORIGINAL PAPER

Ni_3Al Matrix Composite with Lubricious Tungstate at High Temperatures

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Abstract Ni_3Al–Ag–BaF_2/CaF_2–W composites were fabricated by the powder metallurgy route, and their tribological properties over a wide temperature range, starting from room temperature up to 800 °C, were investigated. The Ni_3Al matrix composite with 15 wt% BaF_2/CaF_2 exhibited a favorable friction coefficient (range 0.3–0.4) and wear rate (0.2–$6.2 \times 10^{-4} mm^3 N^{-1} m^{-1}$). The formation of $BaWO_4$ and $CaWO_4$ with lubricity on the worn surface due to a tribo-chemical reaction at high temperatures provided excellent lubricating properties. The low friction coefficient over a broad temperature range could be attributed to the synergistic effect of Ag, BaF_2/CaF_2, $BaWO_4$, and $CaWO_4$.

Keywords Ni_3Al · W · Tungstate · Tribology

1 Introduction

A series of self-lubricating composites based on nickel alloys and ceramics have been developed in recent years by plasma spraying or powder metallurgy methods [1–9]. A Ni-based high-temperature self-lubricating composite known as PM 304 has been developed that shows good tribological behavior over a wide range of temperatures (room temperature to 650°C) [6]; however, above 800°C, declines in its mechanical properties reduce its wear resistance. Ceramic matrix self-lubricating composites based on Cr_3C_2, Al_2O_3, Si_3N_4, and ZrO_2–Y_2O_3 also exhibit excellent friction and wear behavior within 800°C and may achieve higher application temperatures [1, 2, 7–9], but their inherent brittleness restricts the manufacture of complex shapes and the reliability of applications. However, intermetallic materials possess excellent high-temperature combination properties [10–13] and may, therefore, be a superior matrix for high-temperature self-lubricating composites.

Several Ni_3Al matrix high-temperature self-lubricating composites have been developed in our laboratory [14–17]. The composites, which consist of a Ni_3Al matrix with Cr or Mo, Ag, and BaF_2/CaF_2 additions, exhibit a low friction coefficient and wear rate over the range of temperatures from room temperature to 800°C. In our previous studies [14–17], we reported that Ag and BaF_2/CaF_2 act as solid lubricants, and that Cr or Mo can act as reinforcements in high-temperature solid lubricants, promoting the strength and also improving tribological performance at high temperatures due to the formation of chromates or molydates.

In the study reported here, the Ni_3Al–Ag–BaF_2/CaF_2–W composite (BaF_2/CaF_2; hereafter referred to as “fluorides”) was selected based on the premise that Ni_3Al intermetallics would act as a favorable high-temperature matrix; silver provided the low friction coefficient at low temperatures; fluorides and tungsten were expected to react with oxygen at high temperatures and create tungstate lubricants on the worn surface. It is well known that tungstate has favorable lubricious property at high temperatures due to low shear strength [18]. Several tungstates have been shown to be as promising solid lubricants, such as $CaWO_4$, $PbWO_4$ and $ZnWO_4$ [18–20]. Furthermore, the addition of tungsten can

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improve mechanical strength of Ni_3Al at elevated temperatures [21]. Thus Ni_3Al–Ag–fluorides–W composites were fabricated by the powder metallurgy route, and their tribological properties from room temperature to 800°C were investigated.

2 Experimental Procedure

Ni_3Al–Ag–BaF_2/CaF_2–W composites were fabricated by the powder metallurgy technique. Table 1 gives the compositions of the sintered samples. WFX denotes the composite, with X representing the percentage mass of fluoride content. The initial powders were commercial BaF_2, CaF_2, Ag, and W powders, together with Ni_3Al powders produced by self-propagating high-temperature synthesis, with an average particle size of 30–70 µm. The fabrication process has been described in detail elsewhere [13].

The Vicker's microindentation hardness of each sample so produced was measured by using an MH-5 Vicker's hardness instrument. Ten tests were conducted and the mean value given. Quasi-static uniaxial compressive tests were performed at room temperature. Each test was repeated three times and the average result reported.

The tribological tests were conducted on an HT-1000 ball-on-disk high-temperature tribometer (made by the Zhong Ke Kai Hua Corp, China). The disk was made from the sintered sample, and the counterpart ball was a commercial Si_3N_4 ceramic ball with a diameter of 6 mm [approx. hardness value (HV) 15 GPa]. The selected experimental temperatures were room temperature and 200, 400, 600, and 800°C. The tribological tests were carried out at an applied load of 10 N, sliding speed of 0.19 m/s, and testing time of 60 min. The cross-section profile of the worn surface was measured using a surface profilometer. The wear volume was determined as $V = AL$, where A and L were the cross-section area and the perimeter of the worn scar, respectively. The wear rate, $W = V/SN$, was calculated as a function of the wear volume divided by the product of sliding distance S and applied load N (units: $mm^3\ N^{-1}\ m^{-1}$). All of the tribological tests were carried out at least three times to guarantee the reproducibility of the experimental results at the same condition, and average results were reported.

The morphology and composition of the worn surfaces at different friction conditions were examined by scanning electron microscopy (SEM; model JSM-5600LV; JEOL, Tokyo, Japan), energy dispersive spectroscopy (EDS; Kevex, Newark, DE), and X-ray diffractometry (XRD; X' Pert-MRD; Philips, Eindhoven, Netherlands).

3 Results and Discussion

The XRD results are given in Fig. 1. No reactants between the Ni_3Al matrix and other additives detected after the hot-sintering process were observed, indicating that the Ni_3Al matrix composite can be employed in a high-temperature environment requiring thermal stability.

The relationship between the mechanical strength of the Ni_3Al matrix composites and the content of fluorides added is shown in Table 1. It can be seen that the microindentation hardness, yield stress, and compressive strength of the composites gradually decreases with increasing fluoride content. WF10 and WF20 exhibit the highest and lowest mechanical properties, respectively.

Figure 2 shows the friction coefficients of the samples over a range of temperatures, from room temperature to 800°C. The friction coefficients of the samples fall within the range of 0.3–0.35 between room temperature and 400°C; at higher temperatures, they increase with increases in the temperature. WF15 had the most favorable friction coefficients among the three samples tested over the wide temperature range.

The evolution in the friction coefficients of the samples with the sliding time at different temperatures is presented in Fig. 3. The friction coefficient is approximately 0.31 up to 400°C; with increasing temperature up to 600°C, it increases to about 0.4, and then falls to 0.36 at 800°C. It is clear that WF15 provides low and stable friction coefficients in the range of 0.3–0.4 from room temperature to 800°C. This result implies that 15 wt% fluorides are the optimal content and that the low friction coefficient of WF15 can be attributed to the balance between strength and lubricity [15, 16].

Figure 4 shows the wear rates of the samples from room temperature to 800°C. The wear rates of the samples clearly increase from room temperature to 400°C, in the range of $0.2–1.8 \times 10^{-4}\ mm^3\ N^{-1}\ m^{-1}$. However, at 600°C, they increase sharply to a peak of about $6 \times 10^{-4}\ mm^3\ N^{-1}\ m^{-1}$. With increasing temperature up to 800°C, the wear rates

Table 1 Compositions and mechanical properties of the sintered Ni_3Al matrix composites

Samples	Compositions (wt%)	Hardness (HV)	Yield stress (MPa)	Compressive strength (MPa)
WF10	Ni_3Al + 12.5% Ag + 15% W + 6.2% BaF_2 + 3.8% CaF_2	315	661	994
WF15	Ni_3Al + 12.5% Ag + 15% W + 9.3% BaF_2 + 5.7% CaF_2	307	617	944
WF20	Ni_3Al + 12.5% Ag + 15% W + 12.4% BaF_2 + 7.6% CaF_2	263	425	596

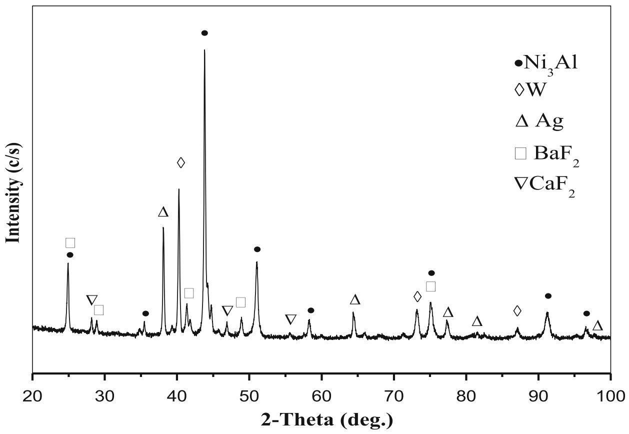


Fig. 1 X-Ray diffractometry spectrum of the sintered sample WF15

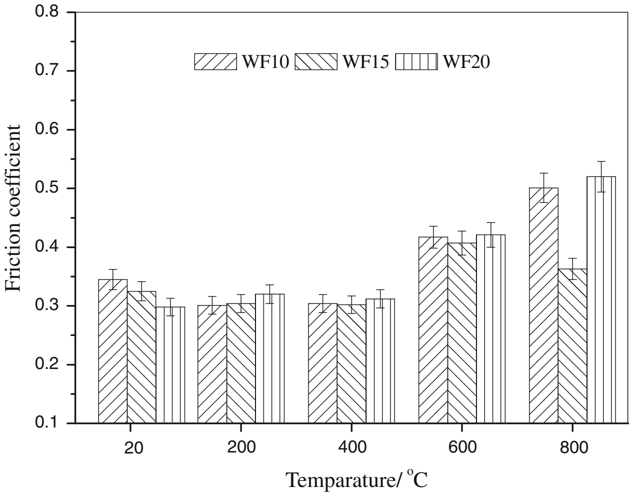


Fig. 2 Variations in the friction coefficient of the sintered samples at different temperatures

decrease in varying degrees, and it is evident that the wear rate depends on the strength of the composites [16].

Based on the above tribological results, WF15 showed the best tribological performance among the three samples. At a wide temperature range, its friction coefficient is in the range of 0.3–0.4, and its wear rate is $0.2–6.2 \times 10^{-4}$ mm^3 N^{-1} m^{-1}. Moreover, at 600°C, it has the highest friction coefficient and wear rate.

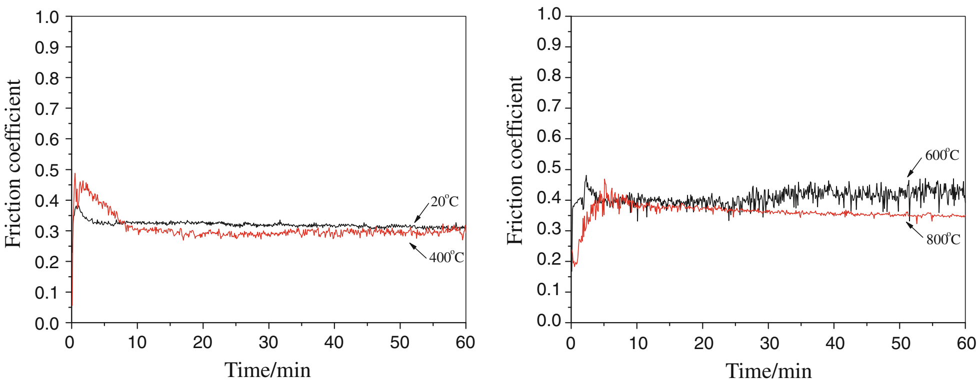
The worn surfaces of WF15 after tests at different temperatures are shown in Fig. 5. Fine grooves and mild delamination are present on the worn tracks below 400°C. At 600°C, a large number of delaminated layers and fine debris are present on the coarse worn track. With increasing temperature up to 800°C, the smooth surface layer acquires some grooves, suggesting the formation of the glaze layer.

Figure 6 presents the XRD results of the worn surfaces of WF15 after tests at different temperatures. No new phases were detected on the worn surfaces at 200 and 400°C, as shown in Fig. 6a, b. However, at 600°C, the peaks of $BaCO_3$ are present on the worn track, as is a little peak for $BaWO_4$. Their occurrence is due to the oxidation of BaF_2 at high temperatures. With increasing temperature to 800°C, the peaks of $BaWO_4$ and $CaWO_4$ become stronger, which suggesting the formation of more tungstates on the worn surface.

The peak values obtained are in good agreement with the JCPDF database PDF #41–1431 ($CaWO_4$) and PDF #43–0646 ($BaWO_4$). Both $CaWO_4$ and $BaWO_4$ have the scheelite structure and belong to the tetragonal crystal system. The lattice parameters are $a = 0.5243$ nm, $b = 0.5243$ nm, and $c = 1.1373$ nm for $CaWO_4$ and $a = 0.5612$ nm, $b = 0.5612$ nm, and $c = 1.2706$ nm for $BaWO_4$. Clearly, both have a high c/a value. In general, the lubricity of a specific solid lubricant is associated with the formation of crystals with a layered atomic structure and weak interplanar bonds [22]. Moreover, the high value of c/a means that the interplanar bonding energy is weak, thereby likely enhancing lubricity. Therefore, similar to the graphite laminated structure, these tungstates should exhibit favorable lubricity.

The formation of tungstate in situ on a worn surface at high temperatures has been reported in several papers [19, 20, 23]. Prasad et al. reported that at 500°C, the WS_2–ZnO nanocomposite exhibited a low steady friction coefficient of 0.22, which was controlled by the formation of a

Fig. 3 Variations in friction coefficients of WF15 with sliding time over a range of temperatures from room temperature to 800°C



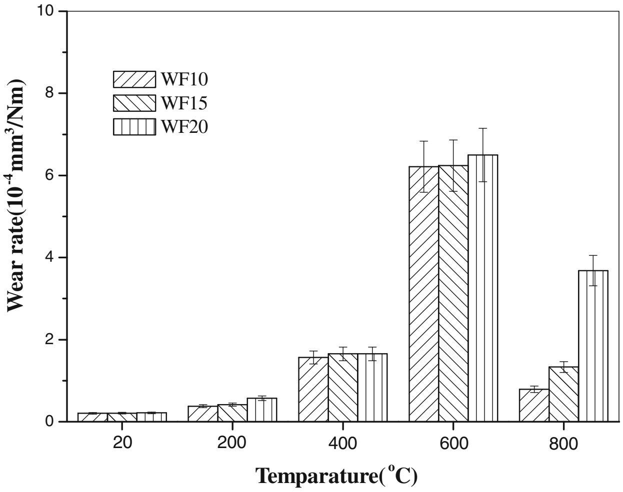


Fig. 4 Variations in wear rates of the sintered samples at different temperatures

tribo-chemical compound $ZnWO_4$ [20]. The high-temperature self-lubricating behavior of the Ni–WC–PbO cermet was attributed to the formation of $PbWO_4$ on the friction track at 600°C [19]. On the basis of previously reported results, it can be inferred that tungstate is prone to form during the friction process at an elevated temperature. Therefore, the formation of $BaWO_4$ and $CaWO_4$ is possible given the higher temperature rise at the instantaneous contacting surface in the rubbing process at high temperatures.

It is well known that the soft metal Ag acts as a solid lubricant at temperatures below 500°C, while fluorides have a good reduced friction above 450°C [5, 6]. As shown in Figs. 2 and 3, the sintered samples exhibited a low friction coefficient of about 0.3–0.35 between room temperature and 400°C due to the lubricious property of Ag. At 600°C, a high friction coefficient was obtained (see Figs. 2 and 3) due to the formation of $BaCO_3$ at high temperatures, which reduces the amount of BaF_2 and accounts for the increase in the friction coefficient because $BaCO_3$ is not a confirmed solid lubricant. With increasing temperature to 800°C, the friction coefficient once again decreases. As expected, barium and calcium tungstates with lubricious properties contribute to the low friction coefficient at 800°C. Therefore, we attribute the low friction coefficient over a wide temperature range from room temperature to 800°C to the synergistic effect of Ag, BaF_2/CaF_2, $BaWO_4$, and $CaWO_4$.

The wear rate of the samples increased with increasing temperature from room temperature to 400 °C, as shown in Fig. 4. This can be attributed to the decrease in strength with increasing temperature. However, the wear rate dramatically increased at 600°C, due to the formation of $BaCO_3$. The formation of $BaCO_3$ can degrade the lubricity of the samples, as shown in Fig. 5d, so that a coarse surface

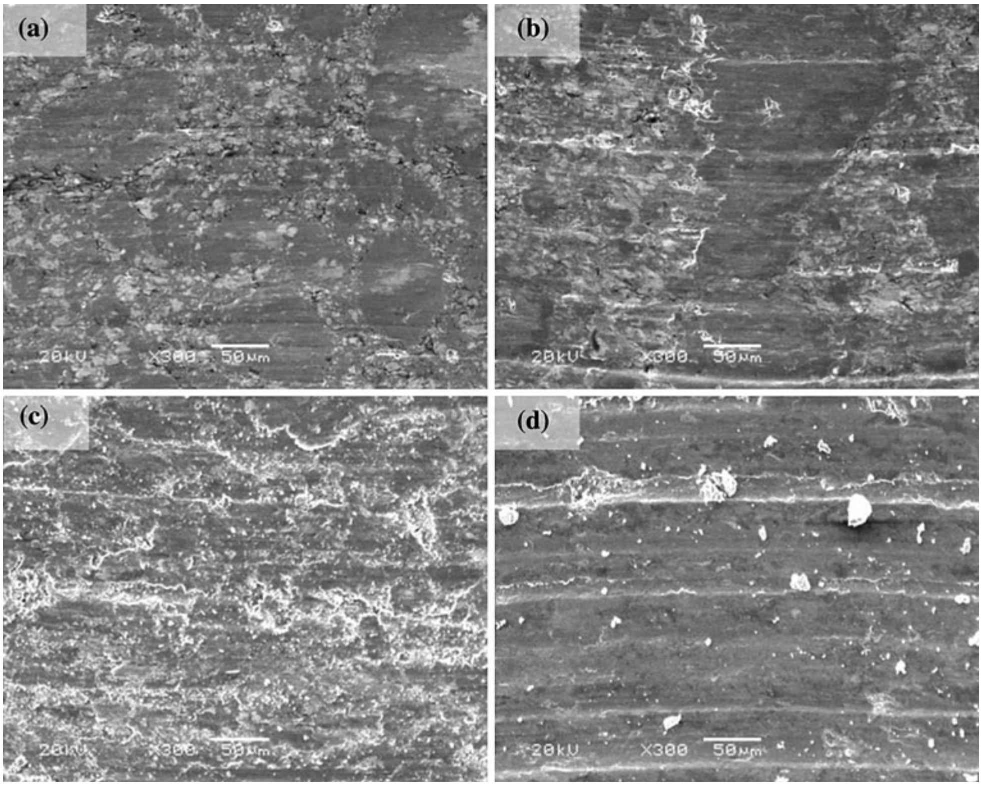


Fig. 5 Worn surfaces of WF15 after tests at different temperatures: **a** room temperature, **b** 400°C, **c** 600°C, **d** 800°C

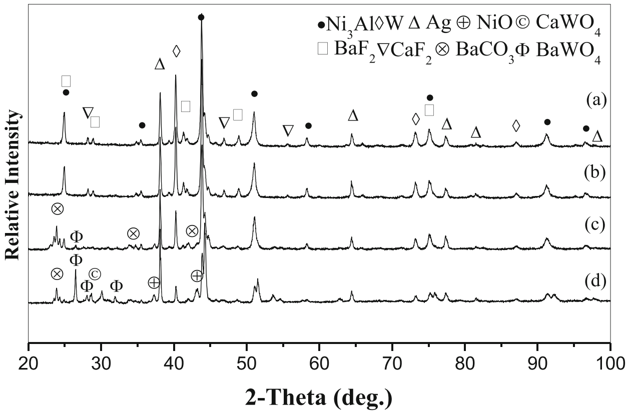


Fig. 6 X-ray diffractometry patterns of the worn surfaces of WF15 after tests at different temperatures: **a** 200°C, **b** 400°C, **c** 600°C, **d** 800°C

develops on the worn track and can reduce the strength of the samples. When the temperature increases to 800°C, the development of the glaze layer, which mainly consisted of $BaWO_4$ and $CaWO_4$, plays a significant role in the improvement of wear performance (Figs. 5e, 6).

4 Conclusions

Ni_3Al–Ag–BaF_2/CaF_2–W composites were fabricated by powder metallurgy route. Over a wide temperature range, the Ni_3Al matrix composite with 15 wt% BaF_2/CaF_2 exhibited favorable tribological properties. Its friction coefficient was in the range of 0.3–0.4, and its wear rate was $0.2–6.2 \times 10^{-4}$ mm^3 N^{-1} m^{-1}.

The low friction coefficient over a broad temperature range between room temperature and 800°C can be attributed to the synergistic effect of Ag, BaF_2/CaF_2, $BaWO_4$ and $CaWO_4$.

At a high temperature of 800°C, the glaze layer mainly consisting of $BaWO_4$ and $CaWO_4$ played a significant role in the improvement of tribological behavior. Moreover, the formation of $BaCO_3$ led to high friction coefficient and wear rate at 600°C.

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