Influence of Silver Contents on the Tribological Properties of Ni-Based Self-Lubricating Coatings by Atmospheric Plasma Spraying

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Abstract The NiCrAlY–Mo–Ag composite coatings were prepared by atmospheric plasma spraying. The tribological properties of the composite coatings were investigated from 25 to 900 °C in details. The tribo-layer formed on the worn surface of the composite coatings and influenced the tribological properties at different temperatures. The addition of silver could effectively decrease the friction coefficient and wear rate of the coatings at the wide range of temperature. The rubbing process could form the nickel molybdate and promote the formation of silver molybdate within the worn surfaces at high temperature. The synergistic lubricating effects of nickel molybdate and silver molybdate are attributed to the improvement of the tribological properties of coatings at high temperature.

KEY WORDS: Plasma spraying; Tribological properties; Synergistic lubricating; High temperature

1 Introduction

MCrAlY ($M = \text{Co}$ or/and Ni) coatings prepared by thermal spraying technique have been diffusely used in the industries of nuclear power, aerospace and automotive owing to the excellent high-temperature corrosion and oxidation resistance and it could withstand the high thermal and mechanical loads due to possessing excellent high-temperature self-lubricating properties [1–6]. Graphite and molybdenum disulfide usually acted as solid lubricants

could improve the tribological properties of the composites [7–15]. But this kind of solid lubricants would be oxidized or decomposed above 500 °C, and therefore lose their lubricating effects [16]. Silver could decrease the wear rate and friction coefficient of the composites and provide the excellent lubricating effect below 400 °C due to a low shear strength and large diffusion coefficient on the worn surfaces during the sliding process [16–21]. An et al. [19] prepared the NiMoAl–Cr₃C₂–Ag composite coatings by high-velocity oxy-fuel (HVOF) and demonstrated that the incorporation of silver could efficiently improve the tribological properties of the composite coatings. Our previous studies showed that increasing the silver contents could decrease the wear rate and friction coefficient of the composites by power metallurgical sintered [16]. In recent years, due to excellent lubrication performance in wide temperature range, Ag–Mo dual-lubricant has been investigated by several researchers [22–25]. Chen et al. fabricated the NiCrAlY–Ag–Mo composite coatings by atmospheric plasma spraying (APS), which possesses excellent tribological properties at the wide range of temperature [25], but there are few studies on the influence of

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the silver contents on the mechanical properties and tribological properties of the coatings.

In the present work, we investigated the microstructure, tribological and mechanical properties of NiCrAlY–Ag–Mo composite coatings with different mass fractions of silver prepared by APS at a wide temperature range. The tribological properties of composite coatings were researched from room temperature (RT) to 900 °C. In the meantime, the silver molybdate and nickel molybdate tribo-chemical reaction films formed on worn surface and their influences on the tribological properties of composite coatings were discussed.

2 Experimental

2.1 Preparation of Composite Coatings

The NiCrAlY–Mo–Ag composite coatings with different silver contents were fabricated by APS. The NiAl powder was applied as bond coat. Commercially, available feedstock powders of Ni₂₂Cr₁₀Al_{11.0}Y, Mo and NiAl were gained from Sulzer Metco. The powder of Ag was obtained from Beijing Research Institute of Mining and Metallurgy. The Inconel 718 alloys acted as the substrate and were cleaned by ultrasonic cleaner with acetone after sand-blasted. The compositions of each composite coating are listed in Table 1. The main spraying parameters employed were: H₂ flow rate, 5 L/min; Ar flow rate, 40 L/min; power feed rate, 42 g/min; voltage, 55 V; current, 500 A.

2.2 Characterization

The microhardness was measured by using a MH-5-VM microhardness tester with a normal load of 300 g and a dwell time of 5 s. The measurement was at least ten times on each sample. The adhesive strength of the composite coating was measured in conformity to the standard of ASTM C633. The specimen diameter was 25.4 mm, and the tensile rate was 0.5 mm/min. Scanning electron microscopy (SEM) was used to observe the microstructures of composite coatings. The X-ray diffraction (XRD) was used to determine the phase composition and structures of

composite coatings. The micro-Raman was used to research the phase compositions of worn surfaces of composite coatings. The processes of friction and wear tests have been described in detail elsewhere [6].

3 Results and Discussion

3.1 Microstructure of the Coatings

Figure 1 shows the morphologies of feedstock powders of NiCrAlY, Ag, Mo and NiAl. It can be clearly seen that all feedstock powders have the similar size and very excellent spherical shape. The feedstock powders are mixed uniformly and insure the good flow ability, which is useful to the stability of powder feed rate [6, 25].

The XRD patterns of composite coatings with different mass fractions of silver are presented in Fig. 2. It is obvious that the components of composite coatings and feedstock powders have an excellent accordance, and the Ni₃Al (JCPDS file No. 09-0097) phase is the main phase in all coatings. The diffraction peaks of the single-phase Mo (JCPDS file No. 42-1120) and Ag (JCPDS file No. 04-0783) exist in composite coatings, which indicates that the Mo and Ag cannot be alloyed in NiCrAlY during thermal spray process. The diffraction peaks of Y₂O₃ (JCPDS file No. 43-1036) are identified in all composite coatings. The Y₂O₃ phase is an oxide dispersion strengthening phase which can improve the strength of the composite coatings [6].

Figure 3 shows the microstructures of polished cross section of composite coatings. It has the NiAl bond coat between the substrate and coating, in addition, they adhere well. It can be observed in Fig. 3a that the NiCrAlY coating contains many cracks and pores, which shows the existence of typical lamellar structure. We can find from Fig. 3b that the NiCrAlY–Mo–Ag composite coating mainly consists of white Ag phase, gray Mo phase and dark gray NiCrAlY phase. These components are all metallic in nature which is disadvantageous to the adhesive strength of composite coatings [25]. It can be obviously seen that the three components distribute equably and combine with each other tightly without any evident cracks at the interface of any two phases.

3.2 Mechanical Properties of the Coatings

Table 2 shows the microhardness of the composite coatings with different mass fractions of silver. The microhardness of NMA0 coating is higher than that of NMA coating. Addition of Mo could improve the microhardness of the composite coatings. Nevertheless, addition of Ag deteriorates the microhardness of composite coatings.

Table 1 Composition of the coatings

Composite coatings	NiCrAlY (wt%)	Mo (wt%)	Ag (wt%)
NMA	100	0	0
NMA0	90	10	0
NMA1	80	10	10
NMA2	75	10	15
NMA3	70	10	20

Fig. 1 SEM images of NiCrAlY **a**, Mo **b**, Ag **c**, NiAl **d**

Fig. 2 XRD patterns of the coatings

This may be because that the silver is a kind of soft metal and could decrease the microhardness of composite coatings [16].

The adhesive strength is an important performance for plasma-sprayed coatings. In order to enhance the adhesive strength of composite coatings, the NiAl is used to the bond coating. It can be obviously seen that the NiAl bond coating adheres well with substrate and coating (Fig. 3) which could effectively enhance the adhesive strength of coatings. Figure 4 displays the adhesive strength of composite coatings with different mass fractions of silver. And with increasing Ag content, the adhesive strength of composite coatings is deteriorated. For the plasma-sprayed coatings, the adhesive strength between the substrate and bond coating often exceeds the adhesion of the coating itself and the adhesion between the epoxy and coating [26]. The detachments occur in the interior of NMA0, NMA1, NMA2 and NMA3 coatings, while for the NMA coating, the detachment occurs at the interface between the bond coating and substrate. It is because that the NiCrAlY, Mo and Ag are all metallic in nature in the composite coatings, which could obviously deteriorate the adhesive strength of composite coatings [25].

Fig. 3 Micrographs of polished cross section of NMA **a**, NMA1 **b**, NMA3 **c** coatings

Table 2 Vickers hardness of the composite coatings

Composite coatings	NMA	NMA0	NMA1	NMA2	NMA3
Vickers hardness (HV)	329.8 ± 31.6	342.5 ± 34.5	297.4 ± 30.2	273.9 ± 28.6	241.1 ± 23.9

Fig. 4 Adhesive strength of the composite coatings

3.3 Tribological Properties of Composite Coatings

Figure 5 presents the friction coefficients of composite coatings with different mass fractions of silver from RT to 900 °C. The NMA coating shows higher friction coefficient than NMA0, NMA1, NMA2 and NMA3 composite coatings at all test temperature except RT. The friction coefficient of NMA1 coating is higher than those of NMA and NMA0 coatings. It may be because that the melt of silver during the thermal spray process makes the residual silver not enough to play the lubricating role. The friction coefficients of all composite coatings reduce continuously with increasing temperature except NMA2 and NMA3 composite coatings at 500 °C. At RT and 300 °C, the NMA3 exhibits the lowest friction coefficient. Nevertheless, the NMA2 and NMA3 coatings exhibit similar friction

Fig. 5 Friction coefficients of the composite coatings at different test temperatures

coefficient as NMA coating at 500 °C. This may be because that the silver will be softened and loses its lubricating effects at 500 °C [19, 22]. At 700 and 900 °C, the friction coefficients of NMA1, NMA2 and NMA3 composite coatings are lower than those of NMA and NMA0 coatings. It illustrates that the addition of silver could obviously decrease the friction coefficients of composite coatings at the wide range of temperature. It is seen distinctly that the NMA3 exhibits lower friction coefficient than any other composite coatings at the wide range of temperature.

Figure 6 shows the wear rates of composite coatings with different mass fractions of silver from RT to 900 °C. The wear rates of all coatings obviously decrease from RT

to 300 °C. The wear rates of NMA1, NMA2 and NMA3 coatings increase obviously at 900 °C. It is probably because that the worn surfaces of coatings have severe plastic deformation at 900 °C [6]. The NMA1, NMA2 and NMA3 composite coatings show lower wear rate than those of NMA and NMA0 coatings at all test temperatures. The NMA3 composite coating presents the lowest wear rate at RT and 300 °C. This implies that the addition of silver could obviously improve the tribological properties of composite coatings at low temperature.

The SEM micrographs of worn surfaces of composite coatings at different test temperatures are presented in Fig. 7. At RT, for the NMA0 coating (Fig. 7a), the worn surface shows a severe brittle fracture compared with those in NMA1 (Fig. 7e) and NMA3 (Fig. 7i), corresponding to the higher friction coefficient (Fig. 5) and wear rate (Fig. 6). Therefore, the wear mechanism is dominated by abrasive wear. When adding the silver, the worn surface of NMA3 is covered with fine detachments. On account of the smoothest worn surface at RT, the friction coefficient (Fig. 5) and wear rate (Fig. 6) of the NMA3 composite coating are the lowest. At 300 °C, the worn surfaces of all coatings become smoother than those at RT. So the friction coefficient (Fig. 5) and wear rate (Fig. 6) of all coatings are lower than those at RT. At 500 °C, the worn surfaces of all coatings show continuous glaze film with some detachment smears. The worn surfaces of NMA1 (Fig. 7g) and NMA3 (Fig. 7k) coatings show the severe brittle fracture and surface deformation than those at 300 °C. So the friction coefficient (Fig. 5) and wear rate (Fig. 6) of NMA1 and NMA3 are increased from 300 to 500 °C. At 900 °C, the worn surfaces of NMA1 (Fig. 7h) and NMA3 (Fig. 7l) composite coatings form some high-temperature lubricating films. The lubricating films are composed of silver molybdate, nickel molybdate and NiO shown in Figs. 8 and

10. The worn surface of NMA0 coating (Fig. 7d) has the obvious delamination. The wear mechanism of coating is characterized by microfractures.

Figure 8 shows the XRD patterns of worn surfaces of NMA3 composite coatings at different temperatures. It can be obviously seen that the diffraction peaks of composite coating after friction test at 300 °C are nearly the same as that at RT. It clearly illustrates that the components of the composite coating have no obvious change between at RT and 300 °C. Interestingly, the new peaks of silver molybdate can be detected when test runs at 700 °C. At the same time, the diffraction peaks of Mo (JCPDS file No. 42-1120) disappear and Ag (JCPDS file No. 04-0783) peaks weaken. Sliding test after 700 °C, molybdenum and silver can react and form silver molybdate which could effectively decrease the friction coefficient and wear rate of composite coatings at high temperature [16]. Except as the silver molybdate, the diffraction peaks of NiO (JCPDS file No. 47-1049), Cr_2O_3 (JCPDS file No. 04-0787) and CrO_2 (JCPDS file No. 09-0332) appear on the worn surface of coating. It has been approved that the CrO_2 , Cr_2O_3 and NiO could also enhance tribological properties of composite coatings at high temperature [6, 14, 16, 25]. So the composite coating has lower friction coefficient (Fig. 5) and wear rate (Fig. 6). At 900 °C, the Ag_2O (JCPDS file No. 19-1155) peaks appear on the worn surface of composite coating. Although the CrO_2 , Cr_2O_3 and NiO are well lubricant phases at high temperature and can improve the tribological properties of composite coatings, the worn surface has the severe plastic deformation (Fig. 7), which increases wear rate (Fig. 6) of composite coating at 900 °C [6].

In order to further determine the tribo-chemical changes of composite coatings at high temperature, the micro-Raman spectra of NMA1 and NMA3 composite coatings are presented in Figs. 9 and 10. For the NMA1 coating, it can be clearly seen that the silver molybdate and nickel molybdate peaks were detected inside the wear track area after 700 and 900 °C, which are ascribed to the Ag_2MoO_4 , $\text{Ag}_2\text{Mo}_4\text{O}_{13}$, $\text{Ag}_2\text{Mo}_2\text{O}_7$ and NiMoO_4 peaks. In contrast, there are no silver molybdate and nickel molybdate peaks outside the worn surface (Fig. 9). For the NMA3 coating, the micro-Raman spectra obtained within the worn surface are similar to the NMA1 coating at 700 °C. However, it has the Ag_2MoO_4 peak outside the worn surface (Fig. 10a). At 900 °C, the micro-Raman spectra obtained on the worn surface are similar to that obtained outside the worn surface, which consist of Ag_2MoO_4 and nickel molybdate peaks. It can be clearly understood that the rubbing process could form the nickel molybdate and thus promote the formation of the silver molybdate on the worn surface at high temperature. When adding the silver, the Ag_2MoO_4 is determined outside the worn surface of composite coatings,

Fig. 6 Wear rates of the composite coatings at different test temperatures

Fig. 7 SEM images of worn surfaces of composite coatings: **a–d** NMA0 coating, **e–h** NMA1 coating, **i–l** NMA3 coating

Fig. 8 XRD patterns of worn surfaces of NMA3 composite coating at different temperatures: **a** 25 °C, **b** 300 °C, **c** 500 °C, **d** 700 °C, **e** 900 °C

which could effectively improve the tribological properties of composite coatings and has the better lubricating performance than $\text{Ag}_2\text{Mo}_4\text{O}_{13}$ and $\text{Ag}_2\text{Mo}_2\text{O}_7$ at high temperature [14, 16]. So the NMA3 coating has the better tribological properties than NMA1 at high temperature.

The structural changes on the worn surface of NMA3 composite coating at different temperatures are evaluated by micro-Raman spectra, as shown in Fig. 11. Raman spectra show the lubricating action and mechanism at different temperatures. From RT to 500 °C, the Ag_2MoO_4 peak was detected on the rubbing surface. The Ag_2MoO_4 could act as a thermal chemically stable solid lubricant at moderate and high temperatures [27]. So the NMA3 coating possesses the better tribological properties than NMA1 coating at low temperature. While at 700 °C, the peaks of Ag_2MoO_4 , $\text{Ag}_2\text{Mo}_4\text{O}_{13}$, $\text{Ag}_2\text{Mo}_2\text{O}_7$ and NiMoO_4 appear on the worn surface. It can be clearly illustrated that the tribochemical reaction occur on the worn surface and form the silver molybdate and nickel molybdate lubricating composite layer during the sliding process at high temperature.

Fig. 9 Micro-Raman spectra of worn surfaces of NMA1 composite coatings tested at **a** 700 °C, **b** 900 °C

Fig. 10 Micro-Raman spectra of worn surfaces of NMA3 composite coatings tested at **a** 700 °C, **b** 900 °C

Fig. 11 Micro-Raman spectra of within the wear track of NMA3 composite coatings tested at different temperatures

At 900 °C, the peaks of $\text{Ag}_2\text{Mo}_4\text{O}_{13}$ and $\text{Ag}_2\text{Mo}_2\text{O}_7$ disappear and the intensity of the Ag_2MoO_4 phase increases substantially.

The silver molybdate and nickel molybdate tribochemical reaction films were reproduced during rubbing test at high temperature and can lower friction coefficients and wear rates since the silver molybdate and nickel molybdate can be acted as a lubricating phase and then can effectively improve the tribological properties of composite coatings [27, 28]. The lubricating films could effectively reduce the direct contact between ball and disk and further improve the tribological properties of composite coatings [16].

4 Conclusions

1. The composite coatings are composed of Ni_3Al , NiAl , Ni and Y_2O_3 phases. The Y_2O_3 phase is the oxide dispersion strengthening phase which can improve the strength of the composite coatings.
2. The addition of silver can effectively improve the tribological properties of composite coatings at a wide range of temperature.

3. The rubbing process could form the nickel molybdate and promote the formation of the silver molybdate on the worn surface at high temperature.
4. The silver molybdate and nickel molybdate tribochemical reaction films could effectively improve the tribological properties of composite coatings at high temperature.

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