Preparation and characterization of atmospheric plasma-sprayed NiCr/Cr\textsubscript{3}C\textsubscript{2}–BaF\textsubscript{2}·CaF\textsubscript{2} composite coating

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A B S T R A C T

NiCr alloy-coated BaF\textsubscript{2}·CaF\textsubscript{2} eutectic and Cr\textsubscript{3}C\textsubscript{2} powders were respectively prepared by both pressurized hydrogen reduction and solid state alloying technology. Using this NiCr/Cr\textsubscript{3}C\textsubscript{2}–BaF\textsubscript{2}·CaF\textsubscript{2} composite powder, a derived coating was produced by atmospheric plasma spray (APS) technology. Microstructures and phase compositions of the powders, as well as the deposited coating, were analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The friction and wear behavior of the coatings from ambient temperature to 800 °C was evaluated using a ball-on-disk tribometer. The results show that the NiCr/Cr\textsubscript{3}C\textsubscript{2}–BaF\textsubscript{2}·CaF\textsubscript{2} composite coating exhibited low porosity, high microhardness and high cohesive strength, which result in good friction reduction and excellent anti-wear ability at elevated temperatures up to 800 °C. The friction coefficient of NiCr/Cr\textsubscript{3}C\textsubscript{2}–BaF\textsubscript{2}·CaF\textsubscript{2} coating decreases with increasing temperature. The wear rates of both coating and couple balls are significantly lower at temperatures above 500 °C than those tested at room temperature. From the investigation of worn surfaces, it was concluded that brittle fracture and delamination were the dominant wear mechanisms of the coatings at low temperature. A transition stage from brittle to plastic state with decreased shear strength was observed for BaF\textsubscript{2}·CaF\textsubscript{2} eutectic at high temperatures, which resulted in the formation of a continuous lubricating layer in the wear track above 500 °C. The excellent mechanical properties of the coating were partially attributed to the protection of NiCr layer of the composite powders which decreased the oxidation, decarburization and ablation of Cr\textsubscript{3}C\textsubscript{2}–BaF\textsubscript{2}·CaF\textsubscript{2} during spraying.

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1. Introduction

Tribological components working at high temperatures and in aggressive environments are greatly required in advanced gas turbines, energy processing and power generation industries. To meet these application expectations, coatings with self-lubrication properties, exceptional high-temperature wear and oxidation resistance properties are a necessity [1]. Thermally sprayed Cr\textsubscript{3}C\textsubscript{2}–NiCr coating is promising because of its very high hardness and oxidation resistance behavior up to 800 °C [2–7]. However, the Cr\textsubscript{3}C\textsubscript{2}–NiCr coating exhibits significantly high wear rates to the counter materials during long sliding process due to its high sliding friction coefficient, which significantly limits its application on high speed rotation devices. In order to reduce the friction coefficient of wear-resistant composite coatings, soft noble metals (Au, Ag, etc), inorganic fluorides (LiF\textsubscript{2}, CaF\textsubscript{2}, etc) and some metal oxides (NiO, MoO\textsubscript{3}, Cr\textsubscript{2}O\textsubscript{3}, etc) have been employed as solid lubricants [8–12]. CaF\textsubscript{2}/BaF\textsubscript{2} eutectic has also been used as a solid lubricant to improve the tribological properties of Cr\textsubscript{3}C\textsubscript{2}–NiCr coating because it is stable with low shear strength properties at elevated temperatures [13–15].

Some problems still exist during the plasma spray process of mechanical mixed–sintered powders. It was found that decarburization and oxidation of carbide can not be avoided during flighting in flame and depositing of spray droplets from impact on surface to cooling down, which have adverse effects on the microstructures, hardness and tribological properties of carbide coatings [16–20]. In our laboratory, the chemical-coated composite powders were made for reducing the occurrence of ablation and oxidation during plasma spray to a certain extent. Pressurized hydrogen reduction technology has been used for large scale development. Production of the powder by this method is easy to implement to obtain well controlled powder composition, and proportions in the group are straightforward to adjust.

Based on the above considerations, BaF\textsubscript{2}·CaF\textsubscript{2} eutectic and Cr\textsubscript{3}C\textsubscript{2} powders which were coated with NiCr alloy were prepared by the hydrogen reduction hydrothermal process combined with a solid state alloying method to overcome the problems occurred in the plasma spray process. Then the processed NiCr/Cr\textsubscript{3}C\textsubscript{2} and NiCr/BaF\textsubscript{2}·CaF\textsubscript{2}
particles were used as hard wear-resistant phase and high-temperature solid lubricant to prepare NiCr/Cr3C2–BaF2–CaF2 self-lubrication wear-resistant coating by plasma spray.

2. Experimental

Fluoride eutectic powder was prepared by mixing reagent grade BaF2 and CaF2 powders in the eutectic ratio 62:38 in mass, then melted in a graphite crucible at 1100 °C in a hydrogen atmosphere for 2 h. The cooled eutectic was crushed and milled into an average particle size range from 44 to 74 μm.

Nickel-coated Cr3C2 powders and BaF2–CaF2 eutectic powders were prepared by pressurized hydrogen reduction in a 10L autoclave with magnetic stirring apparatus, respectively. Chemically pure nickel sulfate, ammonium sulfate and ammonia were mixed proportionally, and then put into autoclave with Cr3C2 (or BaF2–CaF2 eutectic) particles and activator. The autoclave was then sealed, temperature charged and hydrogen pressurized for complete reaction. The basic reactions of this process are shown below, which in essence is hydrogen reduction at high pressure with Cr3C2 (or BaF2–CaF2 eutectic) particles as cores:

\[
\left[ \text{Ni}(\text{NH}_4)_2\text{SO}_4 + \text{H}_2 + \text{Cr}_3\text{C}_2 \text{ surfactant} \right] \rightarrow \text{Ni}/\text{Cr}_3\text{C}_2 + (\text{NH}_4)_2\text{SO}_4 + (n-2)\text{NH}_3 (n \geq 2) \\
\left[ \text{Ni}(\text{NH}_4)_2\text{SO}_4 + \text{H}_2 + \text{eutectic surfactant} \right] \rightarrow \text{Ni}/\text{eutectic} + (\text{NH}_4)_2\text{SO}_4 + (n-2)\text{NH}_3 (n \geq 2).
\]

Chromizing process of nickel-coated Cr3C2 powders and BaF2–CaF2 eutectic powders were carried out in a tube furnace in an inert argon atmosphere at 950 °C for 4 h by using solid state alloying technology.

The sprayed coatings were deposited on low carbon steel substrates (40 mm × 30 mm × 3 mm) by APS-2000 K plasma spray system. The spray power was 30–40 kW, spraying distance was 110 mm, with a powder feed rate of 30 g–40 g/min. Before being coated, the substrate was blast cleaned with coarse Al2O3 particles and plasma-sprayed with a NiAl bond coat about 0.1 mm thick. The NiCr/Cr3C2–BaF2–CaF2 coatings were then applied at a thickness of no less than 0.4 mm.

Microstructural characterization of the as-sprayed coating was observed using FEI Quanta 200 FEI scanning electron microscope (SEM), equipped with energy dispersive X-ray analysis system (EDX). For SEM observations, plasma-sprayed specimens were carefully sectioned using an abrasive wheel flooded with water. The cross-sectioned samples were grounded and then polished using a special metallographic procedure. The constituents of the powder and coating were characterized by X-ray diffraction (XRD) in a Philips X’Pert Pro diffractometer using filtered CuKα radiation (λ = 0.1541 nm) at 40 kW, 30 mA.

The carbon and oxygen contents in both the feedstock powder and as-sprayed coating were analyzed using Leco carbon/sulphur determinator (Model CS-344) and nitrogen/oxygen determinator (ModelTC--136), respectively. The coating for the carbon and oxygen analysis was detached from substrate after spraying. A HX-1000TM Vickers hardness tester with 1.96 N test load and a dwell time of 15 s on polished cross-sections was used to test the coating’s microhardness. To evaluate coating’s tensile strength, a commercial WDW-100E microcomputer controlled universal material testing machine was used at a cross head speed of 1 mm/min. The sample size is Ø25 mm × 5 mm.

The friction and wear tests were carried out using an HT-1000 ball-on-disk high-temperature tribometer as shown in Fig. 1, consisting of a stationary ball and rotating disk assembled in the test housing surrounded by an electric resistance furnace. The disk was made of the plasma spray coatings of size of 18.5 mm × 18.5 mm × 3.9 mm, while the counterpart ball, diameter 6 mm, was made of Si3N4 ceramic. The specimen size is Ø25 mm × 5 mm. The sample size is Ø25 mm × 5 mm. The cross head speed of 1 mm/min. The load of 9.8 N and sliding speed of 0.188 m/s, for duration of 20 min. The friction torque generated between the contacting ball and disc was measured continuously using a strain-gauge transducer during the test. The friction coefficient was calculated from the measured friction torque and the applied normal load. At the end of the test, the specimens were cooled back down to room temperature. The wear volumes of coatings were measured using the Rank Taylor Hobson Talysurf 5P-120 system. The wear rates of specimens were calculated as \( w = \frac{V}{S} \), where w is the wear volume in mm², S is the normal load in Newton, and V is the total sliding distance in meter. Repeat tests were performed for each frictional pair and the averaged results of the three repeat tests are reported in this article. The surface morphologies of the coatings before and after wear testing were observed by SEM with EDX.

3. Results and discussion

3.1. Characteristics of powder and coating

The feedstock powder consists of a high chrome nickel alloy matrix, Cr3C2 reinforced phase and BaF2–CaF2 eutectic solid lubricant. The nickel alloy, 80% Ni–20% Cr, offers excellent high-temperature oxidation/corrosion resistance and mechanical strength. The high-
temperature strength is further enhanced by chromium carbide particles, which functions as a hardener to enhance the anti-wear performance of the coating. BaF₂·CaF₂ eutectic functions as a solid lubricant. Table 1 shows the nominal composition and some properties of the feedstock powder. It can be seen that the powder has excellent flowability and apparent density, which influences the spraying process and coating quality. Excellent powder flowability can guarantee uniform powder feeding in the spraying process to avoid nozzle clogging. High apparent density of powder can ensure the powder to feed into flame center to maintain well melting characteristics.

Fig. 2(a) presents the typical morphology of feedstock powders, it shows very fine and uniform particles, with a size range from 38 to 90 μm. The powder is clearly seen to be irregular in shape and possesses sharp edges. From Fig. 2(b) and Fig. 2(c), it can be seen that BaF₂·CaF₂ eutectic and Cr₃C₂ particles were dense coated with NiCr layer. Electron microscope measurements show that the protective layer thickness of NiCr is about 3–5 μm. EDX examinations show the dark grains are primarily CaF₂ and the white matrix is mainly BaF₂. This indicates that the CaF₂ precipitates as grains in a matrix of BaF₂ on cooling of the melt, which is the remarkable characteristic of the BaF₂·CaF₂ eutectic [21].

In the spraying process, NiCr was in a melt state, covering the surface of the core particles, which can effectively isolate its contact with O₂. Compared to core particles directly exposed to the atmospheric environment, oxidation and decomposition have fewer opportunities, which can significantly reduce the decarbonization and oxidation of carbide, as well as the ablation of fluoride eutectic, to ensure the integrality of all designed compositions. These often reflect on the variation of carbon and oxygen content between feedstock powder and deposited coating. Table 2 shows the carbon and oxygen contents in both the deposited coating and the original feedstock powders. It can be seen that the carbon content in the deposited coating was lower compared with that in feedstock powders. This implies that the decarburization still occurred during in-flight particles and the deposition process. The main mechanism for the carbon loss of in-flight particles is the oxidation of the carbon dissolved in the matrix and carbides in the particle. However, compared with the change rate of carbon and oxygen in thermal spray Cr₃C₂–NiCr coatings in other literature [16,22], this result is equivalent to HVOF process but lower than that in other plasma spray process. This result indicates that the dense coated NiCr layer plays an important role in plasma spraying process and the feedstock powder preparation method will be of significant influence on the carbon loss of Cr₃C₂ carbide during plasma spraying.

Results of XRD analysis, as shown in Fig. 3, indicate that the major constitutional phases of the plasma-sprayed composite coatings are nearly the same as in the precursor ceramic powder mixtures. This demonstrated that no significant decomposition and oxidation of materials occurred during the plasma spray and re-solidification process. From XRD analysis of feedstock-powder in Fig. 3(a), it can be seen that in feedstock powders there are no other

<table>
<thead>
<tr>
<th>NiCr (wt.%)</th>
<th>Cr₃C₂ (wt.%)</th>
<th>BaF₂·CaF₂ (wt.%)</th>
<th>Apparent density (g/cm³)</th>
<th>Flowability (s/50 g)</th>
<th>Shape</th>
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<tr>
<td>20–26</td>
<td>64–70</td>
<td>10</td>
<td>2.377</td>
<td>33</td>
<td>Angular</td>
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impurities. From Fig. 3(b), it can be found that compared with feedstock powder, only a small amount of oxide (Cr$_2$O$_3$ and NiO) peaks appear, and no obvious Cr$_7$C$_3$ and Cr$_{23}$C$_6$ peaks are found, which indicates that small amount decarburization and oxidation occur due to the protection of NiCr layer. XRD analysis is in reasonable agreement with the former carbon and oxygen content analyses.

The typical micro-structural features of as-sprayed NiCr/Cr$_3$C$_2$–BaF$_2$•CaF$_2$ coating are shown in Fig. 4. From Fig. 4(a), the substrate, NiAl bonding layer and composite coating can all be clearly seen from left to right. Coating and substrate had a very good mechanical and metallurgical bonding, which indicated the coating’s high bonding strength. Coating’s tensile strength tests showed that the average value is 24 MPa, and fracture occurred mainly within the NiCr/Cr$_3$C$_2$–BaF$_2$•CaF$_2$ coating. This indicated the bond strength between substrate and coating was more than 24 MPa. It also can be found that the composite coating exhibited less porosity (less than 5%), and a lamellar structure containing melted, partially melted powder particles (Fig. 4(b)). The main defect structures in the composite coating were pores and internal boundaries. X-ray dot mapping analyses (Fig. 5) showed that the phase boundaries were clearly defined, indicating no evident interdiffusion or reaction between them. The morphology and distribution of different constituents in the NiCr/Cr$_3$C$_2$–BaF$_2$•CaF$_2$ composite also can be found in the Fig. 5. NiCr (bright regions), Cr$_3$C$_2$ (gray regions), BaF$_2$•CaF$_2$ eutectic and little oxide (dark regions) constituents are evident and can be easily identified, mainly as fine, typical lamellar structures with different gray levels in the backscattered electron (BSE) mode. The element of Ba, Ca, F were in the same splat, which indicated that the eutectic was not decomposed and oxidated during plasma spray process. The micro-hardness (HV$_{0.2}$) of hard and soft phase in coating is 930±50 and about 450, respectively. The order of magnitude for the hardness in the coating is carbide, NiCr alloy and fluoride eutectic. Because carbide has relatively high mass fraction, the mean hardness value of the coating is evaluated to be about 810. The high micro-hardness of coating is very helpful to improve the coating’s wear resistance.

3.2. Sliding friction and wear behavior

Fig. 6 presents the friction coefficient of NiCr/Cr$_3$C$_2$–BaF$_2$•CaF$_2$ coating sliding against Si$_3$N$_4$ from room temperature to 800 °C. It can be seen that the NiCr/Cr$_3$C$_2$–BaF$_2$•CaF$_2$ coating exhibits a peak friction coefficient of 0.7–0.78 between room temperature and 300 °C. With the increase of temperature, the friction coefficient decreases and remains to about 0.4 at 800 °C. The friction coefficient decreases slowly from 300 °C to 500 °C, however it decreases sharply when temperature is above 500 °C. This may be due to the lubricating effect of this coating’s high-temperature lubricant additive, BaF$_2$•CaF$_2$ eutectic. The eutectic has been shown to be an effective solid lubricant above 400 °C [21] and plays an important role in the variation of friction coefficient. The friction reduction with temperature may also be affected by the
presence of the Cr₂O₃ which is an intrinsic solid lubricant above 500 °C. However, Cr₃C₂ and NiCr alloys are stable below 700 °C, and mild oxidation may happen only when temperature is above 800 °C.

Fig. 7 shows the effect of temperature on the wear rates of the NiCr/Cr₃C₂–BaF₂•CaF₂ coating as well as the Si₃N₄ ball. It can be seen that at room temperature, the wear rates of NiCr/Cr₃C₂–BaF₂•CaF₂ coating and the Si₃N₄ ball are 9.2×10⁻⁶ mm³/N m and 9.6×10⁻⁶ mm³/N m, respectively. The wear rates of coating and ball increase and decrease somewhat respectively with the increasing temperature from room temperature to 500 °C. The increased wear rate of coating may be due to slight oxidation wear and adhesive wear, which induced by high flash temperature at the contact area and plastic deformation. Above 500 °C,
the wear rates of both coating and Si$_3$N$_4$ ball decrease significantly. The wear rate of coating remains almost a constant of $5 \times 10^{-6}$ mm$^3$/N m, and the wear rate of Si$_3$N$_4$ ball stays at a value of $2.5$ to $3 \times 10^{-6}$ mm$^3$/N m between 600 °C and 800 °C. Above 500 °C, the friction coefficient of coating and the wear rates of both coating and ball have significant variation of decrease. It is clearly illustrated that the incorporation of relative ‘soft’ BaF$_2$-CaF$_2$ high-temperature solid lubricating phase in the composite coating leads to surprising enhancements of both self-lubricating and especially wear resisting properties under high-temperature sliding wear test conditions. On the other hand, the interfacial bond between the matrix and the particle reinforcement plays a significant role in the wear process. Sakai and Karamakas [23] have found that wear resistance decreased with increased alumina contents for copper–alumina composites. The detrimental effects of alumina particles on the wear resistance of the composites have been attributed to poor interfacial bond between copper and alumina. Similar observations have been made in case of TiC reinforced composites [24]. From Figs. 4 and 5, it can be found that particles and matrix have a good interfacial bond, which contributed to the good wear resistance of the NiCr/Cr$_3$C$_2$–BaF$_2$–CaF$_2$ coating.

3.3. Worn morphology analysis

Fig. 8(a) and (b) show the worn surface micrographs of the NiCr/Cr$_3$C$_2$–BaF$_2$–CaF$_2$ coating tested at room temperature and 500 °C. For the as-sprayed NiCr/Cr$_3$C$_2$–BaF$_2$–CaF$_2$ coating, pores, intersplat boundaries and other low density areas pre-existed, as mentioned in Section 3.1. On further deformation during wear tests carried out at room temperature, all these voids elongated and linked to form long cracks in a direction almost parallel to the wear surface. At a critical length, these cracks shear to the surface, yielding large wear debris. The worn surface at room temperature appeared to be critical length, these cracks shear to the surface, yielding large wear long cracks in a direction almost parallel to the wear surface. At a critical length, these cracks shear to the surface, yielding large wear

![Image](image-url)

Fig. 6. Effect of temperature on the friction coefficients of the NiCr/Cr$_3$C$_2$–BaF$_2$–CaF$_2$ coating.

![Image](image-url)

Fig. 7. Influence of temperature on the wear rates of NiCr/Cr$_3$C$_2$–BaF$_2$–CaF$_2$ coatings and Si$_3$N$_4$ balls.

and cause high wear rate. At 500 °C, the wear surface became smoother than room temperature due to grinding action and plastic formation of metal phase.

Fig. 8(c) presents the typical morphology of the worn surface of the NiCr/Cr$_3$C$_2$–BaF$_2$–CaF$_2$ coating tested at 600 °C, which shows the worn surface being covered with smooth BaF$_2$-CaF$_2$ eutectic material-transfer films. EDX revealed that the film contained large amounts of Ba, Ca, F, Cr, Ni, O, suggesting fluoride particles were forced out of the reservoirs due to plastic deformation, forming a compact film on the surface. BaF$_2$-CaF$_2$ well known for its excellent self-lubricating properties at temperatures higher than 400 °C when it underwent the brittle to ductile transformation, forming a fully ductile phase with very low shear strength [21]. Under the actions of friction and pressure, it can form a thin film on the worn surface due to the plastic deformation. The higher superficial temperature rise at the contacting surface effectively activated the self-lubrication property of the BaF$_2$-CaF$_2$ phase and subsequently significantly enhanced the wear resistance and reduced the friction coefficient of the coating. Plastic deformation and continuous formation of BaF$_2$-CaF$_2$ transfer films became the dominant wear mechanism at 600 °C.

Fig. 8(d) shows the typical morphology of the worn surface of the NiCr/Cr$_3$C$_2$–BaF$_2$–CaF$_2$ coating tested at 800 °C. When the testing temperature is 800 °C, a continuous glaze lubricating film plus small wear debris and mild scratches are a general feature of the worn surface. Coating material transfer, local adhesion and viscous flow are clearly evident. EDX indicated that more and more self-lubricants flowed and formed glaze film. However, at 800 °C high-temperature wear rate was not greatly reduced by the BaF$_2$-CaF$_2$ lubricant under these experimental conditions when compared to that at 600 °C. This may be due to adhesive transfer and viscous deformation of the coating. The coating materials were severely softened by local extremely high temperature.

EDX analysis of the worn surface of Si$_3$N$_4$ balls at room temperature shows that little or no detectable transfer of eutectic occurs during room temperature sliding. As the ambient temperature is increased, the fluorides soften and are able to develop a lubricous transfer film on the Si$_3$N$_4$ counterface as fluorides do wet ceramics. At 600 °C, the temperature at the asperities could be sufficiently high to greatly soften the self-lubricating films, part of films transferred to the surface of the Si$_3$N$_4$ ball during sliding process. Noticeable X-ray signals from the lubricants Ba, Ca, Ni and Cr are, however, detected on tribological Si$_3$N$_4$ specimens from high-temperature tests. BaF$_2$-CaF$_2$ eutectic was non-lubricating in the brittle condition, but became...
lubricating above 500 °C, when it underwent internal structural changes and a brittle to ductile transition, which functions to reduce abrasive wear.

4. Conclusions

NiCr alloy-coated powders are prepared by pressurized hydrogen reduction and solid state alloying process. These powders can reduce the decarburization of carbide, oxidation and ablation in plasma spray process, which leads to an improved quality of the derived coating. For example, the microstructure of plasma-sprayed NiCr/Cr3C2–BaF2•CaF2 coating was fine and dense with low porosity, high micro-hardness and cohesive strength. Therefore, the NiCr/Cr3C2–BaF2•CaF2 composite coating exhibited an improvement in tribological properties at high temperature. It was found that the brittle fracture and delamination of the NiCr/Cr3C2–BaF2•CaF2 composite were the dominant wear mechanisms of the coatings at low temperature. BaF2•CaF2 eutectic acts as a solid lubricant at above 500 °C, which effectively reduces friction and wear by creating a lubricating layer in the wear track, and a very important plastic deformation and continuous formation of BaF2•CaF2 transfer films became the dominant wear mechanism at elevated temperatures.

References


