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Preparation and characterization of atmospheric plasma-sprayed $NiCr/Cr_3C_2–BaF_2·CaF_2$ composite coating

Chuanbing Huang [a,b], Lingzhong Du [a], Weigang Zhang [a,*]

[a] State Key Laboratory of Multi-phase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China
[b] Graduate University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

NiCr alloy-coated $BaF_2•CaF_2$ eutectic and Cr_3C_2 powders were respectively prepared by both pressurized hydrogen reduction and solid state alloying technology. Using this $NiCr/Cr_3C_2–BaF_2•CaF_2$ 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 $NiCr/Cr_3C_2–BaF_2•CaF_2$ 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 $NiCr/Cr_3C_2–BaF_2•CaF_2$ 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 $BaF_2•CaF_2$ 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 $Cr_3C_2–BaF_2•CaF_2$ during spraying.

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_3C_2–NiCr coating is promising because of its very high hardness and oxidation resistance behavior up to 800 °C [2–7]. However, the Cr_3C_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_2, CaF_2, etc) and some metal oxides (NiO, MoO_3, Cr_2O_3, etc) have been employed as solid lubricants [8–12]. CaF_2/BaF_2 eutectic has also been used as a solid lubricant to improve the tribological properties of Cr_3C_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, $BaF_2•CaF_2$ eutectic and Cr_3C_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 $NiCr/Cr_3C_2$ and $NiCr/BaF_2•CaF_2$

* Corresponding author. Tel./fax: +86 21 6252 0135.
E-mail address: wgzhang@home.ipe.ac.cn (W. Zhang).

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particles were used as hard wear-resistant phase and high-temperature solid lubricant to prepare NiCr/Cr_3C_2–BaF_2•CaF_2 self-lubrication wear-resistant coating by plasma spray.

2. Experimental

Fluoride eutectic powder was prepared by mixing reagent grade BaF_2 and CaF_2 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 Cr_3C_2 powders and BaF_2•CaF_2 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 Cr_3C_2 (or BaF_2•CaF_2 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 Cr_3C_2 (or BaF_2•CaF_2 eutectic) particles as cores:

$$[Ni(NH_3)_n]SO_4 + H_2 + Cr_3C_2 \xrightarrow{\text{surfactant}} Ni/Cr_3C_2 + (NH_4)_2SO_4 + (n-2)NH_3 \ (n \geq 2)$$

$$[Ni(NH_3)_n]SO_4 + H_2 + \text{eutectic} \xrightarrow{\text{surfactant}} Ni/\text{eutectic} + (NH_4)_2SO_4 + (n-2)NH_3 \ (n \geq 2).$$

Chromizing process of nickel-coated Cr_3C_2 powders and BaF_2•CaF_2 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 Al_2O_3 particles and plasma-sprayed with a NiAl bond coat about 0.1 mm thick. The NiCr/Cr_3C_2–BaF_2•CaF_2 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 FEG 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 ($\lambda = 0.1541$ nm) at 40 kV, 30 mA.

The carbon and oxygen contents in both the feedstock powder and as-sprayed coating were analyzed using a 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 micro-computer 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 surround 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 Si_3N_4 ceramic. The

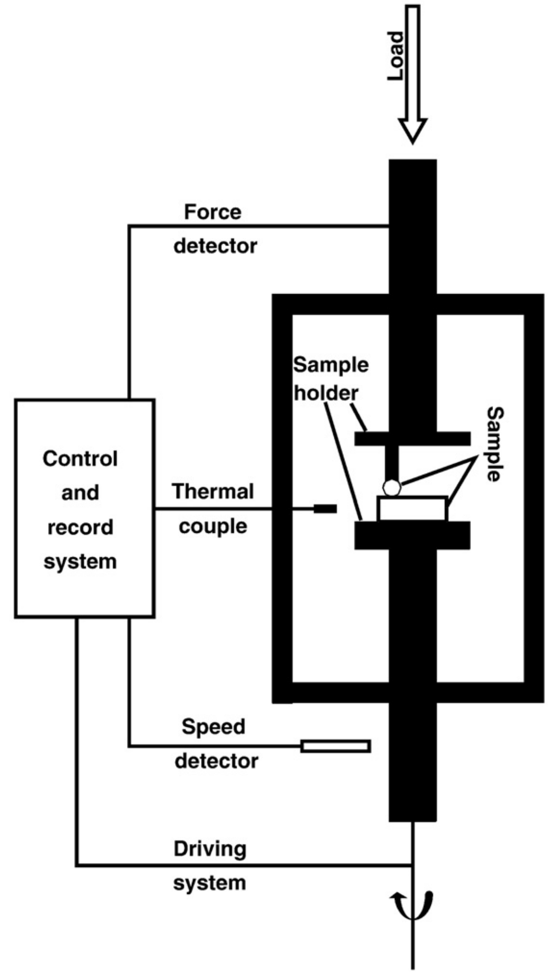

Fig. 1. Schematic diagram of the high-temperature friction and wear tester.

temperature in the furnace, monitored using a thermocouple, was raised at rate of 10–12 °C/min to the pre-set test temperature, the temperature deviation was controlled to be within ±2 °C. The friction and wear tests were carried out with a load of 9.8 N and sliding speed of 0.188m/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 $w = V/FS$, where w is the wear volume in mm^3, F is the normal load in Newton, and S 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, Cr_3C_2 reinforced phase and BaF_2•CaF_2 eutectic solid lubricant. The nickel alloy, 80% Ni–20% Cr, offers excellent high-temperature oxidation/corrosion resistance and mechanical strength. The high-