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Effect of boron on enhancing infrared emissivity of Ni-Cr system coating

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ABSTRACT

High infrared emissivity coating possesses great value in practical application, whether in the military or civilian areas. In this study, B-NiCr precursor powder containing NiO, Cr_2O_3 and ZrB_2 was calcined at 1300 °C and then used to prepare a high infrared emissivity B-NiCr coating via atmospheric plasma spraying. A large number of test methods were employed to analyze the powder and coating, including TG-DSC, XRD, FE-SEM, infrared spectrometer and so on. The result of infrared emissivity measurement indicates that the coating possesses maximum infrared emissivity of 0.908 at 1000 °C while the infrared emissivity is 0.901 after thermal shock test. Comparing with NiCr coating, $Ni_2CrO_2(BO_3)$ formed during calcination may be the main factor to improve the infrared emissivity of B-NiCr coating. The B-NiCr coating possesses good thermal shock resistance and can withstand 50 times thermal shock at least without falling off, from 800 °C to room temperature.

1. Introduction

According to the Kirchhoff's law, emissivity ε of material is equal with absorptivity α [1,2]. Due to high application value, high infrared emitting materials have attracted a lot of attention from researchers all over the world. For instance, a high infrared emissivity coating, US patent, is based on rare earth oxide, such as cerium oxide (CeO_2) and terbium oxide (Tb_2O_3) [3,4]. There are many application areas for high infrared emitting material, such as industrial furnace field. Coated with a high infrared emitting material, inner wall of industrial furnace can absorb most of heat energy that will lose and reradiate them into furnace. Another application area is aerospace field. A nuclear reactor is used as a power source of spacecraft, but there is no air in outer space, no heat conduction and heat convection. Therefore, residual heat in spacecraft can only be dissipated through heat radiation [5]. High infrared emitting material applied to outer surface of spacecraft can emit heat efficiently and quickly.

Because of special crystal structure, infrared emissivity of spinel (AB_2O_4) can reach 0.87 and above. Xudong Cheng et al. sprayed nickel-chromium spinel ($NiCr_2O_4$) on the surface of stainless steel by atmospheric plasma spraying (APS) and the infrared emissivity of $NiCr_2O_4$ coating was 0.87 at room temperature [6]. Subsequently, he doped a series of transition metal oxides and rare earth oxides into Ni-Cr spinel, which increased the infrared emissivity to 0.91 at high temperature [7,8]. Zirconium diboride (ZrB_2) possesses low electrical resistivity (9.2 $\mu\Omega\cdot$cm) [9] and there are four electrons outside boron ion (B^-), each B^- with three of B^- to form covalent bonds and remaining electrons to form delocalized π-conjugated structure, which can enhance infrared radiation of material [10]. ZrB_2 is easy to be oxidized, but the addition of 20–30 vol% of SiC can greatly increase oxidation resistance of ZrB_2 [10,11]. Therefore, in the application area of middle temperature (about 800 °C), we believe it is a good way to improve infrared emissivity of coating by adding ZrB_2 into the Ni-Cr system.

2. Experiment and measurement

2.1. Experimental procedure

Raw powders used in the experiment were chromic oxide with purity of 99.0% (Cr_2O_3, 0.5–1.5 μm), nickel monoxide with purity of 99.0% (NiO, 0.5–1.5 μm), zirconium boride with purity of 99.9% (ZrB_2, 1 μm) and silicon dioxide with purity of 99.9% (SiO_2, 1 μm). The all materials mentioned above were from Sinopharm Chemical Reagent Co., Ltd, China. Binder (organics) was self-made in the laboratory. Firstly, four kinds of raw powders were mixed in accordance with the ratio showed in Table 1. After adding appropriate amount of deionized water, the mixture was ground in a sand mill machine for half an hour. Waiting for several hours, the slurry contained of four kinds of powders deposited in the bottom of container. Taking out dirty water and adding appropriate amount of deionized water and binder, the slurry was ground in

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Table 1
The mass ratio of raw powders of coating. (The mole ratio of Cr_2O_3 to NiO is 1: 1, the mole ratio of ZrB_2 to SiO_2 is 1: 1 and the mass of ZrB_2 is 15% of total mass of Cr_2O_3 and NiO).

Sample	Cr_2O_3/g	NiO/g	ZrB_2/g	SiO_2/g
B-NiCr	268.18	131.82	60	32
NiCr	268.18	131.82	0	0

a rubber mill machine for 15 min. Then, a lab spray dryer was employed to produce precursor powder through suspension feed. The precursor powder was sieved and powder with particle size of 40–63 μm was collected. In order to obtain calcined powder, the collected precursor powder was calcined for 2 h in a muffle furnace at 1300 °C. Finally, ceramic coatings were sprayed on the surface of stainless steel substrate (316L, 30 mm × 40 mm × 1 mm) by atmospheric plasma spraying equipment. For each ceramic powder, ten test samples were prepared. It's important to note that, before the spraying, the stainless steel substrate needed to spray a bonding layer (layer of aluminum coated by nickel) in order to enhance the tensile adhesive strength of ceramic coating and substrate.

2.2. Analysis and measurement

Thermogravimetric analysis-differential scanning calorimetry (TG-DSC, STA449F3, Netzsch Group, Germany) was employed to determine mass and heat energy changes of precursor powder in air atmosphere with a heating rate of 10 °C/min and maximum temperature of 1350 °C. Crystal structure of powder was analyzed by X-ray diffraction (XRD, D8 Adwance, Bruker Corporation, US). Using Cu K_α radiation, its scanning speed and step size were 5°/min and 0.02°, respectively. Surface and cross-section morphologies of coatings were analyzed by scanning electron microscope (SEM, JSM-IT300, Japan Electron Optics Laboratory co., Ltd, Japan) while surface element distribution of coatings was analyzed by field emission scanning electron microscope equipped with EDS (FE-SEM, Zeiss Ultra Plus, Carl Zeiss AG, Germany). An infrared spectrometer (Tensor27, Bruker Corporation, US) was used to calculate normal infrared emissivity at room temperature and the normal infrared emissivity at high temperature (600–1000 °C, step of 100 °C) was measured by China National Supervision and Test Center for Infrared and Industry Galvanothermy Product Quality (Wuhan, China). The infrared emissivity valves in this paper are average emissivity values. Tensile adhesive strength of coating and substrate was tested by an universal testing machine (HUT305D, Wance Group, China) with a load rate of 900 N/s. Thermal shock experiment was accomplished in muffle furnace. The coatings were heated cyclically to 800 °C and then cooled to room temperature.

Technological process is showed in Fig. 1. The coating adding ZrB_2 is named as B-NiCr coating while another is called as NiCr coating.

3. Result and discussion

3.1. Analysis of TG-DSC

Test temperature of precursor powder is from 30 °C to 1350 °C for the reason that the formation temperature of Ni-Cr spinel is between 900 and 1200 °C. TG-DSC curves of B-NiCr precursor powder and NiCr precursor powder are showed in Fig. 2. There is a mass reduction at 296.3 °C on TG curve of NiCr powder (Fig. 2(a)), which corresponds to an endothermic peaks at the same temperature on DSC curve. It is obvious that binder decomposes at around 296.3 °C. The chemical reaction to form Ni-Cr spinel is as follow (Eq. (1)):

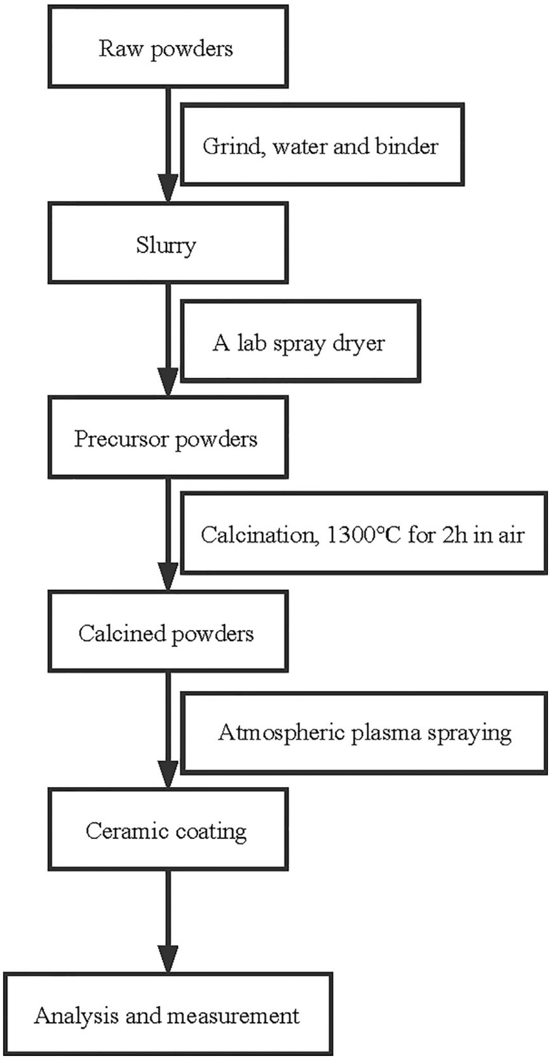

Fig. 1. Technological process for preparing ceramic coating.

$$Cr_2O_3 + NiO \rightarrow NiCr_2O_4 \quad (1)$$

Therefore, it is reasonable to assume that there is almost no mass change in the formation of Ni-Cr spinel, but an exothermic peak will occur because of the chemical reaction. In Fig. 2(a), changes of TG curve and DSC curve at 900–1200 °C are good to confirm the above speculation. The culmination of exothermic peak, namely 1060.7 °C, is the temperature that the above chemical reaction is the most violent. The NiCr powder calcined at 1300 °C for 2 h was detected by XRD and the result of analysis of XRD indicates that there are a large number of $NiCr_2O_4$ in the calcined powder.

Fig. 2(a) and (b) show that B-NiCr precursor powder has the same changes of the TG curve and DSC curve with the NiCr precursor powder at around 300 °C, which indicates the binder inside of B-NiCr powder decomposing. The above has mentioned that ZrB_2 is easily oxidized and the exothermic peak of the DSC curve at 729.9 °C (Fig. 2(b)) is correspond to the oxidation of ZrB_2. It is confirmed by the mass increase showed on TG curve (Fig. 2(b)) at 600–800 °C. There are two endothermic peaks in Fig. 2(b), respectively, at 1042.6 °C and 1145.3 °C. It is clear to know that the endothermic peak at 1042.6 °C corresponds to the formation of $NiCr_2O_4$ and