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Microstructure and properties of composite coatings prepared by plasma spraying ZrO_2-B_2O_3-Al composite powders

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ABSTRACT

The composite coatings containing ZrB_2 were prepared by plasma spraying ZrO_2-B_2O_3-Al system, and the effects of ZrO_2 particles size on the microstructure and properties of the as-prepared coating were investigated. The results show that ZrO_2, B_2O_3 and Al reacted with each other to form ZrB_2 during the plasma spraying process. The reaction degree of ZrO_2-B_2O_3-Al composite powders with nano-sized ZrO_2 particles was greater than that of the micro-sized ZrO_2 particles, and there was more ZrB_2 formed in the coating plasma sprayed with nano-sized ZrO_2 particles. The coating prepared by plasma spraying ZrO_2-B_2O_3-Al composite powder with micro-sized ZrO_2 showed the characteristics of stacking of partially melted or unmelted feedstock particles, loose microstructure, high porosity, and poor quality. However, the coating prepared by plasma spraying ZrO_2-B_2O_3-Al composite powder with nano-sized ZrO_2 displayed lamellar structure, homogenous distribution of ZrB_2 particles, dense microstructure and better quality. The hardness of the coating prepared by nano-sized ZrO_2 was much higher than that of the coating prepared by micro-sized ZrO_2, which is attributed to the high density and the homogeneously distributed reinforcement phase ZrB_2 formed in the coating. Meanwhile, the coating prepared by plasma spraying ZrO_2-B_2O_3-Al composite powder with nano-sized ZrO_2 possessed high toughness.

1. Introduction

With the development of modern technology such as aerospace, nuclear and metallurgy technology, there are more requirements for structural materials with high performance at high temperature. Plasma spraying technology can be used to deposit coatings on surfaces of a series of metal and nonmetallic materials, which can improve the wear, corrosion and oxidation resistance of substrate materials [1,2]. The materials used for plasma spraying include oxide ceramics such as Al_2O_3 and ZrO_2, transition metal boride ceramics such as TiB_2 and ZrB_2, metals and alloys such as nickel-chromium, and intermetallics such as NiAl, FeAl, etc. Reactive plasma spraying (RPS) is a versatile technology that has been successfully used as a reliable cost effective solution for many industrial problems. The most important characteristic of the reactive plasma spraying technique, which combines atmospheric plasma spraying (APS) with self-propagation high temperature synthesis (SHS), is that the desired phases for the coating could be formed in-situ by the SHS reaction during the plasma spraying process [3,4]. Compared to APS, the coating fabricated by RPS has a high deposition rate and hence the possibility of preparing thick coatings, high cohesive strength between phases due to in-situ formation, and a low cost due to the cheap feedstock powders. Y. Han et al. [3] compared the TiB_2-TiC composite coatings prepared by direct plasma spraying TiB_2+TiC composite powder and reactive plasma spraying Ti+B_4C composite powder. The results showed that the coating prepared by reactive plasma spraying Ti+B_4C composite powder showed better quality and higher properties than the coating prepared by plasma spraying TiB_2+TiC composite powder. X. Dai et al. [4] fabricated in-situ $(Al,Cr)_2O_3$-Cr composite coating by reactive plasma spraying Al-Cr_2O_3 composite powder. It was found that the microstructure of the coating consisted of $[(Al, Cr)_2O_3+Cr]$ eutectic and $Cr+[(Al,Cr)_2O_3+Cr]$ hypoeutectic.

ZrB_2 owning a series of excellent properties, such as high

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melting point (3245 °C), high hardness (22 GPa), good thermal conductivity and electrical conductivity, good chemical stability, excellent corrosion resistance and oxidation resistance, and good neutron control property [5–9], has been widely used in many fields such as cutting tools, drilling, grinding and oxidation components, refractory crucibles, spacecraft engine nozzles, high temperature protection accessories and plasma arc electrodes, etc [9,10].

At present, there are three main methods for preparing ZrB_2, including direct synthesis method, non-metal reduction method and metal thermal reduction method [11–17]. Direct synthesis method is to synthesize ZrB_2 using Zr as the raw material and B_4C, B_2O_3 or B as the boron sources. The main reactions are as follows, $3Zr+B_4C\rightarrow 2ZrB_2+ZrC$, $5Zr+2B_2O_3\rightarrow 2ZrB_2+3ZrO_2$ and $Zr+2B\rightarrow 2ZrB_2$. Xu et al. [11] produced ZrB_2-ZrC/Ni composite powders from Ni-Zr-B_4C system by self-propagating high-temperature synthesis (SHS). ZrB_2-ZrC/Ni cermet coating was deposited on a magnesium alloy substrate by atmospheric plasma spraying (APS) using the SHS derived powders as feedstocks. The coating exhibited lamellar and porous structure, and mainly consisted of ZrB_2, ZrC, Ni and by-product ZrO_2.

Non-metal reduction method is to prepare ZrB_2 by thermal reduction reaction using ZrO_2 as raw material and B_4C, B_2O_3, B and C as boron sources and reducing agent. The main reactions are as follows, $8ZrO_2+5B_4C\rightarrow 8ZrB_2+5CO_2+2B_2O_3$, $2ZrO_2+2B_2O_3+5C\rightarrow 2ZrB_2+5CO_2$ and $3ZrO_2+10B\rightarrow 3ZrB_2+2B_2O_3$. P. Karuna Purnapu Rupa et al. [12] studied the effect of B_4C content on microstructure and hardness of plasma sprayed zirconia (ZrO_2) coatings. ZrO_2-ZrB_2 composite coatings were obtained from the ZrO_2-B_4C powder mixtures. The coatings exhibited a porous microstructure. The reaction between B_4C and ZrO_2 resulted in the formation of ZrB_2 phase. Guo et al. [13] studied the effects of ZrO_2 particle size on synthesis of ZrB_2 powders via new borothermal reduction. The process consisted of two-step heat treatment (first-step at 1000 °C and second-step at 1600 °C) plus intermediate step of water washing. Based on the process, submicrosized ZrB_2 powders were synthesized using nano-sized ZrO_2.

Metal thermal reduction method is to prepare ZrB_2 using ZrO_2, B_2O_3 or B_4C, and Al or Mg as raw materials. S.K. Mishra et al. [14,15] used Al, ZrO_2 and B_2O_3 as raw materials and synthesized the Al_2O_3-ZrB_2 composite by SHS dynamic compaction. Addition of titanium as diluent during the SHS synthesis could change the phases and microstructure of the composite. Yu et al. [16] synthesized ZrB_2/Al_2O_3 composite powders from B_2O_3-ZrO_2-Al system. The results showed the presence of ZrB_2 and Al_2O_3 as the primary phases in the composite powders. Yan et al. [17,18] synthesized ZrB_2-Al_2O_3 in situ composite powders at 1550 °C via a solid-state precursor route using ZrO_2, Al, and BN as raw materials. The final ZrB_2-Al_2O_3 composite powders consisted of large crystal Al_2O_3 particles (several micrometers) and fine ZrB_2 particles (100–400 nm).

In recent years, many researches have been conducted on the preparation of transition metal boride coatings by plasma spraying using metal thermal reduction. Cagri Tekmen et al. [19] deposited mechanically alloyed Al-12Si, B_2O_3 and TiO_2 powders onto aluminum substrate using APS. It was observed that, during the spraying process, TiB_2 and Al_2O_3 were in-situ formed through the reactions between starting powders and finely dispersed in Al-Si matrix alloy. In the present investigation, the composite coatings containing ZrB_2 were prepared by plasma spraying ZrO_2-B_2O_3-Al system, and the effects of ZrO_2 particle size on the microstructure and properties of the as-prepared coating were investigated.

2. Material and methods

As-received powders are two kinds of t-ZrO_2 with average particle size about 40 nm and 6–9 μm, Al with average particle size about 6–9 μm, and B_2O_3 with average particle size about 10 μm. The powders were agglomerated uniformly to produce powder mixtures, and the ratio of ZrO_2-B_2O_3-Al system was chosen as 3:3:10, which was selected according to the chemical reaction equation '$3ZrO_2+3B_2O_3+10Al\rightarrow 3ZrB_2+5Al_2O_3$'. The powder mixtures were then dried at 120 °C and sieved through the sieve of 200–300 mesh. The composite powder prepared by nano-sized zirconia is represented by ZrO_2(nm)-B_2O_3-Al, and the composite powder prepared with micro-sized zirconia is represented by ZrO_2(μm)-B_2O_3-Al.

The carbon steel (~0.45 wt%C) coupons were used as substrates. A bond coating of Ni-10 wt%Al self-melting alloy with thickness about 50–100 μm was deposited onto the substrates. The as-prepared ZrO_2(nm)-B_2O_3-Al composite powder and ZrO_2(μm)-B_2O_3-Al composite powder were then plasma sprayed onto the bond coating for about 250 μm in thickness, respectively. The coatings were prepared using a GDP-2 type 50 kW plasma spraying system (Jiu Jiang Spraying Device Co., Ltd., China). The plasma spraying parameters were as follows: (a) primary gas (Ar) flow rate was 80 L min^{-1}, (b) secondary gas (H_2) flow rate was 20 L min^{-1}, (c) powder flow rate was 0.4 L min^{-1}, (d) current was 500 A, (e) voltage was 70 V and (f) spray distance was ~100 mm.

Cross-sections of the as-prepared coatings were ground and polished. The phase constitutions of the composite powders and as-prepared coatings were characterized by X-ray diffraction (XRD, Rigaku DMAX-2500) with Cu Kα radiation. A scanning electron microscope (SEM, Hitachi S-4800) equipped with X-ray energy dispersive spectroscope (EDS) was employed to characterize the morphologies of the composite powders and the cross-sections of the coatings. Thermal analysis of the composite powders was carried out by TG/DTA 6300 type comprehensive thermal analyzer with Ar as the protective gas. The heating rate was 10 °C min^{-1}, and the highest temperature was 1300 °C. The porosity of the coatings was obtained by image analyzing method. The microhardness of the coatings was tested on the polished surface of the coatings by a SHIMADZU HMV-2 Microhardness Tester under an indent load of 100 g with a dwell time of 15 s (ten indents for each sample).

3. Results and discussion

3.1. Effect of particle size of ZrO_2 on phase evolution of the composite powders during plasma spraying

Fig. 1 shows the XRD patterns of ZrO_2(μm)-B_2O_3-Al and ZrO_2(nm)-B_2O_3-Al composite powders. It can be seen that both of the composite powders contained Al, ZrO_2 and B_2O_3. ZrO_2 had two kinds of crystal structures, which were tetragonal and monoclinic, respectively. Fig. 2 shows the metallographic morphology of ZrO_2-B_2O_3-Al composite powders. It can be seen that two kinds of composite powders exhibited spherical or ellipsoidal shapes, and their sizes were in the range of 30–90 μm. Fig. 3 shows the SEM image with EDS map distribution of elements in the ZrO_2(nm)-B_2O_3-Al composite powder. It can be seen that the raw materials (ZrO_2, B_2O_3 and Al) distributed homogeneously in the composite powder.

Fig. 4 shows the XRD patterns of the coatings prepared by plasma spraying ZrO_2-B_2O_3-Al composite powders. It can be seen from Fig. 4a that the main phases of the coating prepared by the ZrO_2(μm)-B_2O_3-Al composite powder were t-ZrO_2 and Al, and the second phases were ZrB_2 and Al_2O_3. Fig. 4b shows that the main phases of the coating prepared by the ZrO_2(nm)-B_2O_3-Al composite powder were $Zr_{0.99}Al_{0.01}O_{1.995}$ and Al, and the second phase was ZrB_2. $Zr_{0.99}Al_{0.01}O_{1.995}$ is a solid solution phase formed by γ-Al_2O_3 dissolved into t-ZrO_2. Comparing Fig. 4 with Fig. 1, it can be seen