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Microstructure and properties of in-situ ceramic matrix eutectic nanocomposite coating prepared by plasma spraying Al-Cr_2O_3-Al_2O_3 powder

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ABSTRACT

According to the characteristic of eutectic solidification, the [Cr+$(Cr,Al)_2O_3$] eutectic nanocomposite coating was in-situ synthesized by reactive plasma spraying Al-Cr_2O_3-Al_2O_3 powder. The microstructure of the [Cr+$(Cr,Al)_2O_3$] coating shows the characteristic of nanostructure, in which Cr with granular and rod shape distributed homogeneously in $(Cr,Al)_2O_3$ matrix. The particle size of Cr was less than 10 nm, and the diameter of Cr with rod shape was less than 20 nm and the length of the rod was less than 100 nm. The microhardness of the [Cr+$(Cr,Al)_2O_3$] eutectic nanocomposite coating and the $(Cr,Al)_2O_3$ coating were $HV_{0.3}$ 1764 and $HV_{0.3}$ 1129, respectively. The toughness of the eutectic nanocomposite coating was higher than that of the $(Cr,Al)_2O_3$ coating. The wear resistance of the eutectic nanocomposite coating was 5.57 times of the $(Cr,Al)_2O_3$ coating.

1. Introduction

Al_2O_3 ceramic coating has high hardness, high chemical stability, and high wear resistance [1]. Cr_2O_3 exhibits excellent wear and friction characteristics due to its low friction coefficient [2], and it can resist high temperature corrosion due to its high melting point (about 2435 °C) [3,4]. Cr_2O_3 coating is superior to traditional wear resistant hard chromium coating [5–8]. Cr_2O_3 coating can be conveniently deposited on piston ring and cylinder liners in the automotive industry, where it reduces fuel and oil consumption and increases the engine life [9,10].

Al_2O_3 and Cr_2O_3 can form a $(Cr,Al)_2O_3$ infinite solid solution due to their similar crystal structure. K. Pedersen et al. [11] prepared the α-$(Cr,Al)_2O_3$ metastable solid solution coating by reactive codeposition of Cr_2O_3 and Al. Hardness values of the coating were in the range of 24–27 GPa, which were somewhat lower than that of the pure chromia films (29 GPa). However, the low toughness of Al_2O_3, Cr_2O_3 and $(Cr,Al)_2O_3$ ceramic coatings limit their application. Generally, the following ways were used to improve the toughness of Al_2O_3, Cr_2O_3 and $(Cr,Al)_2O_3$ ceramic coatings. The first method is to prepare the coating with nanostructure, and the second method is to introduce metallic phase with high toughness into the coatings [12,13]. Preparation of nanostructured materials is an important way for toughening ceramic coatings. It was reported that nanostructured coatings prepared by plasma spraying showed improvement of resistance to wear, erosion, corrosion and mechanical properties as compared to their conventional counterparts [14–16]. Researchers have successfully obtained the nanostructured coatings by thermal spraying with reconstituted nanostructured powders [17,18]. The mechanical properties of the nanostructured coatings were greatly improved as compared with those of the corresponding conventional coatings. Shi et al. found that the crack extension force (G_C) of the nanostructured coating increased by 80% as compared with that of the conventional coating [19,20].

Although toughness of the ceramic coatings were improved by preparation of the nanostructured coatings, researches found that

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the microstructure of the coatings were uneven and the porosity of the coating was increased owing to the high porosity of the reconstituted composite powders, which weakened the toughening effect of the nanostructured coatings. Reactive plasma spraying (RPS) combining plasma spraying with self-propagating high-temperature synthesis was carried out to synthesize ceramic/metal composite coatings in-situ. Yan et al. prepared $FeAl_2O_4$-Fe-Al_2O_3 nanocomposite coating by plasma spray Al-Fe_2O_3 composite powder [21,22]. The $FeAl_2O_4$-Fe-Al_2O_3 composite coating had higher toughness and wear resistance than the conventional Al_2O_3. However, the distribution of Fe particles was heterogeneous owing to the aggregate of Fe particles during solidification. So far, there are still some questions for fabricating metallic/ceramic composite coatings by RPS, because co-deposition of metallic phase and ceramic phase could not occur at the same time due to their different melting temperature and poor wetability between metal and ceramic. In addition, there is the mismatch of thermal expansion coefficient of metal and ceramic, which results in decreasing of the bonding strength between metal and ceramic, therefore the toughening effect is weakened.

It is necessary to study how to obtain nanocomposite coatings with nano-sized ductile metallic phases distributed homogeneously in ceramic matrix. In this paper, we report a new method for preparing metal/ceramic composite coating. Cr-$(Cr,Al)_2O_3$ composite coating, which had eutectic nanostructure characteristic, was synthesized following the eutectic reaction $L \rightarrow \alpha+\beta$. According to the Cr_2O_3-Al_2O_3 and Cr-Cr_2O_3 phase diagrams [23], an infinite solid solution $(Cr,Al)_2O_3$ could be formed and the eutectic reaction $L \rightarrow (Cr+Cr_2O_3)$ occur, in which Cr and Cr_2O_3 phases could form at the constant temperature and same time. During the process of reactive plasma spraying Al-Cr_2O_3-Al_2O_3 composite powder, the infinite solid solution and eutectic reactions occur at the same time, and $[Cr+(Cr,Al)_2O_3]$ eutectic nanocomposite coating was synthesized. The microstructure and properties of the $[Cr+(Cr,Al)_2O_3]$ eutectic nanocomposite coating were investigated in detail.

2. Materials and methods

The raw powders used to prepare the $[Cr+(Cr,Al)_2O_3]$ eutectic nanocomposite coating were Cr_2O_3, Al and Al_2O_3 powders. Cr_2O_3 powder with analytical grade and average particle size of 0.2–0.5 μm was obtained from the Third Chemical Reagent Company of Tianjin, China. Al powder with particle size of 6–9 μm and Al_2O_3 powder with particle size about 2–10 μm were obtained from Anshan Micropowder Co. Ltd. China and Jinzhou Jinjiang spraying materials Co. Ltd. China, respectively. The raw powders were blended uniformly to produce a powder mixture by wet ball-milling. The mixed powder slurries were then spray dried to form agglomerated Al-Cr_2O_3-Al_2O_3 composite powders. The coatings were prepared using GDP-2 type plasma spraying device made by Jiu Jiang Spraying Device Company, China. Q235 steel (0.14–0.22 wt %C) was used as substrate and machined into samples of 30 mm × 25 mm × 10 mm size. The samples were grit-blasted by using alumina grit before spraying for improving the bonding strength between coating and steel substrate. Ni-20 wt%Al alloy powder was plasma sprayed on the surface of the substrate to form a bonding layer between substrate and composite coating. The thickness of the bonding layer and top ceramic layer were about 100 μm and 300 μm, respectively. The plasma spraying parameters were as follows: (a) primary gas (Ar) flow rate was 60 $Lmin^{-1}$, (b) secondary gas (H_2) flow rate was 20 $Lmin^{-1}$, (c) carrier gas (N_2) flow rate was 8 $Lmin^{-1}$, (d) current was 500 A, (e) voltage was 65 V and (f) spray distance was ~100 mm. The phase compositions of the powders and the coatings were identified by X-ray diffraction installation (XRD, Rigaku Smartlab 2500/PC) with Cu Kα radiation. The microstructure of the surface and cross-section of the coatings and the powders were examined using scanning electron microscope (SEM, HITACHI S4800) and transmission electron microscopy (TEM, Philips Tec-nai G2) equipped with energy dispersive spectroscopy (EDS). Surfaces of the as-prepared composite coating were ground and polished. Specimens for transmission electron microscopy (TEM) were prepared with grinding and ion milling to electron transparency by using a Gatan 656 dimple grinder and a Gatan 691 Ion-Miller. The hardness of the coatings was measured with a Vickers indenter (SHIMADZU HMV-2) at a load of 2.94 N with a dwell time of 15 s (ten indents for each sample). Wear testing was performed in a SFT-2M tribometer (Zhong Ke Kai Hua Science and Technology Development Co. Ltd., Lanzhou, China) using the ball-on-disc geometry. Commercial bearing grade Si_3N_4 balls of diameter 3.969 mm were used to rotate in contact with each disc specimen. The normal load on each disc was 2.94 N. The rotation speed was 955 rpm, corresponding to a sliding velocity of 0.3 m/s. There was no lubricant used in the wear testing process, and the wear tests were done in air. After wear testing, the width and depth of the circular wear track on each disc was measured using the profile meter. The wear volume (W_V) was determined using the wear track data measured by the profile meter, and the wear rate was calculated. The worn surfaces of the coatings were characterized by SEM.

3. Results and discussion

3.1. The composition of the composite powder for preparing $[Cr+(Cr,Al)_2O_3]$ eutectic nanocomposite coating

According to Cr-Cr_2O_3 eutectic phase diagram and Cr_2O_3-Al_2O_3 uniform crystallization phase diagram, eutectic reaction $L \rightarrow (Cr+Cr_2O_3)$ and uniform crystallization reaction $L \rightarrow (Cr,Al)_2O_3$ could occur during solidification process of liquid. $(Cr,Al)_2O_3$ is an complete miscibility solid solution of Cr_2O_3 and Al_2O_3. Therefore, when the two reactions of $L \rightarrow (Cr,Al)_2O_3$ and $L \rightarrow (Cr+Cr_2O_3)$ take place at same time, Cr and $(Cr,Al)_2O_3$ can be formed at the same time. In order to synthesize $[Cr+(Cr,Al)_2O_3]$ eutectic coating, reactive plasma spraying Al-Cr_2O_3-Al_2O_3 composite powder was used and the composition of Al-Cr_2O_3-Al_2O_3 composite powder was designed and calculated. Al-Cr_2O_3 thermite reaction (Eq. (1) [24]) was used to form Cr in situ, and meanwhile, the heat released by the thermal reaction could help to melt the composite powder completely during the spraying process.

$$2Al + Cr_2O_3 = Al_2O_3 + 2Cr + 544\ kJ \quad (1)$$

On the basis of Al-Cr_2O_3 reaction, a certain amount of additives (Al_2O_3+Cr_2O_3) were added to make the composition of the composite powder to the eutectic composition. The reasons for the selection of (Cr_2O_3 + Al_2O_3) as additives are as follows. First, the composition of $(Cr,Al)_2O_3$ can be changed by adjusting the proportion of Cr_2O_3/Al_2O_3, which may regulate the performance of $(Cr,Al)_2O_3$. Second, the wetability between Cr and Cr_2O_3 is better than that of Cr and Al_2O_3, which may be helpful for forming Cr nanocrystals. Addition amount of the additives of Cr_2O_3 and Al_2O_3 was calculated from Eq. (2).

$$(2Al+Cr_2O_3)+(aAl_2O_3+bCr_2O_3) = Al_2O_3+2Cr+(aAl_2O_3+bCr_2O_3) \quad (2)$$

where $(2Al+Cr_2O_3)$ is the reaction system, and the molar ratio of Al and Cr_2O_3 is 2:1. $(aAl_2O_3+bCr_2O_3)$ is the additives. According to Eq. (2) and Cr-Cr_2O_3 phase diagram, the molar ratio of $(aAl_2O_3+bCr_2O_3)/(2Al+Cr_2O_3)$ is 1.5, and a/b is determined to 3/7.