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Formation mechanism of supersonic plasma-sprayed nanostructured composite ceramic coatings

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ABSTRACT

In this paper, nanostructured composite ceramic coatings (NCs) were prepared by supersonic plasma spray technology, and their surface, cross-section and fracture morphologies were observed by scanning electron microscope (SEM). The phase composition and high resolution morphology are analyzed by X-ray diffraction (XRD) and transmission electron microscope (TEM). In the final, the formation mechanisms of microstructure and micro-defects were concluded. The results show that a great deal of metastable γ-Al_2O_3 phase and a few amount of Al_2TiO_5 phase were generated after the spraying. Fully melted regions (FM regions) and partially melted regions (PM regions) are interlocked and piled up without obvious boundaries. The bimodal distributional microstructure is formed in the form of lamellae, which is relative to position of particles injected into plasma jet, melting points about composite phase and thermal conductivity of particles in the process of spraying. Reducing the gap in particle diameter and changing tap density of agglomerated particles can improve effectively performances of NCs. The increases of velocity and tap density of particles are the effective ways to reducing micro-defects and improving quality of NCs.

1. Introduction

Plasma spraying technology is an indispensable surface engineering technology in the field of engineering technology [1–3]. In the process of plasma spraying, a single fused aggregated powder is the basic unit to form the coating. The behavior of the individual powder includes three basic processes, as followings: 1) the process of powder entering into plasma arc flame; 2) the process of interaction of powder and plasma arc flame, where powder is heated and melted under the action of the plasma arc flame; 3) the process of interaction of substrate and particles or droplets with high temperature and high speed (or the deposited coating), including the collisions between substrate and particles or droplets, flattening of particles or droplets and the rapid solidification [4].

Due to surface effect, small dimension effect and quantum dimension effect, physical and chemical properties of nano materials are different from many features of the macro material [5], for instance high strength, high toughness, high specific heat and thermal expansion rate, high electrical conductivity, magnetic conductivity, high frequency wave absorption, etc. [6–8]. These features have become important research field of frontier science and technology in the new century.

Therefore, the way of combining the thermal spraying technology and nanotechnology to prepare nanostructured coating can make the application of nano materials gradually enter a stage of large-scale practical. The preparation of nanostructured coating has become an important development direction of thermal spraying technology. In comparison with traditional coatings, the nanostructured coatings , such as WC-Co, Al_2O_3, TiO_2, NiCr–Cr_3C_2, ZrO_2, etc., have been significantly improved in the aspects of strength, toughness, corrosion resistance, wear resistance, thermal barrier, thermal fatigue, etc., and even part of the above coatings simultaneously possess many kinds of mentioned performances [9–12].

In recent years, the supersonic plasma spraying technique has been successfully used for the preparation of coatings with excellent performances (low porosity, high bonding strength). In this paper, supersonic plasma spraying technique was used for preparing NCs. Through thorough analysis of the surface morphology, cross-section morphology and fracture morphology, the formation mechanisms of microstructure and micro-defects are summarized,

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which is expected to produce a great significance on the further study of its performances and expanding its application range.

2. Experimental procedures

2.1. Spraying materials

An iron-base alloy, AISI 1045, previously cleaned with acetone or alcohol solution, sand-blasted with alumina particles, was used as the substrate with the dimensions of 40 mm × 10 mm × 6 mm. A commercially available Ni/Al coated powder with the composition of Al-20, Ni-balance (wt.%) was sprayed as bonding coating and its micro morphology was shown in Fig. 1(a). The bonding coating decreased the difference in physical properties between ceramic coating and metal substrate and then the bonding strength was increased significantly. The agglomerated nanostructured Al_2O_3–13 wt.%TiO_2 composite powder was used for preparing NCs and its micro morphology was shown in Fig. 1(b).

2.2. Spraying process and equipment

The bonding coating with a thickness of about 80 μm and NCs with a thickness of about 300 μm were fabricated by high-efficiency supersonic plasma spray system developed by National Key Laboratory for Remanufacturing, China. The advanced system was composed of plasma torch, gas supply, powder feeder, and water cooling circulatory and so on. The advanced, novel plasma torch with a Laval nozzle was a key part of this system and played a significant role in heating and accelerating particles. Particles were directly injected into the plasma jet by an internal injection port with different slop to control the position of powder in plasma jet. More detailed information about the system was available elsewhere [13]. In the process of spraying, the gun was perpendicular to the surface of specimen and moved at a speed of 12 mm/s to guarantee coating uniformity. Simultaneously, the cooling air was used for lowering temperature to avoid coating overheat, otherwise it was deleterious to the coating quality. Velocity, temperature and distribution state of particles were monitored by Spray Watch-2I system. Detailed spraying parameters were listed in Table 1.

2.3. Characterization of NCs

The phase composition of NCs and powder were examined by XRD with Cu Kα (1.54056 Å) radiation on a Philips analytical diffract meter. The high resolution morphologies and chemical composition were analyzed by Tecnai F20 field emission TEM equipped with energy dispersive X-ray detector (EDX). The surface morphology, cross-section morphology and fracture morphology of coating were observed by Nova Nano 450/650 environmental SEM, which was equipped with the Feature Max X-ray spectrometer produced by OXFORD company.

3. Results and discussion

3.1. Phase composition and TEM analysis

Fig. 2 presents the analysis results of phase composition of composite powder and NCs. It can be seen that phase composition of powder and coating was different. After spraying, a great deal of metastable γ-Al_2O_3 phase and A few amount of Al_2TiO_5 phase were generated. Previous research proves that γ-Al_2O_3 phase with lower critical nucleation energy is preferentially formed, but part of generated γ-Al_2O_3 phase and Rutile-TiO_2 produce Al_2TiO_5 [2]. In such a case, the generation of Al_2TiO_5 phase makes Rutile-TiO_2 less. Furthermore, compared with diffraction pattern of powder, the diffraction peaks located at about 45.8 and 66.5 (2θ) of coating are broadened. It is believed that the spraying process either cause grain fine or produce the amorphous phase.

In order to further investigate the microstructure of NCs, TEM experiment is carried out. TEM photos, electron diffraction pattern and EDX analysis are shown in Fig. 3. It can be seen from area ‘A’ in Fig. 3(a) that crystal grains with the size of hundreds of nanometers in the shape of stick are possibly columnar crystal, which belong to the structure of FM regions in accordance with EDX analysis shown in Fig. 3(c), size and morphology. On the basis of the calculation for the spot pattern of area ‘B’ in Fig. 3(b), equiaxed or regular polygon crystal grains about 100–200 nm in size are γ-Al_2O_3 phase. Globular crystal grains with the diameter of 50–100 nm are enriched or dispersed in matrix without obvious boundary, which belong to the structure of PM regions.

3.2. Microstructure characteristics of NCs

3.2.1. Cross-section morphology

The cross-section morphologies of NCs and EDS analysis are shown in Fig. 4. It can be clearly seen that NCs is a layer structure with a thickness of 2~7 μm as shown in Fig. 4(a), which is the overlap of FM regions (as demonstrated as region ‘A’ in Fig. 4(b)) and PM regions (as demonstrated as region ‘B’ in Fig. 4(b)) and even in some regions it exists both unmelted and partially melted nanoparticles, as shown in Fig. 4(a). Similar to traditional Al_2O_3–13 wt.%TiO_2 coating, FM regions have a uniform and dense lamellae structure. From PM regions, it can be found that a large number of partially melted (melt only happened on surface)

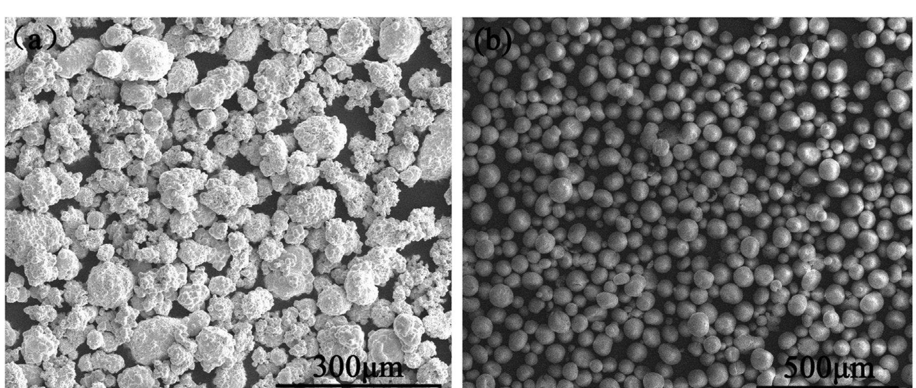

Fig. 1. Micro morphologies of (a) Ni/Al powder and (b) nanostructured Al_2O_3–13 wt.%TiO_2 composite powder.