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Phase evolution of plasma sprayed Al_2O_3−13%TiO_2 coatings derived from nanocrystalline powders

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Abstract: Commercial nanosized alumina and titania particles were selected as raw materials to prepare the blended slurry with composition of Al_2O_3−13%TiO_2 (mass fraction), which were reconstituted into micrometer-sized granules by spray drying, subsequently sintering at different temperatures to form nanostructured feedstock for thermal spraying, and then Al_2O_3−13%TiO_2 nanocoatings were deposited by plasma spraying. The evolution of morphology, microstructure, and phase transformation of the agglomerated powder and as-sprayed coatings were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results show that Al_2O_3 retains the same α phase as the raw material during sintering, while TiO_2 changes from anatase to rutile. During plasma spraying, some α-Al_2O_3 phases solidify to form metastable γ-Al_2O_3, and the volume fraction of α-Al_2O_3 decreases as CPSP increases. However, peaks of the TiO_2 phase are not observed from the as-sprayed coatings except for the coatings sprayed at the lower CPSP. As the CPSP increases, nanostructured TiO_2 is dissolved easily in γ-Al_2O_3 or χ-Al_2O_3·TiO_2 phase. After heat treatment, γ-Al_2O_3 in the coatings transforms to α-Al_2O_3, and rutile is precipitated.
Key words: Al_2O_3−13%TiO_2; nanocrystalline powder; nanocoatings; phase evolution

1 Introduction

In the field of thermal spray, the atmospheric plasma spraying (APS), as a well-established technology, has been widely used to produce various coatings, such as wear, corrosion resistant, hydroxyapatite, and thermal barrier coatings [1]. Plasma spraying ceramic coating technique on metal surface is a promising means to combine advantages of the metal substrate and the ceramic coating, which can simultaneously meet the mechanical properties and environmental service demands, and it has been rapidly developed [2]. However, the application of conventional plasma sprayed ceramic coatings is limited due to their brittleness and poor machining property. The unique properties of nanostructured materials have been reported for both bulk materials and coatings [3]. Plasma sprayed nanostructured ceramic coatings, by taking advantage of properties associated with nanostructures, can improve the performance and durability of conventional plasma sprayed coatings that already have a wide variety of applications in the aerospace, biomedical, automobile and chemical industries [4−7]. For example, nanostructured Al_2O_3−TiO_2 ceramic coatings show much higher wear resistance than the conventional Al_2O_3−TiO_2 coatings [6−8].

The plasma prayed Al_2O_3−TiO_2 nano coatings have been studied on processing, microstructure, interfacial mechanical properties and wear behavior [2−4,6−12]. However, there are few systematic works on the phase evolution of agglomerated Al_2O_3−13%TiO_2 nanocrystalline powder and as-sprayed coatings. In the present study, nanostructured Al_2O_3−13%TiO_2 coatings were prepared by atmosphere plasma spraying nanocrystalline powders, and the evolution of the morphology, microstructure, and phase transformation of the agglomerated powder and as-sprayed coatings were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2 Experimental

Commercial nanosized particles of α-Al_2O_3 with the mean diameter of 50 nm and anatase TiO_2 with the mean diameter of 10 nm were used as the starting powders, and

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the performance parameters of them are shown in Table 1. It is well known that individual nanoparticles cannot be plasma sprayed because of their low mass and inability to be carried in a moving gas stream and deposition on a substrate [13]. So the most important thing using nanoparticles as raw material to generate the nanostructured coatings is to reconstitute individual nanoparticles into sprayable agglomerates, which are large enough for plasma spray deposition. The process of reconstitution consisted of spray drying the slurry that contains nanoparticles in the mass ratio of Al_2O_3−13%TiO_2, and sintering at high temperature (700−1200 °C).

Table 1 Performance parameters of nanopowders

Raw material	Constituent phase	Purity/ %	Mean grain size/nm	Specific surface area/ ($m^2 \cdot g^{-1}$)	Apparent density/ ($g \cdot cm^{-3}$)
Al_2O_3	α-Al_2O_3	≥99.9	50	14	0.1−0.2
TiO_2	Anatase	≥99	10	210±10	0.06−0.07

Plasma spraying was performed on a LP−50B plasma-spraying machine made in China. The critical plasma spray parameter (CPSP) is determined by the plasma output power in the numerator and argon gas flow rate in the denominator. Other processing variables, such as carrier gas flow rate, spray distance, flow rate ratio of argon to H_2, powder feed rate, gun speed, were held constant in this study. Under these controlled processing conditions, CPSP can be directly related to the temperature of plasma and/or particles.

Mild steel substrate samples (Fe−0.45C−0.3Si−0.75Mn−0.03P−0.035S, mass fraction, %) with dimensions of 9 mm × 8 mm × 10 mm were grit-blasted and then coated by plasma spraying Ni/Al powders to form a bonding layer about 100 μm in thickness. The nanostructured Al_2O_3−13%TiO_2 coating was deposited by plasma spray using the agglomerated powders and the coating thickness was about 300 μm.

The phase compositions of the agglomerated powder and as-sprayed coatings were examined using PHILIPS X-PertMPD X-ray diffraction (XRD) with Cu K_α radiation. The microstructures were observed on a Philips XL30 scanning electron microscope (SEM).

3 Results and discussion

3.1 Microstructure of nanostructural agglomerated powders

The morphology and line scanning results of the agglomerated Al_2O_3−13%TiO_2 nanocrystalline powders before sintering are shown in Fig. 1. It can be seen from Fig. 1(a) that the agglomerated powders are well

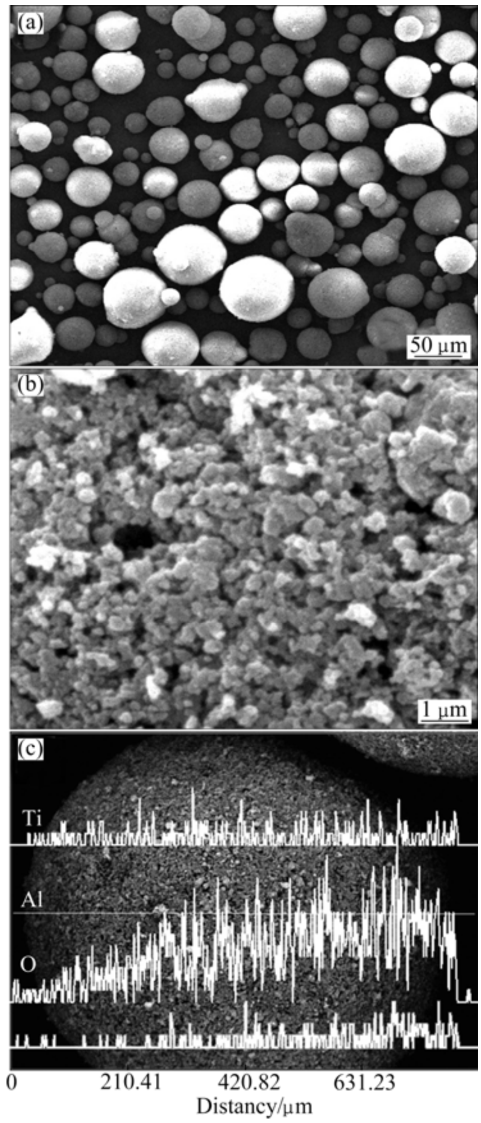

Fig. 1 SEM image (a), high magnification image of surface morphology (b) and line scanning result (c) of agglomerated Al_2O_3−13%TiO_2 powders

spherical and their size ranges from 20 μm to 70 μm, which improves powders feeding behavior during plasma spraying process. Figure 1(b) shows the surface morphology of an agglomerated powder that consists of many small nano-particles combined by the organic binder of PVA. Figure 1(c) shows that the nanosized TiO_2 particles are distributed homogeneously within Al_2O_3 particles.

SEM images of agglomerated Al_2O_3−13%TiO_2 powder sintered at different temperature are shown in Fig. 2. It demonstrates that the nano-particles grow into 100−300 nm in size, and the nano-particles connect together, indicating that sintering of the nano-particles occurs after the organic binder of PVA is burnt. As the sintering temperature increases, the nano-particles grow from nano-size to sub-micron or micron size, and more obvious necking exists between nano-particles due to

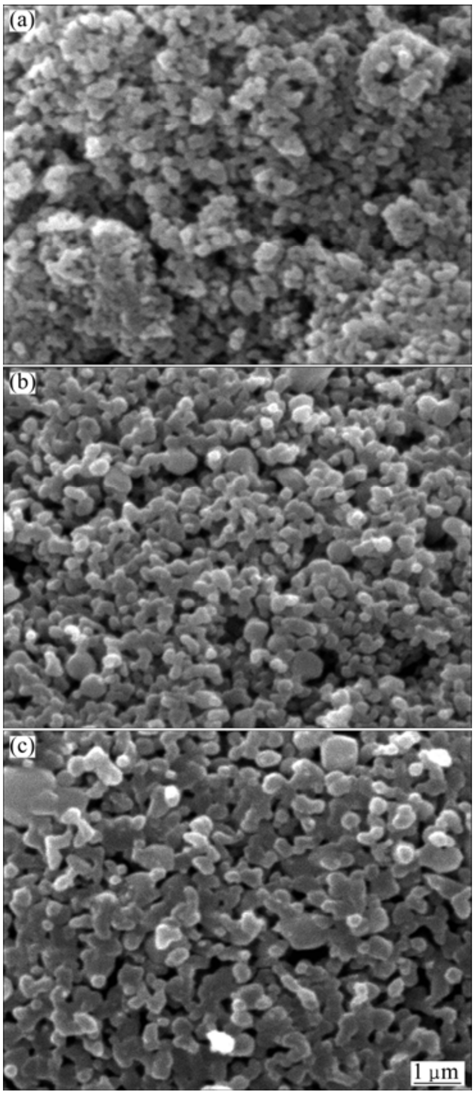

Fig. 2 SEM images of agglomerated Al_2O_3−13%TiO_2 nanocrystalline powder sintered at temperature of 700 °C (a), 900 °C (b) and 1100 °C (c)

sintering effect, which improves the strength of connection between nanoparticles, necessary for plasma spraying.

3.2 Phase evolution of nanostructural agglomerated powders during sintering

Figure 3 presents the XRD patterns of agglomerated Al_2O_3−13%TiO_2 nanocrystalline powders before and after sintering. It can be seen that Al_2O_3 retains the same α phase as the raw material after sintering, while TiO_2 changes from anatase to rutile due to an irreversible phase transition occurring at 610 °C [6]. And the reaction does not occur between alumina and titania to generate a new phase.

3.3 Phase evolution during plasma spraying

To further investigate the phase evolution of

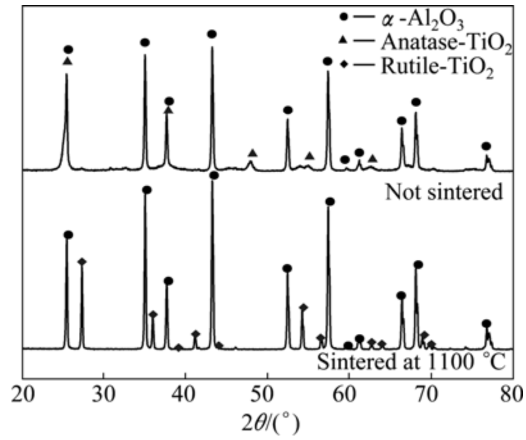

Fig. 3 XRD patterns for agglomerated Al_2O_3−13%TiO_2 nanocrystalline powders before and after sintering

agglomerated Al_2O_3−13%TiO_2 nanocrystalline powders during plasma spraying, various spraying parameters (CPSP) were taken. Figure 4 shows the XRD patterns of the nanostructured Al_2O_3−13%TiO_2 coatings sprayed at different CPSP. It can be seen that during plasma processing, the stable α-Al_2O_3 phase rapidly solidifies to form metastable γ-Al_2O_3, since γ-Al_2O_3 forms more easily from the melt than α-Al_2O_3 at a high cooling rate because of the low interfacial energy between crystal and liquid [14]. Moreover, peaks of α-Al_2O_3 and γ-Al_2O_3 are found in XRD patterns from all the as-sprayed coatings. Melting and rapid solidification is the only processing route available for the formation of γ-Al_2O_3 [10], so the peak of α-Al_2O_3 is certainly due to the presence of unmelted or partially melted alumina. However, peaks of the TiO_2 phase are not observed from the as-sprayed coatings except for the coatings sprayed at lower CPSP (i.e. 312) and only slight TiO_2 peaks exist in the crystal planes (110), (101), (211). As mentioned in Ref. [7], the solubility of TiO_2 in theα-Al_2O_3 is negligible, Ti ions are

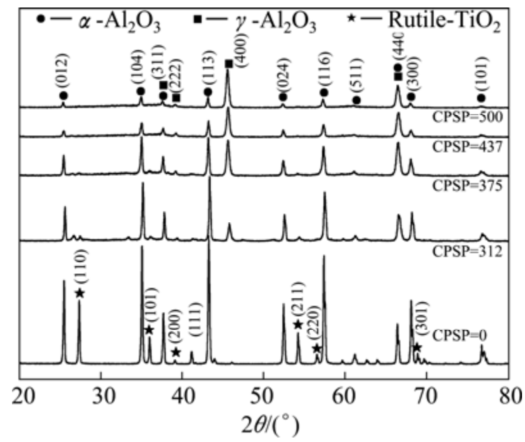

Fig. 4 XRD patterns of nanostructured Al_2O_3−13%TiO_2 coatings sprayed with different CPSP

likely to be in the γ-Al_2O_3 lattice as either an interstitial or substitutional defect. The missing of Ti-containing phase peaks can be attributed to the fact that as the CPSP increases (along with particle/torch temperature), nanostructured TiO_2 is easier to dissolve in γ-Al_2O_3 or χ-Al_2O_3·TiO_2 phase presented in the nanocoatings, which is different from the investigation result of the conventional coatings reported [4,9].

It is also seen from Fig. 4 that the phase component of the coatings is sensitive to the CPSP of the plasma spray gun during production. As the CPSP increases, the intensity of α-Al_2O_3 (113) peak, which is the main peak of α-Al_2O_3, decreases, while the intensity of γ-Al_2O_3 (400) peak increases. According to the results of XRD diffraction, the relative contents of α-Al_2O_3 and γ-Al_2O_3 in nanostructured Al_2O_3−13%TiO_2 coating can be quantitatively calculated by direct *K* value method [7], as shown in Fig. 5. It is clear that as CPSP increases, the volume fraction of α-Al_2O_3 decreases, conversely, the volume fraction of γ-Al_2O_3 increases. Based on the above analysis, the phase transformation of the coatings can be controlled by adjusting critical plasma spray parameter (CPSP), meanwhile the microstructure can be changed, ultimately the purpose to improve the properties of the coatings will be attained.

3.4 Microstructure transformation of as-sprayed coatings

Because the heat input applied to nanopowders increases with increasing CPSP, which is accompanied with higher probability for spray nanopowders to be melted inside the plasma flame, the morphology and microstructure transformation of the coatings can reveal the melting state during plasma spraying at different CPSP, which accords with the phase evolution rule.

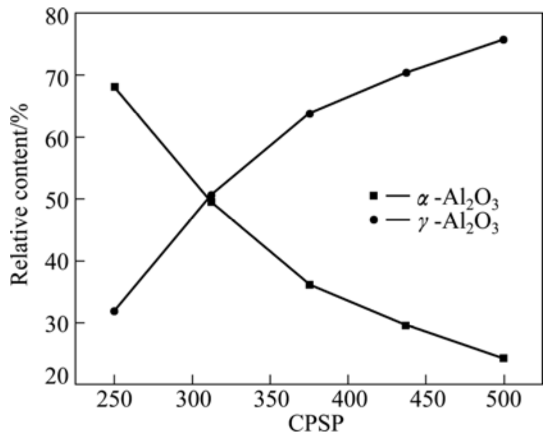

Fig. 5 Relative contents of α-Al_2O_3 and γ-Al_2O_3 in nanostructured Al_2O_3−13%TiO_2 coating as function of CPSP

Figure 6 presents SEM images of the cross-section of the nanostructured Al_2O_3−13%TiO_2 coatings sprayed at different CPSP. In all the coatings, some pores are observed because of the technology characteristics of plasma spraying. And the nanostructured coatings all exhibit a particular bimodal microstructure feature,

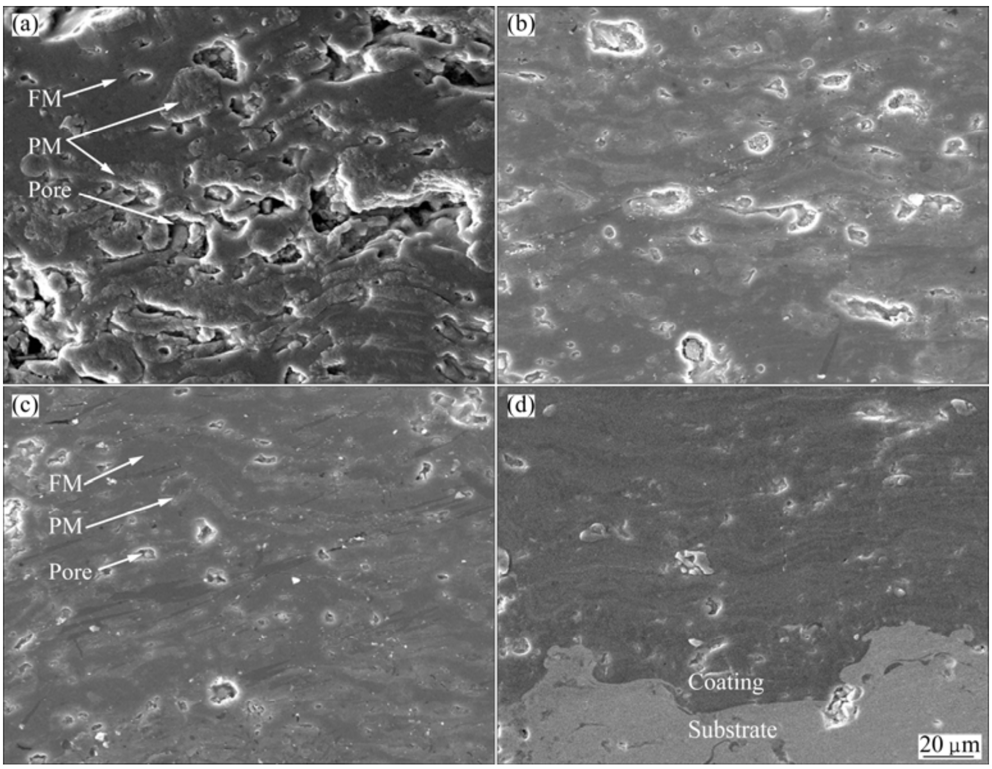

Fig. 6 Cross sectional SEM images of nanostructured Al_2O_3−13%TiO_2 coatings sprayed at different CPSP: (a) CPSP=312; (b) CPSP=375; (c) CPSP=437; (d) CPSP=500

consisting of unmelted or partially melted regions (bright-gray colored, marked with PM in Fig. 6) and fully melted regions (dark-gray colored, marked with FM in Fig. 6). During the process of plasma spraying, a large amount of nanoparticles are fully melted because of high temperature of flames (more than 10^4 K). These melting droplets struck the surface of the substrates or the as-sprayed coatings to form micron-sized lamellar structure under the action of high speed flames. Simultaneously, high speed flames are too fast to melt a part of nanoparticles completely, hence forming the partially melted regions consisting of nanoparticles. Therefore, the as-sprayed nanostructured ceramic composite coatings are composed of lamellar structure and partially unmelted nanoparticles, which can be clearly and detailedly seen from Fig. 7. It is believed that the unique bimodal microstructure contributes to the significantly enhanced mechanical properties of the nanostructured coatings.

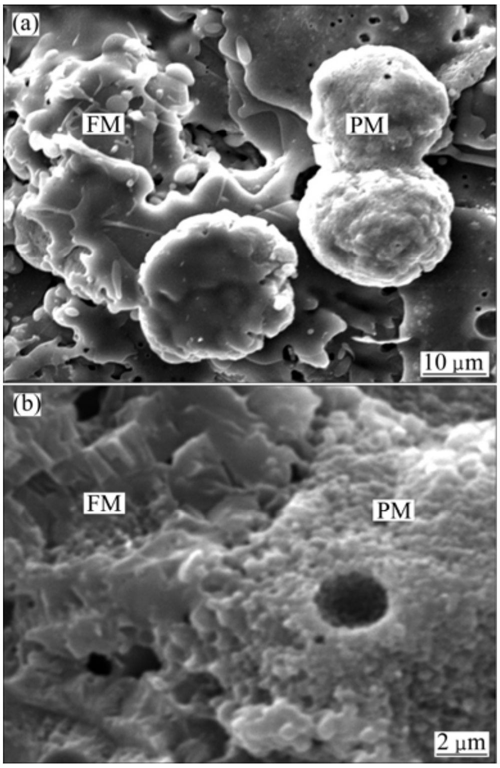

Fig. 7 High magnification SEM images of top surface (a) and fracture surface (b) of nanostructured Al_2O_3−13%TiO_2 coating sprayed at CPSP=437

It is obvious that increasing the CPSP makes more powders fully molten; hence reducing the proportion of the unmelted or partially melted regions in the nanostructured coatings, reducing the proportion and size of the pore, and the coating becomes denser and more uniform at the same time. It can be concluded that the plasma spray parameter (CPSP) plays an essential role in adjusting and controlling the microstructure of the coatings.

3.5 Phase evolution of as-sprayed coatings with post heat treatment

It was reported that γ-Al_2O_3 in as-sprayed Al_2O_3−13%TiO_2 coatings is a metastable phase, and it can easily transform to α-Al_2O_3 in a certain environment or heat treatment process [13]. It can be seen from Fig. 8 that, when the Al_2O_3−13%TiO_2 nano coatings were heat treated at different temperatures, the diffraction peak of α-Al_2O_3 stable phase were significantly enhanced, while the diffraction peaks of γ-Al_2O_3 metastable phase were relatively weakened, and the diffraction peaks of rutile phase appeared, indicating that certain amount of γ-Al_2O_3 transformed to α-Al_2O_3 and TiO_2 phase precipitated during heat treatment. Because of stresses associated with the volume change, the phase transformation will deteriorate thermal shock resistance of the coatings. The higher the heating temperature is, the larger the diffraction peak intensity ratio of α-Al_2O_3 (113) to γ-Al_2O_3 (400) ($I_{K_\alpha}^{\alpha(113)}/I_{K_\alpha}^{\gamma(400)}$) is, and the more the γ-Al_2O_3 transforms to α-Al_2O_3. Then the greater stress will be induced, so that the coating will show a worse performance of thermal shock [15].

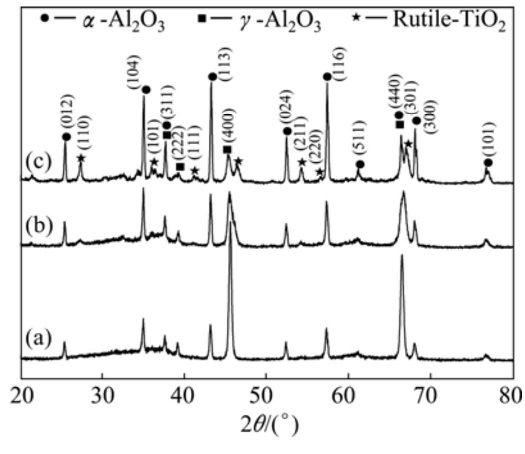

Fig. 8 XRD patterns of Al_2O_3−13%TiO_2 coating (a) and heat treated coatings at temperatures of 900 °C (b) and 1000 °C (c)

4 Conclusions

1) Agglomerated Al_2O_3−13%TiO_2 nanocrystalline powders were prepared by spray drying, and Al_2O_3 retained the same α phase as the raw material during sintering, while TiO_2 changed from anatase to rutile during sintering. The reaction did not occur between alumina and titania to generate a new phase.

2) When the nanostructured Al_2O_3−13%TiO_2

feedstocks were plasma sprayed on the steel, some α-Al_2O_3 solidified to form metastable γ-Al_2O_3, and the volume fraction of α-Al_2O_3 decreased as CPSP increased. However, the peaks of TiO_2 phase were not observed from the as-sprayed coatings except for the coatings sprayed at the lower CPSP. As the CPSP increased, nanostructured TiO_2 was be dissolved easily in γ-Al_2O_3 or χ-Al_2O_3·TiO_2 phase presented in the nanocoatings. The microstructure can be changed because the phase transformation of the coating can be controlled by adjusting critical plasma spray parameter (CPSP).

3) After heat treatment, γ-Al_2O_3 in the coatings transformed to α-Al_2O_3, and rutile will be precipitated.

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纳米 Al_2O_3−13%TiO_2 粉末及其等离子喷涂涂层的相变

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摘　要：将商用纳米 Al_2O_3 与 TiO_2 粉末混合制浆，通过喷雾造粒技术重构成大颗粒纳米 Al_2O_3−13%TiO_2 团聚粉体，然后采用不同加热温度进行烧结，制备用于热喷涂的纳米喂料。采用等离子喷涂技术沉积形成纳米涂层。利用 XRD 和 SEM 对纳米粉末和涂层的形貌、显微结构和晶相进行表征。结果表明，在烧结过程中纳米氧化铝没有发生相变，而纳米氧化钛则由锐钛矿相转变为金红石相；在等离子喷涂过程中，部分 α-Al_2O_3 发生熔化转变为 γ-Al_2O_3，且转变量与喷涂工艺参数有关；而 TiO_2 相只在较低喷涂工艺参数下存在衍射峰，在较高喷涂工艺参数下则以 χ-Al_2O_3·TiO_2 固溶体存在；涂层在热处理过程中会发生 γ-Al_2O_3 向 α-Al_2O_3 的转变，且有 TiO_2 相析出。

关键词：Al_2O_3−13%TiO_2；纳米粉末；纳米涂层；相变

(Edited by Hua YANG)