Phase evolution of plasma sprayed $\text{Al}_2\text{O}_3-13\%\text{TiO}_2$ 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 $\text{Al}_2\text{O}_3-13\%\text{TiO}_2$ (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 $\text{Al}_2\text{O}_3-13\%\text{TiO}_2$ 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 $\text{Al}_2\text{O}_3$ retains the same $\alpha$ phase as the raw material during sintering, while $\text{TiO}_2$ changes from anatase to rutile. During plasma spraying, some $\alpha-\text{Al}_2\text{O}_3$ phases solidify to form metastable $\gamma-\text{Al}_2\text{O}_3$, and the volume fraction of $\alpha-\text{Al}_2\text{O}_3$ 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 $\gamma-\text{Al}_2\text{O}_3$ or $\chi-\text{Al}_2\text{O}_3\cdot\text{TiO}_2$ phase. After heat treatment, $\gamma-\text{Al}_2\text{O}_3$ in the coatings transforms to $\alpha-\text{Al}_2\text{O}_3$, and rutile is precipitated.

Key words: $\text{Al}_2\text{O}_3-13\%\text{TiO}_2$; 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$_2$O$_3$−TiO$_2$ ceramic coatings show much higher wear resistance than the conventional Al$_2$O$_3$−TiO$_2$ coatings [6−8].

The plasma sprayed Al$_2$O$_3$−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$_2$O$_3$−13%TiO$_2$ nano-crystalline powder and as-sprayed coatings. In the present study, nanostructured Al$_2$O$_3$−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 $\alpha$-Al$_2$O$_3$ 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
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$_2$O$_3$–13%TiO$_2$, and sintering at high temperature (700–1200 °C).

<table>
<thead>
<tr>
<th>Table 1 Performance parameters of nanopowders</th>
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<td>Raw material</td>
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<td>Al$_2$O$_3$</td>
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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$_2$O$_3$–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$_\alpha$ 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$_2$O$_3$–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 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$_2$O$_3$ particles.

SEM images of agglomerated Al$_2$O$_3$–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
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$_2$O$_3$–13%TiO$_2$ nanocrystalline powders before and after sintering. It can be seen that Al$_2$O$_3$ 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 agglomerated Al$_2$O$_3$–13%TiO$_2$ nanocrystalline powders during plasma spraying, various spraying parameters (CPSP) were taken. Figure 4 shows the XRD patterns of the nanostructured Al$_2$O$_3$–13%TiO$_2$ coatings sprayed at different CPSP. It can be seen that during plasma processing, the stable α-Al$_2$O$_3$ phase rapidly solidifies to form metastable γ-Al$_2$O$_3$, since γ-Al$_2$O$_3$ forms more easily from the melt than α-Al$_2$O$_3$ at a high cooling rate because of the low interfacial energy between crystal and liquid [14]. Moreover, peaks of α-Al$_2$O$_3$ and γ-Al$_2$O$_3$ 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$_2$O$_3$ [10], so the peak of α-Al$_2$O$_3$ 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$_2$O$_3$ is negligible, Ti ions are
likely to be in the $\gamma$-$\text{Al}_2\text{O}_3$ 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 $\gamma$-$\text{Al}_2\text{O}_3$ or $\chi$-$\text{Al}_2\text{O}_3$·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 $\alpha$-$\text{Al}_2\text{O}_3$ (113) peak, which is the main peak of $\alpha$-$\text{Al}_2\text{O}_3$, decreases, while the intensity of $\gamma$-$\text{Al}_2\text{O}_3$ (400) peak increases. According to the results of XRD diffraction, the relative contents of $\alpha$-$\text{Al}_2\text{O}_3$ and $\gamma$-$\text{Al}_2\text{O}_3$ in nanostructured Al$_2$O$_3$–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 $\alpha$-$\text{Al}_2\text{O}_3$ decreases, conversely, the volume fraction of $\gamma$-$\text{Al}_2\text{O}_3$ 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.

Figure 6 presents SEM images of the cross-section of the nanostructured Al$_2$O$_3$–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,
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.

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

It was reported that $\gamma$-$\text{Al}_2\text{O}_3$ in as-sprayed $\text{Al}_2\text{O}_3$–13%$\text{TiO}_2$ coatings is a metastable phase, and it can easily transform to $\alpha$-$\text{Al}_2\text{O}_3$ in a certain environment or heat treatment process [13]. It can be seen from Fig. 8 that, when the $\text{Al}_2\text{O}_3$–13%$\text{TiO}_2$ nano coatings were heat treated at different temperatures, the diffraction peak of $\alpha$-$\text{Al}_2\text{O}_3$ stable phase were significantly enhanced, while the diffraction peaks of $\gamma$-$\text{Al}_2\text{O}_3$ metastable phase were relatively weakened, and the diffraction peaks of rutile phase appeared, indicating that certain amount of $\gamma$-$\text{Al}_2\text{O}_3$ transformed to $\alpha$-$\text{Al}_2\text{O}_3$ and $\text{TiO}_2$ 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 $\alpha$-$\text{Al}_2\text{O}_3$ (113) to $\gamma$-$\text{Al}_2\text{O}_3$ (400) ($I_{\alpha, 113}/I_{\gamma, 400}$), is, and the more the $\gamma$-$\text{Al}_2\text{O}_3$ transforms to $\alpha$-$\text{Al}_2\text{O}_3$. Then the greater stress will be induced, so that the coating will show a worse performance of thermal shock [15].

4 Conclusions

1) Agglomerated $\text{Al}_2\text{O}_3$–13%$\text{TiO}_2$ nanocrystalline powders were prepared by spray drying, and $\text{Al}_2\text{O}_3$ retained the same $\alpha$ phase as the raw material during sintering, while $\text{TiO}_2$ 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 $\text{Al}_2\text{O}_3$–13%$\text{TiO}_2$
feedstocks were plasma sprayed on the steel, some α-Al2O3 solidified to form metastable γ-Al2O3, and the volume fraction of α-Al2O3 decreased as CPSP increased. However, the peaks of TiO2 phase were not observed from the as-sprayed coatings except for the coatings sprayed at the lower CPSP. As the CPSP increased, nanostructured TiO2 was be dissolved easily in γ-Al2O3 or α-Al2O3-TiO2 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-Al2O3 in the coatings transformed to α-Al2O3, and rutile will be precipitated.

References


