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Solution precursor high-velocity oxy-fuel spray ceramic coatings

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Abstract

For the first time, the solution precursor high-velocity oxy-fuel spray process was used to deposit Al_2O_3–ZrO_2 ceramic coatings. X-ray diffraction analysis and transmission electron microscopy characterization show that the as-sprayed coating is composed of mixed nanocrystalline ZrO_2 and γ-Al_2O_3 as well as amorphous phases. The as-sprayed coating consists of ultrafine splats with diameters ranging from 2 to 5 μm. Few spherical particles, hollow-shell structures are also observed on the coating surface. Polished cross-section shows that the coating is quite dense with a thickness of 40 μm.

Keywords: Alumina; Zirconia; HVOF; Solution precursor spray

1. Introduction

Thermal spray is an effective and flexible method to produce thick coatings (from microns to millimeters) and has been used extensively in aerospace, pulp and paper, machinery manufacturing, petroleum and petrochemical industry, biomedical applications, etc.[1] The plasma spray and high-velocity oxy-fuel (HVOF) spray processes are the most widely used methods to produce a thick coating. Compared to plasma spray, the HVOF spray process produces significantly higher impact velocities (∼800 m/s), but with lower flame temperatures (3000 K).[1] The high velocity impact typically results in superior dense and hard coatings.[2–8] For example, the hardness and toughness of HVOF sprayed alumina/titania ceramic coatings are higher than those of the plasma sprayed coatings.[7] However, the significantly low temperature of the HVOF jet typically only allows processing of metals, cements and low melting point ceramics materials.

In both the plasma spray and HVOF spray process, powders with some specific features are often used as feedstock. Recently, the solution precursor plasma spray (SPPS) process has been successfully developed to deposit highly durable thermal barrier coatings,[9,10] dense ceramic coatings[11] as well as bioactive coatings.[12] In the SPPS process, liquid-precursor solutions instead of powder are injected directly into the plasma jet. The atomized droplets undergo a series of physical and chemical reactions prior to deposition on the substrate as a coating. Similar to the SPPS process, solution precursor can also be injected into a high-velocity oxy-fuel (HVOF) flame to obtain coatings. Since the solution precursors are molecularly mixed, more uniform phase composition and properties are expected in the as-sprayed coatings. The solution precursor HVOF process may offer several advantages over the conventional HVOF method, such as circumvention of the powder-feedstock preparation step, better control over the chemistry of the deposit and deposition of nanostructured coatings.

Alumina–zirconia composites have gained wide applications as structural ceramics or protective coatings due to their excellent mechanical and thermal properties.[13–15] In the Al_2O_3–ZrO_2 binary system, there is a eutectic with composition of Al_2O_3–40wt%ZrO_2 at 1880 °C. Because the eutectic temperature is lower than the melting points of pure zirconia (∼2700 °C) and pure alumina (∼2100 °C), the droplets with this eutectic composition will be easily melted/softened compared to the pure zirconia and alumina in the low temperature HVOF flame. In this research, Al_2O_3–ZrO_2 coating with eutectic composition was deposited using the solution precursor HVOF process. The phase composition and microstructure of the as-deposited coating were investigated.

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Table 1
Parameters of solution precursor HVOF spraying Al_2O_3–ZrO_2 coating.

Parameters	Value
Propylene flow (SLPM)	85
Oxygen flow (SLPM)	152
Air flow (SLPM)	384
Gun traverse speed (mm/s)	750
Liquid feed rate (ml/min)	15
Standoff distance (cm)	17.5
No. of pass deposited	40

2. Experimental procedures

2.1. Precursor

The precursor is an aqueous solution containing aluminum, yttrium, and zirconium salts that are mixed based on molar volumes to produce a ceramic composition of Al_2O_3–40wt% 7YSZ (7 wt% Y_2O_3).

2.2. HVOF spray

The HVOF torch used here is the DJ-2700 hybrid (Sulzer Metco, Westbury, NY, USA), which is attached to a six-axis robotic arm. Propylene and oxygen are used as the fuel gas and oxidant gas, respectively. The solution precursor was axially injected into the combustion chamber of HVOF system. The coating was deposited on type 304 stainless steel substrates (disks 25 mm diameter, 3 mm thickness), surfaces of which were previously roughened by grit blasting (Al_2O_3 grit of #30 mesh size). The spraying parameters are presented in Table 1.

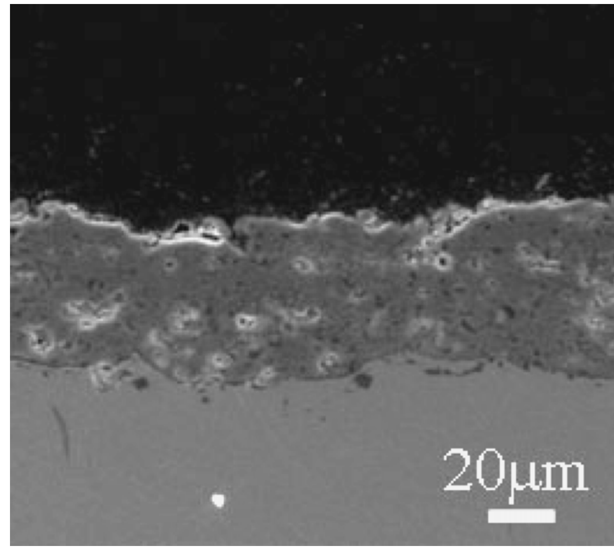

Fig. 1. Polished cross-section of the as-sprayed coatings.

2.3. Characterization

The phase composition of the as-sprayed coating was determined using X-ray diffraction (XRD, Cu Kα radiation; D5005,

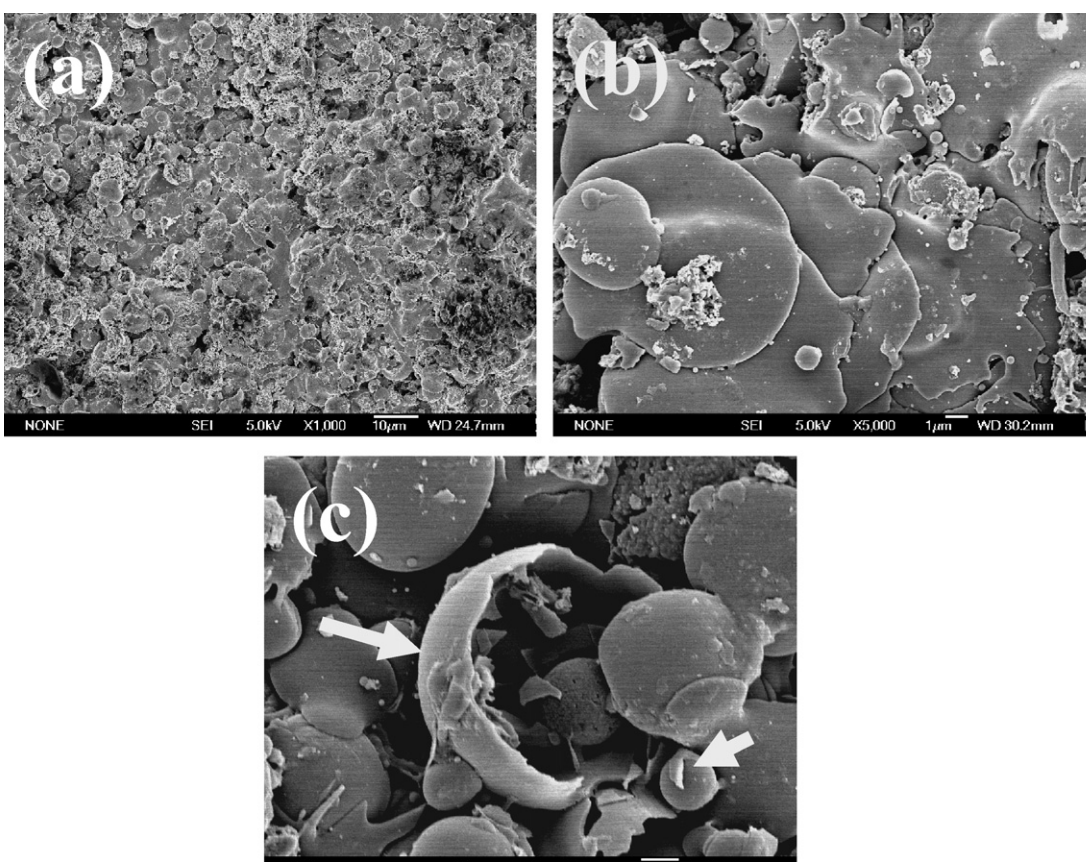

Fig. 2. Surface morphologies of the as-sprayed coating: (a) low magnification; (b and c) high magnification of different morphologies observed at the coating surface.

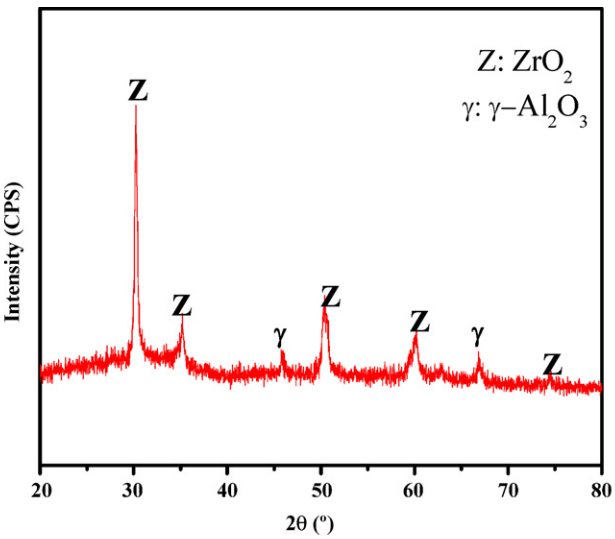

Fig. 3. XRD pattern of the as-sprayed coating.

Bruker AXS, Karlsruhe, Germany). The XRD patterns were collected in a 2θ range from 20° to 80° with a scanning rate of $2^{\circ}\,\mathrm{min}^{-1}$.

An environmental scanning electron microscope (ESEM 2020, Philips Electron Optics, Eindhoven, The Netherlands) and a JEOL JSM-6335F field emission scanning electron microscope (FESEM, Tokyo, Japan) were used to characterize the coating microstructure. Coating microstructures were also observed in a transmission electron microscope (JEOL JEM 2100F TEM) equipped with energy dispersive X-ray spectroscopy (EDS) capabilities. TEM specimen was prepared by crushing the coating and dispersing the resulting particles onto carbon-coated copper grids.

3. Results and discussion

In the solution precursor HVOF process, 40 coating scans were carried out. A typical polished cross-section of the as-sprayed Al_2O_3–ZrO_2 coating is shown in Fig. 1. The coating is quite dense with a thickness of ∼40 μm. There are no cracks in the as-sprayed coating. The coating is well bonded to the substrate. In addition, there are no coarse splat boundaries or layered structures through the coating.

Fig. 2a–c shows the representative surface morphologies of the as-sprayed coating. The coating is mainly composed of pancake-like ultrafine splats with diameters ranging from 2 to 5 μm (Fig. 2b), which are about ten times smaller than the splats (30–50 μm) in conventional HVOF coatings.[8] Few spherical particles as well as the hollow-shell structures are also observed on the coating surface (arrows indicated in Fig. 2c). Because there is no atomizing process during delivering the liquid into the HVOF system, the formed fine splats and solid particles during HVOF spray process clearly indicated that the liquid precursor undergoes significant in situ break-up and forms small droplets in the high velocity HVOF flame. In addition, these splats and spherical particles clearly indicate that the liquid droplets have experienced the solvent evaporation, pyrolysis, melting/semi-melting and solidification process in the HVOF flame jet. When these molten/semi-molten particles impacted on the substrate with high velocity, they will spread and form the splats. About the formation of fractured hollow-shell structure, a model has been developed based on aerodynamic droplet break-up, evaporation of droplets and solute precipitation.[16] It indicates that solute precipitates begin near the droplet surface when the saturation concentration is reached. The high solute concentration precipitates developed near the surface of the droplet is likely to form a thin layer shell. Since the shell will prevent further evaporation, consequently, vapor buildup inside the droplet due to subsequent heating leads to inflate and rupture.

Fig. 3 shows the XRD pattern of the as-sprayed coating. The coating is composed of ZrO_2 and γ-Al_2O_3 crystalline phases. There is no α-Al_2O_3 phase identified. However, the broad and weak peaks imply poor crystallinity. As is well established, γ-Al_2O_3 is one of the intermediate phases formed when alumina is melted. Upon rapid cooling from the melting temperature of alu-

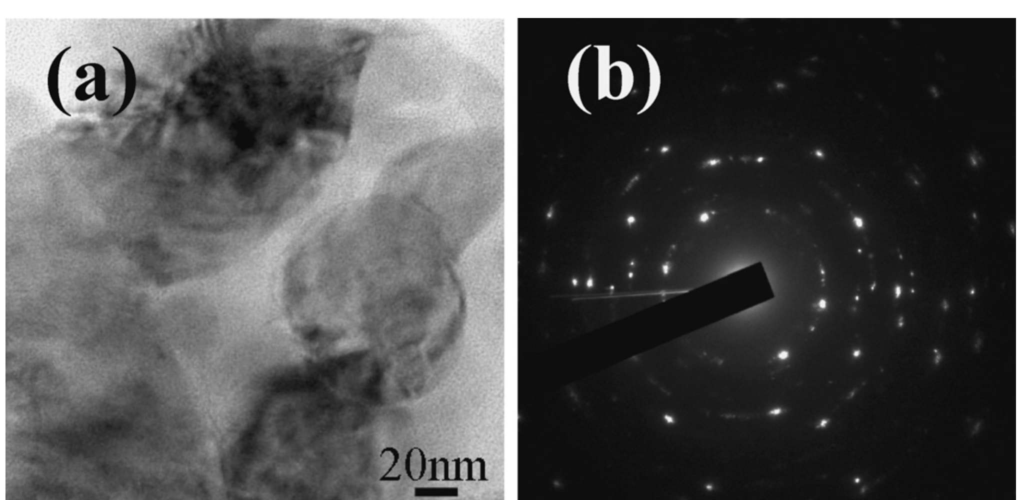

Fig. 4. (a) TEM bright-field image of the as-sprayed coating showing the fine nanostructure region; (b) the SAEDP confirms the t-ZrO_2 and γ-Al_2O_3 phases.

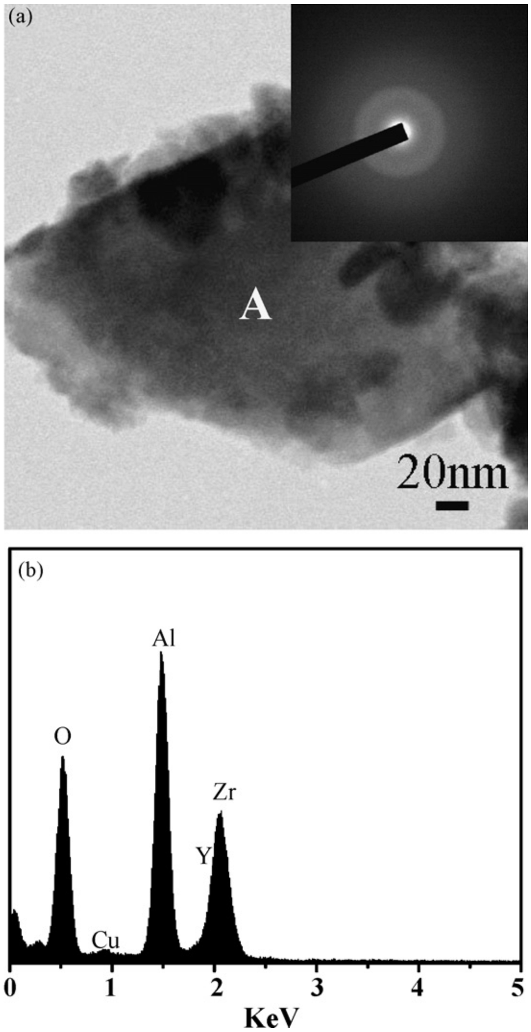

Fig. 5. (a) TEM bright-field image of the as-sprayed coating showing the amorphous region A, inset is the SAED pattern of region A; (b) EDS spectrum on region A.

mina, γ-Al_2O_3 nucleates first over α-Al_2O_3; therefore, γ-Al_2O_3 typically appears in the thermally sprayed alumina coatings.[5,17]

Fig. 4a is a TEM bright-field image of the as-sprayed coating showing its polycrystalline nature with an average grain size of ~20 nm; the corresponding selected area electron diffraction pattern (Fig. 4b) indicated that the nanocrystallites are t-ZrO_2 and γ-Al_2O_3 phases. However, in the as-sprayed coatings, some amorphous phases are also observed. Fig. 5a is a bright-field TEM image of a region (region A in Fig. 5) within the as-sprayed coating showing the presence of amorphous structure, which is evidenced by the selected area electron diffraction pattern (inset in Fig. 5a). Results of chemical analysis by EDS indicated that the amorphous region is composed of Al, Zr elements (Fig. 5b). The above TEM investigation indicated that both ZrO_2 and Al_2O_3 exist in the form of crystalline and amorphous states in the as-sprayed coating.

The formation of mixed nanocrystalline and amorphous microstructure in the as-sprayed coatings can be ascribed to the high cooling rate of HVOF process. It is estimated that the cooling rate of the HVOF splat is on the order of between 10^8 and 10^{10} K/s.[18] The rapid cooling rate causes the molten/semi-molten particles solidify very quickly and they do not have enough time to finish the complete crystallization process. Therefore, some amorphous structures are observed in the as-sprayed coating. Actually, amorphous Al_2O_3 phase in the HVOF sprayed Al_2O_3 splats was also observed by Li et al.[18]; in their experiment, it was confirmed that most of alumina splats displayed full amorphous or mixed amorphous nanocrystalline microstructure due to the rapid cooling of molten particles.

4. Conclusions

In summary, it has been demonstrated experimentally that nanostructured dense ceramic coating could be manufactured using the novel solution precursor high-velocity oxy-fuel spray process. In the as-sprayed Al_2O_3–ZrO_2 composite coatings, the liquid precursor droplets experience extensive break-up, solvent evaporation, pyrolysis, and melting/semi-melting in the HVOF flame and form ultra fine splats (2–5 μm) upon impacting on the substrate. The as-sprayed coating is composed of mixed amorphous and nanocrystalline microstructure.

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