Novel structured yttria-stabilized zirconia coatings fabricated by hybrid thermal plasma spraying

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Abstract

Yttria-stabilized ZrO$_2$ powders with initial sizes of 5–22 μm were chosen as feedstock for hybrid thermal plasma deposition. At 100 kW RF input power, the microstructures of the deposited coatings varied from mostly sprayed splats to physical-vapor-deposited nanostructures when the powder feeding rate was reduced from 4 to 1 g/min. At a powder feeding rate of 2 g/min, a peculiar layered coating consisting of both structures was deposited at a rate over 50 μm/min, which is promising for the fabrication of next-generation novel thermal barrier coatings.

Keywords: Plasma physical vapor deposition; Plasma spraying; Thermal barrier coatings; Hybrid plasma

1. Introduction

In the field of thermal barrier coating (TBC) technology, two main processing methods have been adopted over the last decade. One is vapor deposition, which includes EB-PVD (electron-beam physical vapor deposition), PE-CVD (plasma enhanced chemical vapor deposition), and LCVD (laser chemical vapor deposition). The other is molten particle deposition, typically, APS (atmospheric plasma spraying). TBCs made by the former method are characterized by columnar microstructures while splat structures are common in those deposited by APS. Due to this structural difference, the thermal and mechanical properties of such TBCs vary considerably, as summarized in Table 1 [1–3].

The vapor-deposited TBCs have the following merits: (1) excellent strain tolerance; (2) excellent surface finish; (3) good erosion resistance; and (4) relatively long lifetime. However, these merits are gained at the expense of rather high thermal conductivity and high production cost [3–6]. On the other hand, molten-particle-deposited TBCs exhibit: (1) the lowest thermal conductivity and (2) high processing efficiency and low cost, but are not very durable [7]. Each of these two methods has its own unique strong points and shortcomings. Therefore, a new process which is able to combine all the merits would be of high interest.

Although many materials have been thought to be promising for TBCs [8], Y$_2$O$_3$-stabilized ZrO$_2$ (YSZ), owing to its unique thermal and mechanical properties, has been found to be the best material choice to date. A suit of desirable properties which YSZ possesses includes: (i) one of the lowest thermal conductivities at elevated temperature among all ceramics (~2.3 W/mK at 1000 °C for a fully dense material [9]) because of its high concentration of point defects [10]; (ii) a high thermal-expansion coefficient (~11 × 10$^{-6}$/°C similar to that of the underlying metal (~14 × 10$^{-6}$/°C)), which helps to alleviate the stress arising due to thermal expansion mismatch; (iii) a high melting point (2700 °C) suitable for high-temperature applications; (iv) a relatively low density (6 g/cm$^3$), which is important for aerocraft and rotating engines; and (v) a hardness of ~14 GPa, which makes it resistant to erosion and foreign body impact.

Hybrid thermal plasma, composed of radio-frequency plasma together with a direct-current plasma jet mounted on the torch, has merits such as large plasma volume, high uniformity and stability. It has been intensively investigated by Yoshida [11–13] and has been proven to be a powerful method for various types of thermal plasma spraying.
In this study, an interest has been focused on depositing novel nanostructure YSZ coatings suitable for TBCs at a high rate and high efficiency using hybrid thermal plasma.

2. Apparatus and experimental procedure

Fig. 1 shows the schematic diagram of the experimental apparatus. Substrates are positioned in stages at different heights on a high-speed rotatable substrate holder. With the rotation of the substrate holder, the substrates can pass through the hybrid plasma flame cyclically, thus enabling deposition on all the different substrates in one experiment. The height of the stages can be adjusted and the whole substrate holder can also be raised or lowered to control the distance between the substrates and the exit of the hybrid plasma torch in the range of 0–250 mm. In this paper, the distances from the substrate to the torch exit were set to 10, 20, 30, 40 and 50 mm. The details of the hybrid plasma torch involved in this study are shown in Fig. 2. Table 2 lists the specifications of this hybrid plasma torch. The feedstock powders are fed into the plasma at the center of the torch, which helps to produce a homogeneous thermal history for each particle.

SUS304 stainless steels of 25 mm × 25 mm × 4 mm and Inconel768 of 25 mm × 25 mm × 4.5 mm were mainly used as substrates. Pretreatments such as sand blasting were not performed. Commercial NiCoCrAlY powder (Amperit® 415.6, 44–125 μm, H.C. Starck, Germany) was first sprayed onto the substrates as a bond coat, and then 8YSZ powder (Amperit® 825.09, 5–22 μm, H.C. Starck, Germany) was sprayed when the substrate was heated to the prescribed temperature. The typical experimental

Table 1
Properties of TBCs at room temperature

| Property/characteristic          | EB-PVD | PE-CVD | LCVD | APS |
|----------------------------------|--------|--------|------|-----|
| Thermal conductivity (W/mK)      | 1.5–1.9| 2      | 0.8–1.1| |
| Surface roughness (μm)           | 1      | 10     |      |   |
| Adhesive strength (MPa)          | 400    |        | 20–40|    |
| Young’s modulus (GPa)            | 90     | 200    |      |    |
| Growth rate (μm/h)               | 200–300| 250    | 600  | 10,000|
| Production cost                   | High   | High   | High | Low |

Table 2
Specifications of the hybrid plasma system

| Property                        | Specification |
|---------------------------------|---------------|
| Power input                     | DC power: 15 kW; RF power: 150 kW |
| Torch                           | Water cooled: 80 l/min; inner tube: Si₃N₄, H = 150 mm, Dia. = 60 mm; outer tube: quartz, H = 130 mm, Dia. = 80 mm; RF coil: copper tube, 3-turns, 14 mm; Dia. = 84 mm; H = 55 mm |
| Plasma gas                      | Pure O₂: 100–300 SLM; Ar + H₂: 80 + 40 |
| Vacuum system                   | SLM (at 100 kW) |
| flow rate                       | 1200 l/s; water circulation pump: 2500 l/s × 2 |
| Substrate holder                | SiC coated graphite, 410 mm; rotating speed: ~200 rpm |
parameters are shown in Table 3. The microstructures of the prepared coatings were analyzed using field-emission scanning electron microscope (FE-SEM) and transmission electron microscope (TEM). The phase structure and grain size were identified by X-ray diffractometry.

3. Experimental results

3.1. Effects of powder feeding rate

Fig. 3 shows the FE-SEM image of the 8YSZ powder used in this study. The size distribution concentrates between 10 and 15 μm, as listed in Table 4.

Fig. 4(a)–(c) show the cross-sections of the coatings deposited at different powder feeding rates with the RF input power at 100 kW. At a relatively high powder feeding rate of 4 g/min, the coating was composed mostly of splats (Fig. 4(a)), which indicates that almost all of the injected powder was completely melted and deposited as liquid state. In contrast, when the powder feeding rate was lowered to 1 g/min, splats disappeared. Instead, nanostructures of particles were dominant (Fig. 4(c)), which was the result of vapor deposition by thermal plasma PVD. This kind of microstructure change clearly indicates that the powder feeding rate can significantly affect the plasma conditions. With increasing powder feeding rate, the plasma is cooled and the process can be changed from thermal plasma PVD to thermal plasma powder spraying. On the basis of this point of view, it is not surprising that when the powder feeding rate was 2 g/min, a peculiar layered structure was achieved (Fig. 4(b)). The sprayed splats are in the matrix of the PVD structures. The periodicity of the layer is 0.2–1 μm, the thickness of the columns are 100–500 nm and the width of each column is around 100 nm, which can be seen more clearly in the TEM micrograph in Fig. 5. Typical columnar grain microstructures can be seen in the splats (marked A and B), while the columns of the PVD structure consist of small spherical particles with the size of several tens of nanometers. Many pores also exist in the PVD section. Such a nanoporous matrix is promising for improving both the coating strain tolerance and thermal

![Fig. 3. FE-SEM micrograph of the initial YSZ powder.](image)

![Fig. 4. Cross-sections of the coatings deposited at different powder feeding rate: (a) 4 g/min; (b) 2 g/min; (c) 1 g/min.](image)

Table 3

| Typical experimental conditions |
|--------------------------------|
| (1) Gas flow rate (SLM): DC arc jet = 10; Ar radial sheath = 140; Ar tangential sheath = 30; H2 radial sheath = 30; carrier = 4 |
| (2) Powder injection rate = 0.1–4 g/min |
| (3) Deposition distance = 10–70 mm |
| (4) RF plate power output = 100 kW |
| (5) DC power supply = 8 kW |
| (6) Chamber pressure = 300–500 Torr |

Table 4

| Powder size distribution of Amperit® 825.090 |
|---------------------------------------------|
| Size (μm) | 5.5 | 10 | 15 | 22 |
| Percentage (%) | 13 | 64 | 92 | 100 |
performance, and the splats prevent the heat flux from passing through the channels between the PVD columns easily, and can act as thermal radiation shields. Fig. 6 shows the XRD spectra of the initial powder and the coating deposited with the powder feeding rate at 1 g/min. The spectra show that the monoclinic phase has been transformed to the tetragonal phase after deposition. On comparing the two spectra, no texture is observable in the deposited coating.

Comparing Fig. 4(a) and (b), the PVD structure increases in Fig. 4(b) in conjunction with thinner splats. This is further evidence that better evaporation occurred at the lower powder feeding rate. We should also note that the PVD structure in Fig. 4(b) is less dense than that in Fig. 4(c). With the powder feeding rate of 2 g/min, the PVD structure between splats exhibits columnar structure, although in the columns, fine structure is still spherical. When the powder feeding rate is 1 g/min, the PVD structure is mostly nanoparticles. This means that although the powder feeding rate is higher at 2 g/min, the concentration of YSZ vapor is lower than that at 1 g/min. At a higher YSZ vapor concentration, more clusters are first formed and then deposited on the substrates, leading to a dense nanoparticle structure. At an even lower powder feeding rate of about 0.3 g/min, the columnar structure appears again, as shown in Fig. 7. However, the fine structures of the columns still exhibit elliptical shapes instead of polygons, which is a clue to cluster deposition.

3.2. Growth process of the nanocolumns on splats

Fig. 8(a)–(c) show different parts of the surface of the coating deposited with a powder feeding rate of 2 g/min. Fig. 8(a) reveals a clear splat surface with grain boundaries clearly being seen. Fig. 8(b) shows that some nucleation has occurred at the surface, and in Fig. 8(c), the splat has been covered by the PVD structure and the grains have grown larger to about 100 nm.

Fig. 9 shows the surface morphology of the deposited coating where two splats overlap. The PVD grains on the lower splat are larger than those on the higher one, which indicates that they grew for a longer time. This means that at the powder feeding rate of 2 g/min, when the substrate rotates through the plasma, splats do not cover the whole surface of the substrate in one turn, whereas PVD structure continues to grow in each turn. Therefore, different parts of the surface reveal different stages of growth morphology of the PVD structures as shown in Fig. 10.

3.3. Effect of deposition distance

Fig. 10 shows the surface morphology of the deposited coating where two splats overlap. The PVD grains on the lower splat are larger than those on the higher one, which indicates that they grew for a longer time. This means that at the powder feeding rate of 2 g/min, when the substrate rotates through the plasma, splats do not cover the whole surface of the substrate in one turn, whereas PVD structure continues to grow in each turn. Therefore, different parts of the surface reveal different stages of growth morphology of the PVD structures as shown in Fig. 10.

Fig. 7. Cross-section of the coating deposited at a powder feeding rate of 0.3 g/min.
substrate-to-torch distances, while the thickness decreased slightly with increasing distance, as shown in Fig. 11. The thickest totally thermal plasma PVD coating with a thickness of 50 μm was prepared at a distance of 10 mm in 15 min. Considering the rotation of the substrate, this means that the growth rate over 50 μm/min was achieved, which is about 10 times faster than that by usual EB-PVD. This is because in thermal plasma PVD, the vapor of YSZ is mainly directed to the substrate by the plasma flame, while in low-pressure vapor deposition, such as EB-PVD, the vapor disperses throughout the whole chamber.

4. Conclusion

Experiments of small particle YSZ deposition by hybrid thermal plasma reveal that the powder feeding rate plays an important role in heat transfer between plasma and particles. When the powder feeding rate was reduced from 4 to 1 g/min at 100 kW power input, the process changed from plasma powder spraying to plasma PVD. At the powder feeding rate of 2 g/min, both spraying and PVD occurred, which led to a peculiar layered structure with a periodicity of 0.2–1 μm. This kind of structure is promising for combining both low thermal conductivity and good mechanical properties in TBCs. The results of X-ray diffraction reveal that the thermal plasma PVD nanostructured YSZ coating was composed of tetragonal phase. The growth rate of the coatings deposited by thermal plasma PVD is over 50 μm/min, which is 10 times faster than that
by the conventional EB-PVD process. These results suggest that the use of hybrid thermal plasma is a powerful method for the fabrication of novel TBCs.

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