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Technical Note

Microstructure of Plasma Sprayed La_2O_3-Modified YSZ Coatings

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Yttria-stabilized zirconia (YSZ) has received great attention as a thermal barrier coating (TBC) material for its excellent thermal and mechanical properties. However, the grain growth of YSZ, particularly under temperatures higher than 1200 °C, limits its further applications to a great extent. In our present study, to develop better understanding of the aforementioned phenomenon and explore effective methods to conquer this challenge, TBCs using traditional and La_2O_3-modified YSZ powders were deposited by atmospheric plasma spraying and their microstructures were investigated. The results show that the La_2O_3 addition can effectively alleviate the grain growth of coatings under high temperatures.

Keywords grain growth, heat treatment, microstructure stability, plasma spray, thermal barrier coating

1. Introduction

State-of-the-art aircraft and industrial gas turbine engines should operate at as high temperature as possible to maximize their thrust and fuel efficiency. However, the limits of melting point of hot path alloy components in turbines make increasing the temperature difficult. This problem can be facilitated by three principal methods: improved alloy design, cooling by air flow through internal channels cast into the component, and usage of thermal barrier coatings (TBCs), which is generally considered to be the most economic and feasible method (Ref 1-3).

TBCs are widely applied on transition pieces, combustion liners, first-stage blades and vanes, combustion chambers, and other hot-path components of gas turbines to enable modern gas turbine engines to operate at gas temperatures well above the melting temperature of the super alloy, thereby improving engine efficiency and performance without increasing the surface temperature of the alloy or reducing the requirements for the cooling system. Along with internal cooling of the underlying super alloy component, a 250 μm thick TBC can reduce the average metal temperature by 111 to 167 °C (Ref 4). As a result, it helps to extend the life of alloy components in the hottest sections in an engine (Ref 5-7). Being exposed to extremely aggressive thermal and mechanical environment, TBCs should meet several performance constraints, such as relatively low thermal conductivity and a thermal expansion coefficient comparable to that of the substrate. The coatings should avoid phase transformation during cycling between room temperature and operation temperature. Another less stringent but nevertheless rather practical requirement is that the coating material is thermodynamically compatible with the oxide formed by oxidation of the bond coat. Also, some other factors need to be considered and explored such as high melting point, chemical inertness to the combustion gases, and low sintering rate of the porous microstructure (Ref 1). Among all the requirements for TBC materials, thermal expansion coefficient and low thermal conductivity seem to be the most important (Ref 2). The number of materials that can be used as TBCs is very limited. So far, only a few materials have been found to basically satisfy these requirements (Ref 6).

Yttria-stabilized zirconia (YSZ) possesses a suite of desirable properties that make it proven to be a highly durable TBC material. It is likely to remain the material of choice for turbines with current operating temperatures. First, of all ceramics, YSZ has one of the lowest thermal conductivities at elevated temperature and a relatively high thermal expansion coefficient. Second, it has a relatively low density, which is important for parasitic weight considerations in rotating engine components. It also is resistant to ambient and hot corrosion. Finally, YSZ has a high melting point (2700 °C), making it suitable for high-temperature applications (Ref 5). One of the striking findings from the numerous studies is that yttria-stabilized zirconia coatings containing 7-8 mol% $YO_{1.5}$ having the

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tetragonal-prime structure exhibited the longest lifetime under thermal cycling (Ref 8).

However, a major disadvantage of YSZ is its limited operation temperature (<1200 °C) for long-term application. At higher temperatures, sintering occurs, giving rise to changes in coating morphology and performance. There are two principal concerns. One is that sintering inevitably increases the elastic modulus and thereby decreases the strain compliance of the coating. At the present stage in development, the reduction in strain compliance would generate very large stresses and lead to spontaneous failure on cooling. The other is that densification decreases the volume fraction of porosity, which, in turn, causes the thermal conductivity to increase (Ref 8). So suppressing sintering would be a big challenge in the development of YSZ coatings. Several efforts were made to stabilize the coating microstructural morphology under high temperature (Ref 2, 9). M. Matsumoto and his co-workers (Ref 9) reported that the addition of rare earth oxides could develop TBCs with high resistance to sintering and La_2O_3-containing YSZ coatings have a greatly reduced thermal conductivity as well as high structural stability. A better understanding of the dopant effects will help to develop advanced sintering-resistant TBC coatings in the future. In our present work, TBCs were plasma sprayed using lanthana precursor coated YSZ powders as feedstocks and the effects of lanthana on the sintering process and grain growth of YSZ were evaluated.

2. Experimental Procedures

Commercially available 7-8YSZ (7-8wt.% YSZ) powder and lanthanum nitrate (99% pure) were used as starting materials. The commercial powders have a particle size range of 20-40 μm. YSZ powders were coated with lanthana precursor through a wet chemical method. Commercial YSZ powders were dispersed in $La(NO_3)_3$ and urea mixed solution and then sonicated in an ultrasonic cleaner for 10 min to break up the agglomerates. The suspension was heated in a sealed beaker at 90 °C for 30 h with constant stirring to prevent the YSZ powders from settling down or agglomerating. After reactions, the products were then centrifuged and washed with deionized water and ethanol, in turn, followed by drying in an oven at 70 °C for 24 h. The dried powders were subsequently calcined in an alumina crucible at 800 °C in air for 2 h to obtain La_2O_3-coated YSZ powders. The additive of lanthana was fixed at 10 wt.% of YSZ powder.

Both the pure and lanthana-modified YSZ coatings were prepared by using a Metco A-2000 atmospheric plasma spraying equipment with F4-MB plasma gun (Sulzer Metco AG, Rigackerstrasse 16, CH-5610 Wohlen, Switzerland) with Ar and H_2 as plasma gases at a flow rate of 30 and 15 standard liters per minute (slpm), respectively. More details about the spraying parameters are listed in Table 1. The coatings were sprayed about 3 mm in thickness on nickel-based alloy substrates. After deposition, the coatings were mechanically removed from the substrates.

Table 1 Plasma spraying parameters

Parameters	Value
Arc current intensity, A	660
Primary gas (Ar) flow rate, slpm	30
Secondary gas (H_2) flow rate, slpm	15
Spray distance, mm	130
Powder carrier gas flow rate, slpm	4
Injection diameter, mm	1.8

To investigate the effect of heat treatment on the microstructure of coatings, the freestanding coatings were heated at a rate of 5 K/min, followed by a hold time typically of 50 h, and then cooled in the furnace. For morphology and grain growth studies, scanning electron microscopy (SEM) images of the feedstocks and coatings were collected on a JSM 6700F field emission scanning electron microscope (JEOL Ltd., Tokyo, Japan). The option of energy dispersive X-ray spectroscopy (EDS) was used to determine the chemical composition of the powder within the same equipment that was used for SEM. The element distribution of the coatings was determined with an EPMA-8705QH2 electron probe analyzer (Shimadzu Co., Tokyo, Japan). The phase structure was analyzed on a Japan Rigaku D/max 2550V (Rigaku Co., Tokyo, Japan) X-ray diffractometer using Cu Kα ($\lambda = 0.15406$ nm) radiation at 40 kV and 100 mA.

3. Results and Discussions

3.1 Morphology of Feedstock and As-sprayed Coatings

The morphologies of the commercially available YSZ powders and the as-coated powders are shown in Fig. 1, which reveals that the YSZ powders have a smooth and flat surface. Compared with the starting powders, the modified ones have some tiny grains with particles sizes ranging from 50 to 500 nm. The grains were identified as lanthanum precursor by EDS analysis (at the positioned point in Fig. 1b). According to our XRD results and Ref 10, the lanthanum precursor is affirmed to be lanthanum oxycarbonate, which can be decomposed into lanthana above 720 °C.

The surface and cross-sectional morphologies of the two kinds of coatings were extensively investigated in our experiments. As shown in Fig. 2, the La_2O_3-modified YSZ coatings show a typical morphology of as-sprayed APS coatings. It can be seen that there are many pores and microcracks distributed homogeneously in the coatings (Fig. 2a and b). The pores are isolated and most of them are less than 10 μm in diameter, which offers an effective barrier to heat transportation. Figure 2(c) and (d) presents the fractured cross section of the coatings, demonstrating that the coatings consist of splats aligned predominantly parallel to the substrate surface, which can enhance the thermal insulation property of coatings. The splat structures have a thickness of about 3-6 μm with columnar grains of a diameter of about 1 μm. It can be speculated

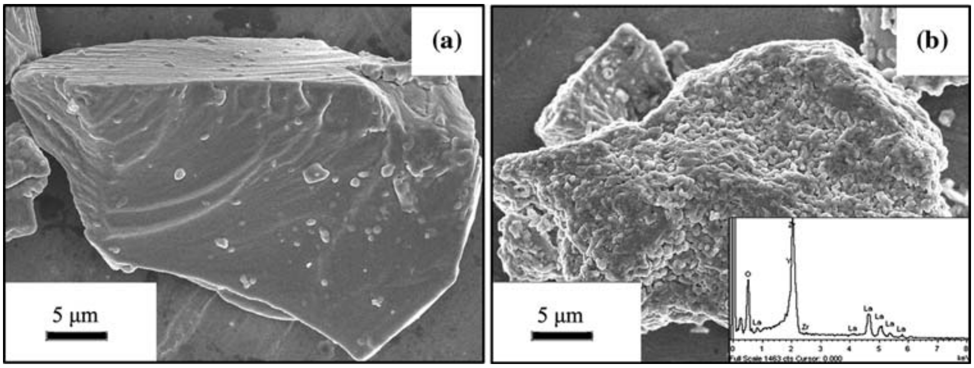

Fig. 1 Morphologies of pure YSZ powders (a) and the modified YSZ powders (b). The inset is EDS profile of A region

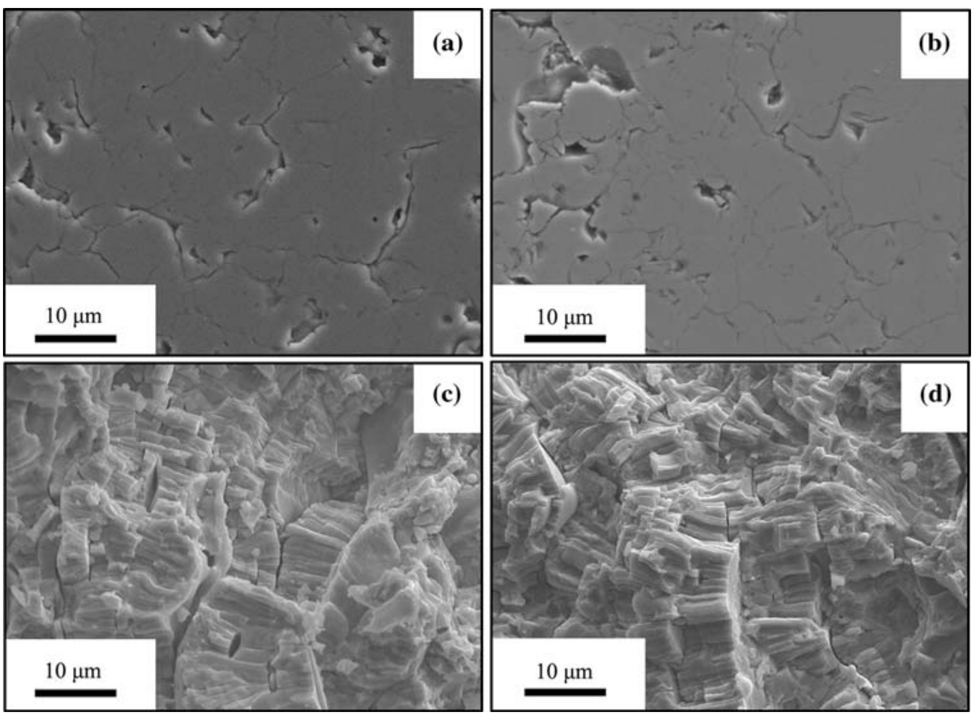

Fig. 2 SEM micrographs of cross section and fractured surface of YSZ coatings (a, c) and lanthana-modified YSZ coatings (b, d)

from the smooth surface perpendicular to the heat flux direction that large pores also exist at the splat boundaries.

3.2 The Effect of Heat Treatment on the Grain Growth of the Coatings

One of the concerns in developing reliable and robust TBCs is how the coating changes during use at high temperatures. Figure 3 and 4 give the SEM micrographs of traditional YSZ coatings and lanthana-modified YSZ coatings after annealing treatment at 1200 °C and 1400 °C for 50 h, respectively. The SEM image reveals that the mean grain size of traditional YSZ coatings aging at 1200 °C for 50 h is about 500 nm with a few abnormal larger ones, whereas a mean grain size under 200 nm was observed for the lanthana-modified YSZ coatings. After annealing at 1400 °C for 50 h, both the kinds of coatings have a grain growth to some degree, but compared with the traditional YSZ coatings, the grains in the lanthana-modified YSZ coatings still have a small grain size distribution and showed a rather slow grain growth rate.

The element of lanthanum probably comprises three kinds of existing state: lanthana, stabilizer dissolved in zirconia, and lanthanum zirconate, which would be formed through the reaction of lanthana and zirconia. The solubility of La_2O_3 in ZrO_2 at equilibrium state is below 1 mol% (Ref 11). There is no visible evidence of $La_2Zr_2O_7$ in the coatings by XRD. Element distribution analysis carried out by electron probe analyzer clearly confirms that a few lanthana particles segregated along the zirconia grain boundaries. As described in the literature

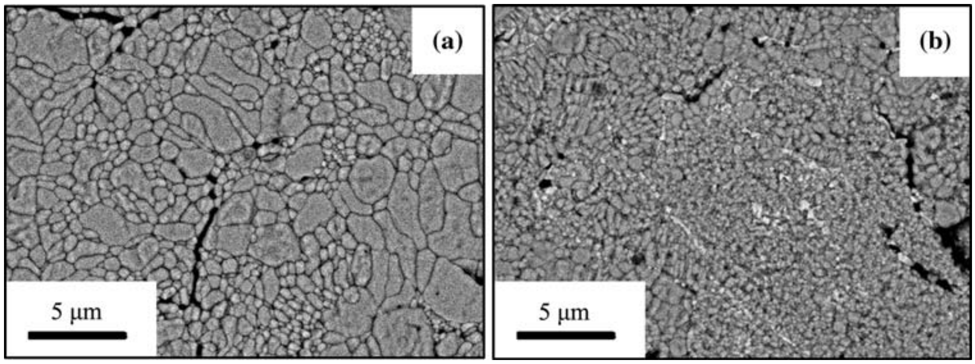

Fig. 3 Microstructures of traditional (a) and La_2O_3-modified YSZ coatings (b) annealed at 1200 °C for 50 h

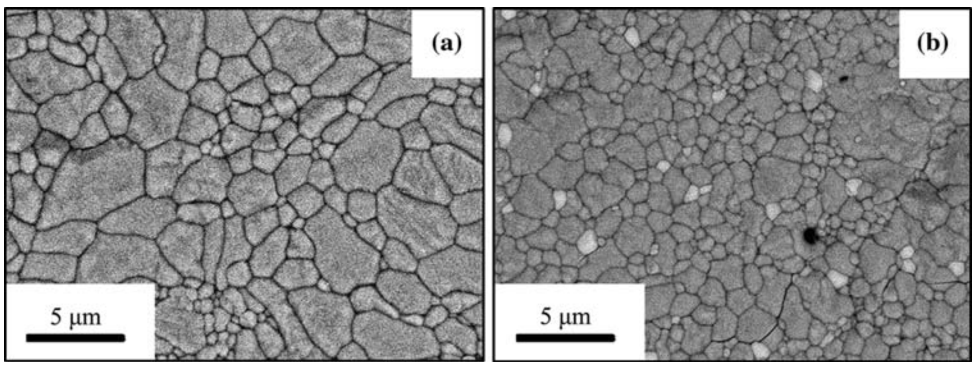

Fig. 4 Microstructures of traditional (a) and La_2O_3-modified YSZ coatings (b) annealed at 1400 °C for 50 h

(Ref 12), trivalent and large cation could segregate on the grain boundaries of zirconia and have a strong effect in suppressing the mobility of grain boundaries and consequently the grain growth. The phenomenon can be satisfactorily rationalized using the space charge concept and the model of impurity drag. This could explain the slow grain growth in the lanthana-modified YSZ coatings under heat treatment.

4. Conclusions

Morphology stability of La_2O_3-modified YSZ coatings under high temperature treatment was investigated. It was revealed that addition of La_2O_3 was effective to suppress the grain growth in TBC. The other thermophysical characterization of the coatings for determining the effects of heat treatment is to be performed and will be reported in our next work.

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