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Thermal barrier coatings from sol–gel-derived spray-grade Y_2O_3–ZrO_2 microspheres

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For the development of ceramic thermal barrier coatings, spray-grade yttria-stabilized zirconia microspheres were prepared by the sol–gel technique. Oxide microspheres were obtained by calcination of the corresponding gel spheres at 1000 °C. Scanning electron microscopic and optical microscopic observations revealed the material thus obtained to have a predominantly spherical morphology and the requisite size distribution (5–50 μm). The dense, calcined microspheres showed good flowability. X-ray diffraction studies indicated the presence of the tetragonal polymorph of ZrO_2 as the major phase, in addition to about 14% monoclinic ZrO_2. The plasma-sprayed YSZ coatings made from the sol–gel-derived microspheres showed a further decrease in the monoclinic ZrO_2 content (6%). The coatings survived 40–50 thermal cycles (30 min at 1200 °C followed by a water quench), indicating good thermal shock resistance.

1. Introduction

Ceramic thermal barrier coatings are being increasingly used for the protection of metal parts which suffer degradation due to corrosion, oxidation or an excessive heat load during service in drastic thermal environments [1–3]. Among the different coating methods, the thermal spraying processes have gained the most widespread industrial application. These methods commonly use ceramic powders directly as the coating material [1, 3, 4]. Atmospheric plasma spraying is a particularly versatile thermal spraying process, and can be used to form protective coatings of any refractory compound [5]. A thermal barrier coating system typically consists of a metallic bond coat in contact with the substrate, and a ceramic overcoat. While the bond coat material should be oxidation/corrosion resistant at the operating temperature, the ceramic material should ideally possess satisfactory characteristics with respect to adherence to the bond coat, thermal stress resistance and stability in the operating environment [2, 4, 6].

Doped zirconia powders are commonly used for the development of thermal barrier coatings because of their low thermal conductivity, relatively high thermal expansion coefficient and excellent chemical resistance [2, 7, 8]. Among the different oxides used as dopants, Y_2O_3 and MgO are the most common for zirconia-based thermal barrier coatings [2, 3]. Y_2O_3-doped zirconia coatings (6–8 wt % Y_2O_3) are used in heat engines and aircraft gas turbines to reduce the substrate temperature, thereby increasing their efficiency [6, 9]. The better solubility of Y_2O_3 in ZrO_2 and superior mechanical stability of the sprayed coatings during thermal cycling conditions typically encountered in gas turbine engine environments [2, 10] makes Y_2O_3 a predominant choice as dopant.

For the development of high-quality coatings of zirconia, ceramic powders of precisely defined specifications are needed, e.g. good flowability, narrow size distribution, homogeneous distribution of the dopant and low monoclinic phase content [3, 7, 11]. For achieving all these properties for spraying, the sol–gel technique has proved to be an excellent means [11] as this method provides an easy control of particle size, shape, material density and the degree of purity. An additional factor in support of the technique is the cost-effectiveness resulting from the relatively low preparation temperature of the powder compared to the other available methods.

The usual commercial YSZ powders for plasma spraying have a Y_2O_3 content of 6–8 wt %; lower addition of Y_2O_3 has been shown to lead to drastic failure of the coatings in thermal cycling [12]. Another relevant factor is the particle shape: spherical particles have been known to perform in a much better way than irregular ones [13]. In view of these facts, an attempt has been made in this work to (i) generate spherical particles of YSZ by sol–gel processing, and (ii) keep the Y_2O_3 content to below 6 wt % with a view to examining the effects of such departure from the usual commercial materials on the properties of the corresponding coatings.

2. Experimental procedure

2.1. Preparation of sol

Zirconia sols with Zr^{4+}/NO_3^- mole ratios of 0.30–0.35 were prepared at 80–90 °C from hydrated zirconia with $ZrOCl_2 \cdot 8H_2O$ as the starting material. The viscosity and pH of the sols were found to be in the range 1.70–1.80 cP and 0.35–0.40, respectively. Yttrium nitrate pentahydrate (equivalent to 5 wt % Y_2O_3) was then added to it. The yttria-containing sol has been termed a "broth" in the text.

2.2. Preparation of support solvent

The support solvent in the present case was a mixture of an organic solvent and an emulsifying agent. To prepare a water-in-oil type emulsion, 1,1,1-trichloroethane was used [11, 14]. Sorbitan monooleate (trade name Span 80), a non-ionic surfactant, was used as the emulsifier [11]. The required amounts of the organic solvent, i.e. 1,1,1-trichloroethane and Span 80, when mixed together under stirring, produced a support solvent for the present study.

2.3. Preparation of the microspheres

To prepare gel microspheres, the broth was emulsified in the support solvent; the method of external gelation was employed [11, 14]. The gel microspheres were washed with methanol, dried at 80 °C and subsequently heat treated at 1000 °C for 1 h.

2.4. Characterization of the microspheres

The particle-size distribution and the average particle size, d_{50}, of the calcined powder in the form of microspheres were determined using a particle size analyser (Microscan, Quantachrome Corporation). Powder morphology and grain size of the gel and calcined materials were examined under optical (Leitz, Ortholux, II POL-BK) and scanning electron (Cambridge, S250) microscopes. Phase content and crystal lattice parameters were determined by X-ray diffraction (XRD) analysis (Philips PW-1730 X-ray unit) using CuK_α radiation. Flow characteristics were examined with a Hall flowmeter, following the ASTM B 213-48 standard. D.c. plasma emission spectroscopy was used to determine the chemical composition of the microspheres. Bulk density was measured following Archimedes' principle.

2.5. Powder evaluation for plasma-spray coating

A METCO 7MB plasma-spray gun was used for application of the coatings. Nimonic-75 flat pieces were used as the substrate. Bond coats of Ni–20Cr and Ni–23Co–17Cr–12Al–0.5Y, each 100μm thick, were deposited on the substrate by plasma spraying. A ceramic overcoat of the sol–gel-derived YSZ powder of varying thickness was then applied over this bond coat, also by plasma spraying. The plasma spraying parameters employed for the application of YSZ ceramic coatings are summarized in Table I. Small pieces (coupons) of the coated Nimonic alloy substrate were subjected to metallographic evaluation and XRD analysis. Using the same procedure, Nimonic-75 coupons, each of approximately 15 mm × 15 mm size, were also coated for thermal cycling studies, aimed at assessing the thermal shock resistance of the coatings.

TABLE I Plasma spraying conditions using a METCO 7MB spraying unit

Spraying parameters	Experimental details
Arc current (A)	500
Primary arc gas	Argon
(i) Pressure (p.s.i.)	100
(ii) Flow rate ($ft^3\ h^{-1}$)	80
Secondary arc gas	Hydrogen
(i) Pressure (p.s.i.)	50
(ii) Flow rate ($ft^3\ h^{-1}$)	15
Powder carrier gas	Argon
Powder feed rate ($g\ min^{-1}$)	~ 50
Spray distance (mm)	75

Note: The substrate was grit blasted, using − 16 + 30 mesh alumina grit, and ultrasonically cleaned prior to coating.
1 p.s.i. = $7.0307 \times 10^5\ g\ m^{-2}$. 1 $ft^3\ h^{-1} = 2.8317 \times 10^{-2}\ m^3\ h^{-1}$.

2.6. Thermal shock resistance test

The small coated specimens (see Section 2.5) were subjected to repeated heating and cooling cycles until the coatings were found to fail due to cracking or peeling. Each cycle consisted of a heating period of 30 min at 1200 °C in an air atmosphere followed by a water quench. Under such conditions, thermal shock resistance was measured by noting the number of cycles withstood by a coating before its ultimate degradation. It may also be noted that the above cycle constitutes an accelerated test, with the thermal cycle far more severe than what is normally encountered in actual operation.

3. Results and discussion

3.1. Microsphere formation via emulsion coprecipitation

In the present external gelation process, the emulsifier prevented the formation of deformed spheres and clustering of the generated gel microspheres by controlling the sol–solvent interfacial tension [15]. In its absence, the particles were found to be devoid of sphericity [7]. The size distribution of the microspheres largely depends on the degree of agitation during droplet formation and neutralization reaction, as also does the emulsion composition. The time required for stable droplet formation is another important point to be considered, because inadequate time periods failed to create discrete spheres and, instead, generated some elongated and dumb-bell shaped particles. Fig. 1a and b show the difference in the nature of the gel materials when the gelation was carried out before and after equilibrium droplet formation.

3.2. Calcination of the gel microspheres

Calcination of the gel microspheres at 1000 °C (with 1 h soak) under controlled conditions produced dense

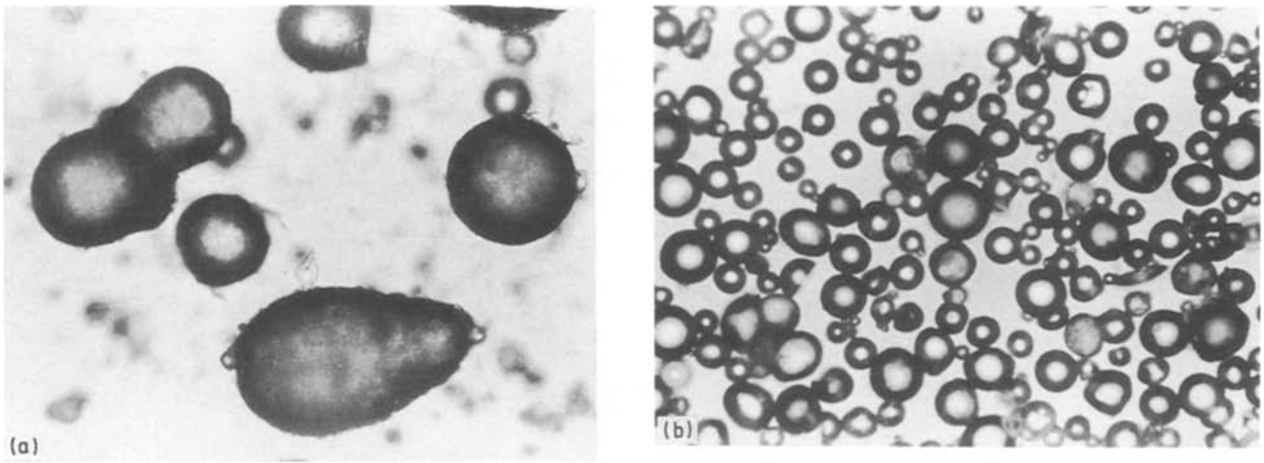

Figure 1 Optical micrographs showing the differences in the nature of gel materials developed (a) before and (b) after equilibrium droplet formation, respectively. × 160

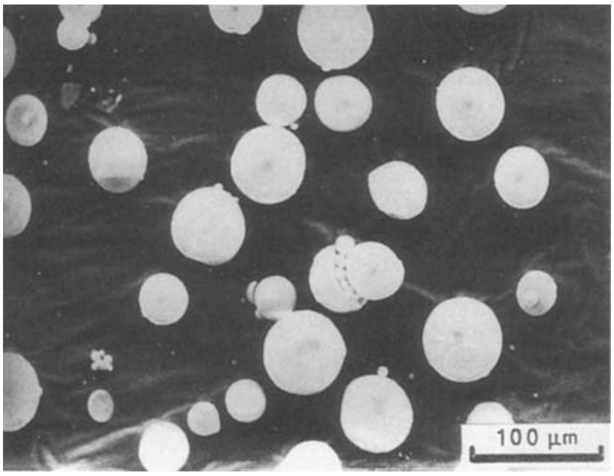

Figure 2 Scanning electron micrograph of typical oxide microspheres.

oxide microspheres with a total weight loss of about 55%. In spite of the removal of such large amounts of adsorbed molecules, the gel spheres retained their integrity and sphericity after calcination. Fig. 2 shows scanning electron micrograph of such oxide microspheres. Calcination up to 1000 °C also reduced the particle size by about 25%–30%.

3.3. Characteristics of the oxide microspheres

Powder properties such as shape, size distribution, flow characteristics and chemical composition, greatly affect the characteristics of the plasma-sprayed coatings. To obtain high-quality coatings, spray-grade ceramic powders showing a size range of 5–50 µm with a spherical morphology and good flow characteristics are preferred. In addition, such powders should not decompose or evaporate at the plasma temperature. Table II summarizes the different properties of the sol–gel-derived oxide microspheres obtained in the present course of study. Fig. 3 shows the particle-size distribution of such microspheres, where about 70% of the product was in the range 20–50 µm and only 8% was finer than 10 µm. This is in good agreement with that required for plasma-spraying operation.

Observation of the gel and the calcined powders under optical and scanning electron microscopes (Figs 1b and 2) revealed their predominantly spherical morphology which generated good flow property in the synthesized powder. When tested with a Hall flowmeter, the powder was found to flow at the rate of 0.83 g s^{-1}. The present powder was found to have an yttria content of 5.07%, as shown by chemical analysis using d.c. plasma emission spectroscopy. The density of the powder was determined to be 6.09 ± 0.02 g cm^{-3}. A similar result was also obtained by Ingel *et al.* [16] and Tsukuma *et al.* [10] for ZrO_2–5 wt % Y_2O_3 single crystal and ceramics, respectively. This value is nearly the same as the theoretical density of the pure tetragonal or cubic phase [9]. This indicates the formation of fully dense oxide microspheres at a relatively low temperature, i.e. 1000 °C [10, 17–19]. From XRD analysis, the monoclinic phase content of the

TABLE II Characteristics of the sol–gel-derived spray-grade Y_2O_3– ZrO_2 microspheres

Particle morphology	Particle size range (µm)	Average particle size, d_{50} (µm)	Flowability (g s^{-1})	Crystal phase (wt %)	Lattice constants (nm)	Chemical composition	Density (g cm^{-3})
Spherical	5–50	22.3	0.83	86% t-ZrO_2; 14%m-ZrO_2	$c = 0.5160$ $a = 0.5096$ $c/a = 1.0126$	ZrO_2– 5.07 wt % Y_2O_3	6.09 ± 0.02

t = tetragonal; m = monoclinic.

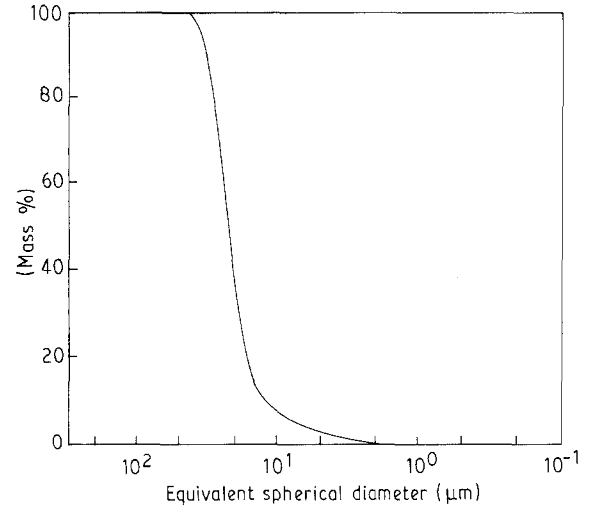

Figure 3 Particle-size distribution of the sol–gel-derived oxide microspheres.

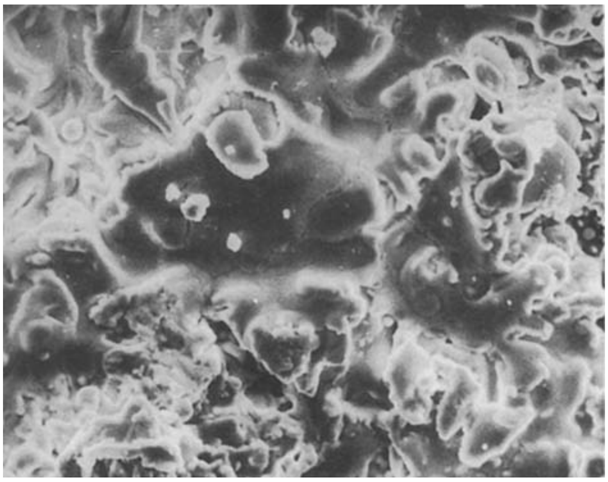

Figure 5 Scanning electron micrograph showing the development of microcracks in the as-sprayed coating. × 1000

powder was estimated to be 14% from the low-angle region of the general scan [20].

3.4. Characteristics and performance of the plasma-sprayed coating

During spraying, the sol–gel derived powder was found to flow well, as might be expected from its shape and size characteristics. Fig. 4 shows a typical microscopic view of the cross-section of a plasma-sprayed coating obtained from this powder. As seen from the micrograph, a well-bonded coating was obtained. When subjected to XRD analysis, the monoclinic phase content in the as-sprayed coating was found to be significantly reduced to only about 6% after spraying, the rest being tetragonal ZrO_2.

The thermal shock resistance test (see Section 2.6) of the five coated coupons with a 100 μm thick Ni–20Cr bond coat and a 550 μm thick YSZ coating showed that under the given conditions, they had an average life of 38 cycles. Such a high value under the severe test conditions is indicative of good thermal shock resistance. The two primary causes of failure of thermal barrier coatings in a high-temperature environment under cycling conditions are oxidation of the underlying bond coat and accumulation of cyclic thermal stresses. The scanning electron micrograph of the as-sprayed coating (Fig. 5) reveals the presence of fine, limited microcracks.

Figure 4 Metallographic cross-section of a coating with a Ni–20 Cr bond coat and a ceramic overlayer of the sol–gel-derived YSZ. × 100

While the dense coating microstructure retards bond-coat oxidation, these microcracks, which are presumably augmented during thermal cycling, provided considerable toughening and increased accommodation of thermal stresses, thereby enhancing coating longevity [5].

A similar thermal cycling test with coupons coated with a 100 μm Ni–23Co–17Cr–12Al–0.5Y bond coat and a 300 μm YSZ overlayer, increased the average life to 50 cycles under identical thermal cycling conditions. Thus, thermal barrier coatings obtained from the YSZ microspheres of this work showed very encouraging performance under accelerated testing.

4. Conclusion

The spray-grade YSZ microspheres, containing 5 wt % Y_2O_3, were synthesized under controlled conditions by the sol–gel technique. The gelation for the development of such powders was carried out in water-in-oil type emulsions. Free-flowing dense oxide microspheres with a size range of 5–50 μm were obtained by calcination of the corresponding gel spheres at 1000 °C.

The powders were evaluated for their efficiency in the preparation of plasma-sprayed coatings. The coatings were found to have a high non-transformable tetragonal zirconia content. They were also observed to have good thermal shock resistance, as indicated by their longevity during a severe thermal cycling test.

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