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Effect of thermal treatment on phase composition and thermal shock resistance of plasma-sprayed calcia-stabilized zirconia–alumina composite coatings

K. P. Sreekumar, P. V. Ananthapadmanabhan and N. Venkatramani
Laser and Plasma Technology Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085 (India)

K. V. Muraleedharan
Applied Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085 (India)

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Abstract

Plasma-sprayed composite coatings of calcia stabilized zirconia–alumina were prepared on stainless steel and sintered alumina substrates. The effect of thermal treatment on the phase composition of the coatings was studied by X-ray diffraction technique. These studies indicate that the thermal treatment of the coatings at temperatures above 1573 K leads to partial destabilization of calcia-stabilized zirconia, resulting in coatings with excellent thermal shock resistance.

1. Introduction

Plasma-sprayed coatings of ceramic materials are widely used for protecting active components in high-tech areas against high-temperature corrosion, erosion and wear [1–6]. These include thermal barrier coatings on internal combustion engine components, rocket nozzles and thrust chambers, corrosion-resistant coatings in chemical reactors, etc. The most frequently used coating materials for high-temperature applications are alumina and stabilized zirconia. Thermally protective coatings of alumina have been used for rocket motor components, jet engine components and a large number of furnace applications [1]. Zirconia coatings, like alumina coatings, have been used primarily for high-temperature applications. The higher melting point of stabilized zirconia extends its range of thermal applications beyond that of alumina.

System components in front-line technologies are often subjected to multiple corrosive influences. In such cases, the protective coatings of the system components should be able to withstand the combined influence of thermal, mechanical and chemical effects. Composite coatings have been developed to meet such requirements. In many high temperature applications, as well as having thermal stability and resistance to corrosion and erosion,

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coatings should possess good thermal shock resistance. Metal–ceramic composite coatings, metal-reinforced ceramic coatings and ceramic composite coatings have been developed to meet these requirements [1, 4, 6]. This present study deals with the preparation of plasma-sprayed composite coatings of calcia-stabilized zirconia (CaSZ) and alumina and the effect of thermal treatment on the structure and thermal properties of these coatings.

2. Specimen preparation

Calcia-stabilized zirconia with various wt.% of alumina was used for plasma spraying. Powders of CaSZ and Al_2O_3 (-325 mesh; H.C. Starck, Berlin) were used as starting materials. The powders were weighed in quantities which gave 3, 4.5, 10 and 15 wt.%Al_2O_3, and mixed in a planetary ball mill for 8 h to homogenize the mixture. These powders were used as feed stock for spraying. A 40 kW non-transferred arc plasma-spray system (see Fig. 1) was used for preparing the specimens. Plasma-sprayed specimens of thickness 200–600 microns were prepared on stainless steel and sintered alumina substrates by the usual technique. A few free-standing specimens were also prepared for thermal shock resistance studies. This preparation consisted of coating a sand-blasted aluminium plate with NaCl followed by the plasma spraying of the composite to a thickness of about 1 mm. The specimen was allowed to cool and the substrate was then dipped in water to remove the undercoat of NaCl, leaving the free-standing CaSZ–Al_2O_3 composite coating. These specimens were cut to a size of 15 mm×10 mm×1 mm before use.

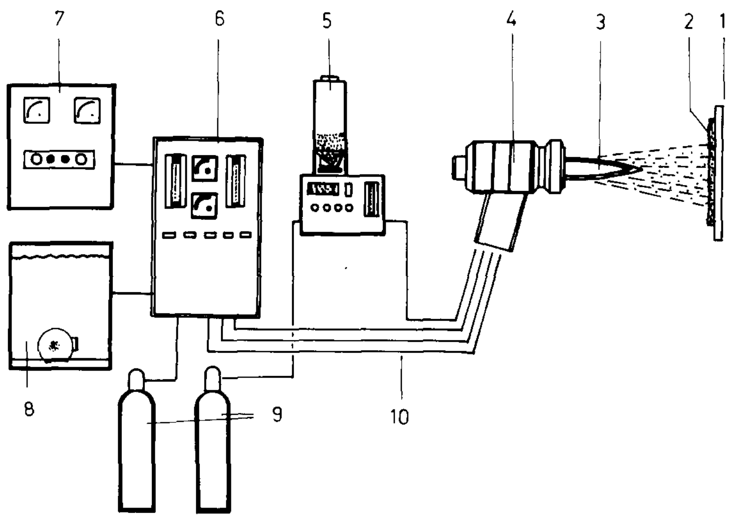

Fig. 1. Schematic diagram of plasma-spray system: 1, substrate; 2, coating; 3, plasma flame; 4, plasma torch; 5, powder feeder; 6, control console; 7, power supply; 8, cooling water; 9, gas supply; 10, feeder lines.

The power level was varied from 10 to 15 kW to test the reaction of the materials in the flame. This was done by maintaining a constant current and by increasing the voltage by increasing the percentage of nitrogen. The specimens were prepared at an input power level of 10 to 15 kW.

In order to study the effect of thermal treatment on the coating properties, the specimens were heat treated in the temperature range 1473–1873 K for soaking periods that varied from 2 to 16 h. The X-ray powder diffraction technique was used to identify phases as well as to study the effect of thermal treatment on the phase composition of the coatings. In order to understand the thermal shock behaviour of these composites, plasma-sprayed specimens of pure CaSZ, as-sprayed and heat-treated specimens of CaSZ–Al_2O_3 composites were introduced into a tubular furnace maintained at 1473 K. The specimens were quenched by dropping them in cold water after they attained thermal equilibrium. This cycle was repeated until the specimen developed visible cracks.

3. Results and discussions

X-powder diffraction of the as-sprayed specimens showed the presence of cubic CaSZ and α alumina. There was no effect on the phase composition of the as-sprayed specimens with increasing amounts of alumina in the powder. Increasing the torch input power from 10 to 15 kW did not affect the phase structure of the coatings.

Adhesion testing specimens as per ASTM standard C 633 were prepared and tested for their adhesion strength [7]. Typical values of the adhesion strength of CaSZ–Al_2O_3 composites with a coating thickness of 380 microns, on a stainless steel substrate, sand blasted with 1 mm quartz sand at a pressure of 2.5 kg cm^{-2} were found to vary from 5 to 12 MPa.

Heat treatment at 1573 K and above has a significant effect on the phase composition of the coatings, as can be seen from Fig. 2 which shows the room temperature powder diffraction patterns of a typical sample before and after heat treatment at 1573 K for 2 h. The reaction of CaSZ and alumina results in the formation of free ZrO_2 and calcium aluminate. The extent of the reaction is expressed by degree of destabilization in terms of the weight percent of free ZrO_2 formed. The degree of destabilization in the heat-treated specimens was determined by means of a calibration curve relating the intensity ratio of the $11\bar{1}$ peak of the monoclinic phase of ZrO_2 to the 111 peak of CaSZ, as described in previous studies [8]. There can be appreciable error in the extent of destabilization determined by the above method in the case of samples containing 10 and 15 wt.% alumina owing to the matrix effect.

Figure 3 shows the variation in degree of destabilization as a function of time for the different compositions fired at 1873 K. It can be seen that there is an initial rapid increase in the degree of destabilization (with time), which then tends to saturate. In other words, the rate of reaction decreases

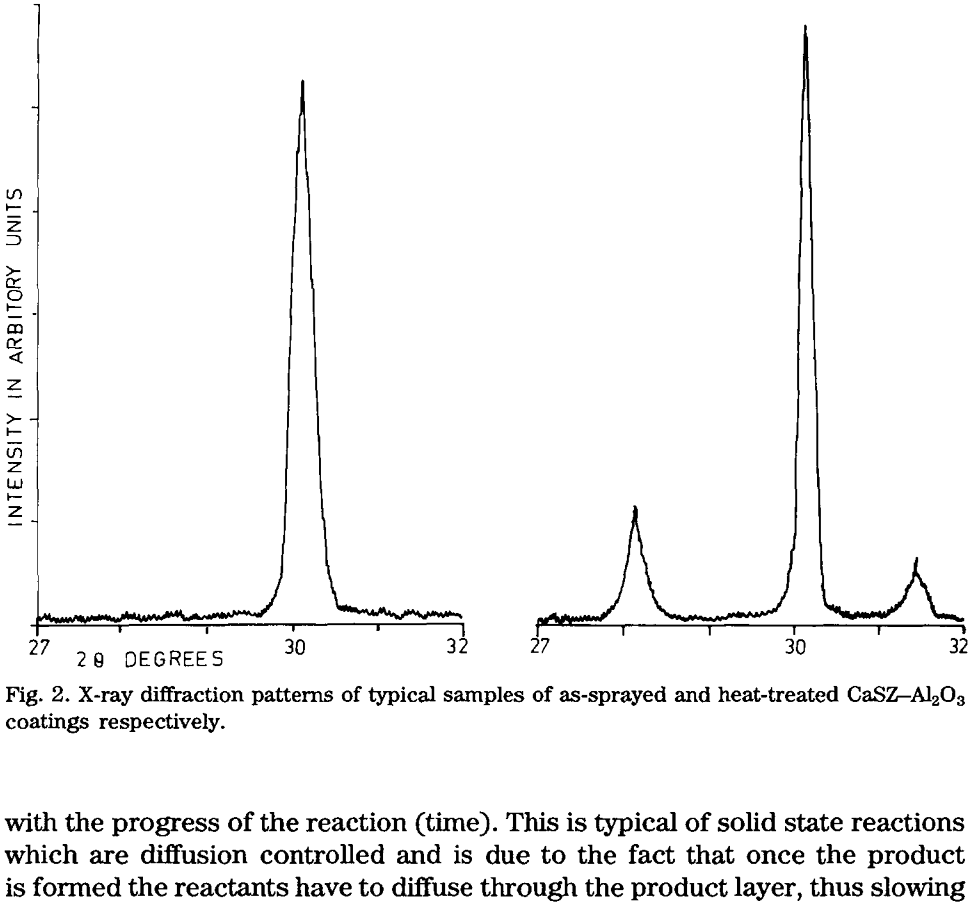

Fig. 2. X-ray diffraction patterns of typical samples of as-sprayed and heat-treated CaSZ–Al_2O_3 coatings respectively.

with the progress of the reaction (time). This is typical of solid state reactions which are diffusion controlled and is due to the fact that once the product is formed the reactants have to diffuse through the product layer, thus slowing down the reaction rate.

The results of the thermal-shock studies, summarized in Table 1, show that plasma-sprayed CaSZ–Al_2O_3 composite coatings have better thermal-shock resistance than that of pure CaSZ coating. As-sprayed samples of CaSZ samples annealed at 1873 K could only withstand about 25 cycles, whereas the composite coatings, heat treated at temperatures above 1573 K, developed an initial crack only after 48 cycles. Continued thermal cycling of these samples did not result in appreciable crack propagation even after 100 cycles. It can also be seen from Table 1 that the as-sprayed specimens of the composites could only withstand about 20 cycles, clearly indicating the influence of destabilization on the thermal shock resistance of the coatings. A significant point to be noted in this context is that the annealed specimens have excellent resistance to thermal shock irrespective of the alumina content in the starting material. Plasma-sprayed coatings of CaSZ–Al_2O_3 powder blends containing 3–15% of Al_2O_3 annealed at different temperatures and time withstood 40–48 thermal cycles, indicating that the amount of free ZrO_2 (generated as a consequence of destabilization of CaSZ by Al_2O_3), which varied from 16 to 52%, did not significantly affect the thermal shock behaviour

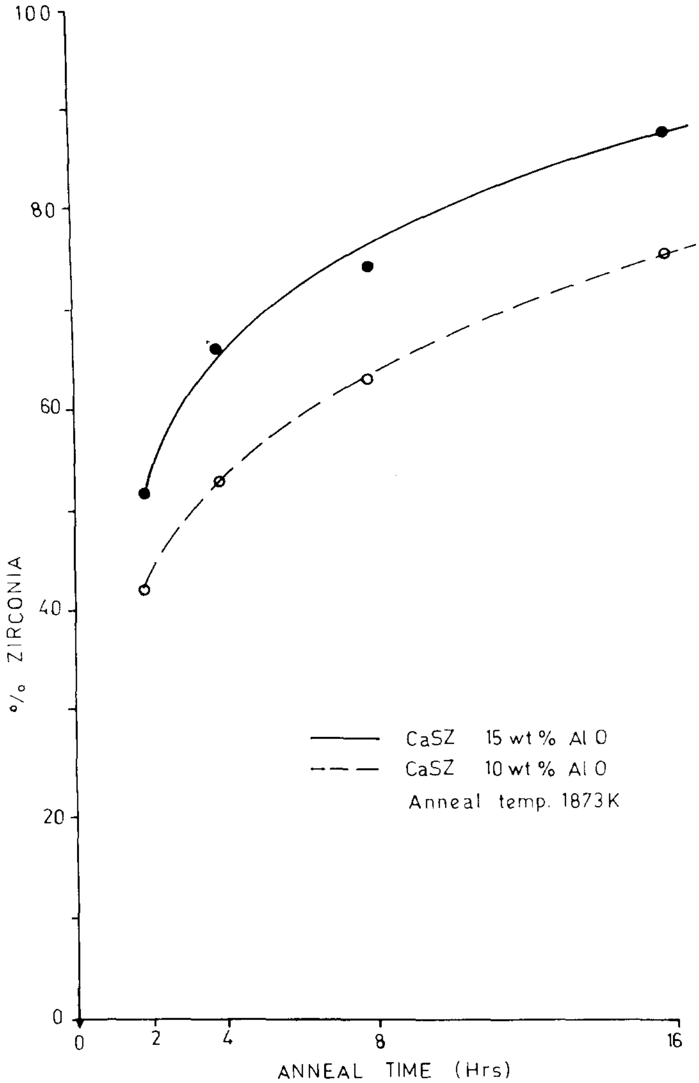

Fig. 3. Variation in degree of destabilization with time.

of the coatings. However, the studies did not show any specific trend or dependence of thermal shock resistance on the degree of destabilization (amount of free ZrO_2).

The enhanced thermal shock resistance of the composite coatings is due to the presence of free zirconia and the phase transition it undergoes during thermal cycling [9]. The phase inversion from the low temperature monoclinic phase to the high temperature tetragonal phase during the heating cycle and the reverse transformation in the cooling cycle generate numerous microcracks which act as thermal stress relief centres. These microcracks

TABLE 1

Thermal shock resistance of CaSZ–Al_2O_3 composite coatings (1473 K) to water at 300 K

Description of coating	Wt.% of zirconia formed	No. of cycles for crack initiation
Annealed at 1873 K		
CaSZ	–	22
CaSZ + 3%Al_2O_3	16	45
CaSZ + 5%Al_2O_3	24	48
CaSZ + 10%Al_2O_3	42	41
CaSZ + 15%Al_2O_3	52	44
Unannealed		
CaSZ	–	25
CaSZ + 3%Al_2O_3	–	21
CaSZ + 5%Al_2O_3	–	24
CaSZ + 10%Al_2O_3	–	15
CaSZ + 15%Al_2O_3	–	20

propagate only quasistatically [10], enabling the body to maintain its mechanical strength even after continuous thermal cycling.

4. Conclusions

The plasma-spraying technique has been used successfully to prepare composite coatings of CaSZ–Al_2O_3. The spray parameters were carefully studied and optimized to get dense, adherent coatings which can be used for high temperature applications. Thermal treatment of the composites results in partial destabilization of the CaSZ phase. An important consequence of the destabilization reaction is the formation of free ZrO_2, resulting in coatings with superior thermal shock resistance.

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References

1 D. A. Gerdeman and N. L. Hecht, *Arc Plasma Technology in Materials Science*, Springer, Berlin, 1972, pp. 10–73.
2 S. Stecura, *Am. Ceram. Soc. Bull.*, *56* (1977) 1082.

3 K. P. Sreekumar, J. Karthikeyan, N. Venkatramani and V. K. Rohatgi, *Proc. Symp. Workshop on Beams and Plasmas: Applications in Materials and Technology, Bombay, 1990*, p. 436.
4 J. Karthikeyan, K. P. Sreekumar, N. Venkatramani and V. K. Rohatgi, *High Temp.-High Pressures, 20* (1989) 653.
5 R. J. Bratton and S. K. Lau, in A. H. Heuer and L. W. Hobbs (eds.), *Advances in Ceramics* Vol. 3, *Sciences and Technology of Zirconia*, American Ceramic Society, Columbus, OH, 1981, p. 226.
6 K. P. Sreekumar, J. Karthikeyan, P. V. Ananthapadmanabhan, N. Venkatramani and U. K. Chatterjee, Plasma Spray Technology: Process Parameters and Applications, *BARC Report No. 1551*, Library and Information Division, Bhabha Atomic Research Centre, Bombay, 1991.
7 Standard Method of Test for Adhesion or Cohesive Strength of Flame Sprayed Coatings, Annual Book of ASTM Standard Part 17, American Society for Testing and Materials, Philadelphia, PA, 1976.
8 P. V. Ananthapadmanabhan, S. B. Menon, V. Venkatramani and V. K. Rohatgi, *J. Mater. Sci., 24* (1989) 4432.
9 P. V. Ananthapadmanabhan, S. B. Menon, N. Venkatramani and V. K. Rohatgi, *Ceram. Int., 12* (1986) 107.
10 D. P. H. Hasselman, in W. W. Kriegel and H. Palmour (eds.), *Materials Science Research*, Vol. 5, *Ceramics in Severe Environments*, Plenum, New York, 1971, p. 89.