Preparation of Plasma Sprayed Coatings of Yttria Stabilized Zirconia and Strontium Zirconate and Studies on Their Interaction with Graphite Substrate

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Abstract

Plasma sprayed coatings are extensively used for high temperature chemical barrier applications. Thermal stability and interaction of the coating material with substrate materials are critical issues that decide coating performance. This paper reports preliminary results of high temperature interaction of plasma sprayed yttria stabilized zirconia and strontium zirconate coatings with graphite substrate.

Introduction

Plasma spray deposition or plasma spraying is a process that combines particle melting, quenching and consolidation in a single operation. The process involves injection of powder particles (metallic, ceramic or cermet powders) into a plasma jet generated by heating an inert gas in an electric arc confined within a water-cooled nozzle. The temperature at the core of the plasma jet is 10,000-15,000 K. Metal or ceramic particles injected into the plasma undergo rapid melting and at the same time are accelerated. These molten droplets moving at high velocities, exceeding 100 metres/second, impact on the surfaces of the substrate forming adherent coating [1-3]. The coating is incrementally built up by the impact of successive particles by the process of flattening, cooling and solidification. By virtue of the high cooling rates, typically $10^5$ to $10^6$ K/sec., the resulting microstructures are fine-grained and homogeneous [3].

Plasma sprayed ceramic coatings are extensively used for thermal barrier, wear and corrosion resistant and chemical barrier applications. The use of ceramic coatings for thermal and chemical barrier applications is well established [4,5]. The choice of the specific ceramic material is decided by its thermal stability, chemical stability in the operating environment, etc. Table I gives some of the prospective ceramic coating materials for high temperature thermal barrier and chemical barrier applications [6,7]. Aluminium oxide, by virtue of
its reasonably high melting point (2300K) and chemically inert nature is the natural choice for thermal and chemical barrier applications. However, the main drawback of alumina is its instability under reducing conditions. Above 1200°C, alumina is reduced to its gaseous suboxides in presence of carbon, hydrogen and other reducing gases. By virtue of their higher melting points and better chemical stability in reducing atmospheres, yttria stabilized zirconia (YSZ) containing about 7 wt% yttrium oxide, CaZrO₃ and SrZrO₃ are expected to perform better in reducing environments. This report deals with the development and evaluation of high temperature stability of plasma sprayed YSZ and SrZrO₃ coatings on graphite substrates.

### Plasma Spray Facility

The 20 kW atmospheric plasma spray system developed at the Laser&Plasma Technology Division was used for preparing the coatings. The system consists of a 20kW DC non-transferred arc plasma torch, DC power supply including RF igniter, powder feeder, plasma gas and cooling water systems. A photograph of the system with the powder laden plasma jet is shown in Figure 1.

<table>
<thead>
<tr>
<th>Coating material</th>
<th>Melting point (K)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium oxide</td>
<td>2327</td>
<td>Widely used ceramic coating for many applications</td>
</tr>
<tr>
<td>Yttrium oxide</td>
<td>2712</td>
<td>Stable in many reactive environments including carbon and molten metals</td>
</tr>
<tr>
<td>Yttria stabilized zirconia</td>
<td>~2600 K</td>
<td>Extensively used for TBC applications in aeroengine components</td>
</tr>
<tr>
<td>Calcium zirconate</td>
<td>2598 K</td>
<td>High melting point and suitable for many molten metal containment</td>
</tr>
<tr>
<td>Strontium zirconate</td>
<td>3000 K</td>
<td>High melting point and suitable for many molten metal containment</td>
</tr>
</tbody>
</table>

Table 1: Prospective ceramic coating materials for high temperature applications

Fig. 1A 20 kW Atmospheric Plasma Spray System

Fig. 1B Powder laden Plasma jet
SrZrO$_3$ and YSZ powders from CERAC Incorporated, USA were used for plasma spray deposition. Particle size distribution, by laser scattering technique showed narrow size distribution with about 60% of the particles having size in the range of 20-40 microns. A mixture of argon and nitrogen was used as the plasmagen gas. Input power to the plasma torch was varied from 10 kW to 18 kW by controlling the arc current. In the range of operating conditions used, the torch efficiency, determined by standard calorimetric method, was found to be 60%. Circular graphite coupons 40mm diameter and 10mm thickness were used as substrates. Experimental parameters are given in Table 2.

### Table 2: Operating Parameters of Plasma Spray Torch

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torch input power</td>
<td>10-18 kW</td>
</tr>
<tr>
<td>Plasma gas (Ar) flow rate</td>
<td>20 LPM</td>
</tr>
<tr>
<td>Secondary gas (N$_2$) flow rate</td>
<td>2 LPM</td>
</tr>
<tr>
<td>Powder feed rate</td>
<td>~10 g/min</td>
</tr>
<tr>
<td>Powder carrier gas flow rate</td>
<td>8 LPM</td>
</tr>
<tr>
<td>Torch to base distance</td>
<td>125 mm</td>
</tr>
<tr>
<td>Anode nozzle diameter</td>
<td>8 mm</td>
</tr>
<tr>
<td>Arc current</td>
<td>250-450 amperes</td>
</tr>
<tr>
<td>Powder injection</td>
<td>Radial injection through nozzle (near the exit)</td>
</tr>
<tr>
<td>Plasma gas injection</td>
<td>Vortex injection</td>
</tr>
</tbody>
</table>

### Coating Characterization

The as-sprayed coatings were characterized by x-ray diffraction technique for identification of the phases. Optical microscopy was used for determining the microstructural and interface features. Reaction with graphite substrate was studied by heating the coated specimens at high temperatures in a specially designed plasma furnace.

### Experimental Setup for Heat-Treatment Studies

High temperature reaction of the coatings with carbon was studied by subjecting the coated graphite specimens to thermal treatments in a plasma furnace. The furnace consists of a DC plasma torch mounted on a water-cooled stainless steel reaction chamber, DC power supply, gas train and control console. A close-fitting graphite tube 40 mm internal diameter, and 2 mm thick is inserted in the chamber. Specimens for thermal treatment are kept on a graphite rod, centrally located inside the graphite insert. The position of the specimen holder can be continuously varied with respect to the torch nozzle. Temperature at the top surface of the graphite rod was monitored by a Pt-Pt-Rh thermocouple. Figure 2 shows schematic of the experimental set-up.

![Fig. 2 Plasma heat treatment furnace](image)

The plasma torch was ignited and the power was maintained constant at a specific level and the reactor was allowed to attain thermal equilibrium as indicated by the constant temperature at the surface of the graphite rod. The plasma power was varied and the equilibrium temperature at the surface of the graphite rod was recorded as before. The hot zone temperature can be varied by varying the plasma power, increasing the distance between the torch nozzle and the graphite rod and the gas flow rate. It was observed that for an input power of 12kW, when the specimen distance from the torch nozzle was 175mm, the equilibrium sample temperature was 1200 ºC.
Sample temperature of 1400°C could be obtained at 10kW and 150mm.

**Results and Discussion**

Results of x-ray powder diffraction of as-sprayed coatings of YSZ using Ni-filtered Cu-Kα radiation showed the characteristic diffraction peaks of the cubic phase. SrZrO₃ coatings showed the diffraction peaks of cubic perovskite structure. Figure 3 shows typical optical micrograph of SrZrO₃ coating. Surface morphology of the coating shows molten and partially molten grains and intergranular porosity characteristic of plasma sprayed coatings.

**Coating Interaction with Substrate**

In order to study chemical interaction of SrZrO₃ and YSZ with carbon, thermodynamic analysis of the systems SrZrO₃-C and Y₂O₃-ZrO₂-C have been studied. Free energy minimization plots for the systems SrZrO₃-C and Y₂O₃-ZrO₂-C developed using CSIRO thermal package [8] are shown in Figures 4 and 5 respectively. The figures show the temperature regions of stability of the different phases. It is seen from Figure 4 that SrZrO₃ is stable only up to 2000K. The reaction of SrZrO₃ with carbon starts above 1750 K resulting in the formation of ZrC and SrO/Sr. This is undesirable as it can lead to delamination and coating failure. It is therefore necessary that the operating temperature should not exceed 1700 K. It is seen from Figure 5 that stabilized zirconia forms ZrC and Y₂O₃ above 1500 K. For better coating performance, it is recommended that the operating temperature does not exceed 1500 K.
Experiments on coating interaction with substrate were carried out by heating specimens of SrZrO₃ and YSZ coatings on graphite in the plasma furnace. The test specimens were kept on top of a graphite rod located centrally in the plasma furnace. The required sample temperature could be obtained by manipulating the input power and distance of sample from torch nozzle. Samples were heated to 1200°C and 1400°C for 3 hours. Heating rate was controlled by slowly increasing the plasma power and the average heating rate was 15°C/minute.

Results showed that coatings were stable at 1200°C indicating no reaction of YSZ and SrZrO₃ with carbon. However, thermal treatment at 1400°C led to coating delamination. The entire coating had separated from the graphite substrate, possibly due to interface stresses arising out of differential thermal expansion of the coating and graphite. However, there was no appreciable chemical reaction between carbon and SrZrO₃ as indicated by x-ray diffraction.

**Conclusion**

Plasma sprayed coatings of SrZrO₃ and Yttria stabilized zirconia have been deposited on graphite substrates. Thermal stability of the coatings on graphite substrates have been studied using a specially designed plasma furnace. Results of experiments show that there was no appreciable chemical interaction of the coatings with carbon up to 1400°C. However, thermal treatment at 1400°C led to complete delamination of the coatings. The coating adhesion can be improved by using iron as intermediate coating.

**References**

4. C. Funke, J.C. Mailand B. Siebert, R vassen and D. Stover, Surface & Coatings Technology, 94-95(1997), 106
About the authors ...

Mr K.P Sreekumar is a senior scientist engaged in development of plasma sprayed ceramic/metalllic/duplex coatings for various industrial and special research applications including strategic nuclear applications. His research work spanning 25 years in BARC includes design & development of plasma torches of various capacities for different plasma systems and building various thermal plasma equipments used for coating applications, mineral processing, aerosol generation, nano-particle synthesis, etc. He has more than 100 publications to his credit.

Mr R.U. Satpute is currently engaged in the development programmes of plasma spraying and plasma processing.

Dr P.V. Ananthapadmanabhan joined BARC after graduating from the 20th batch of the Training School in August 1977. He is engaged in Materials Processing by Thermal Plasma Technology. He has developed many novel materials and coatings for various specialized applications including strategic nuclear applications. His research interests include reactive plasma processing, high temperature materials, nano-particle synthesis, etc. He has also developed thermal plasma devices for mineral processing, aerosol generation, nano-particle synthesis, etc. He has more than 100 publications to his credit.

Dr S. Ramanathan joined BARC in 1976 through 19th batch of Training School and works on processing of advanced ceramic materials. He worked on the development of thoria-yttria solid oxide electrolyte for oxygen sensor applications and obtained PhD in Materials Science from IIT Mumbai. He worked on synthesis of controlled morphology sub-micron sized oxide powders by homogeneous precipitation technique and impervious oxidation resistant and porous catalytic coatings by sol-gel technique. Presently, he is working on the formation of ceramic shapes by liquid based fabrication technique (slip and tape casting). He has about forty-five publications to his credit.

Dr N. Venkatramani is Director of Beam Technology Development Group in BARC. He is the architect of high power plasma, particle and laser beam research and development programmes in India. He has pioneered the thermal and non-thermal applications of these beams including some of the novel material processing techniques. He also directs nuclear and defense oriented projects like high power microwaves and industrially intensive beams.

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