Influence of in-flight particle state diagnostics on properties of plasma sprayed YSZ-CeO$_2$ nanocomposite coatings

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(Received 12 November 2013; final version received 29 June 2014)

This article describes the influence of controlling in-flight hot particle characteristics on properties of plasma sprayed nanostructured yttria stabilized zirconia (YSZ) coatings. This article depicts dependence of adhesion strength of as-sprayed nanostructured YSZ coatings on particle temperature, velocity and size of the splat prior to impact on the metallic substrate. Particle temperature measurement is based on two-color pyrometry and particle velocities are measured from the length of the particle traces during known exposure times. The microstructure and adhesion strength of as-sprayed nano-YSZ coatings were studied. Field emission scanning electron microscopy results revealed that morphology of coating exhibits bimodal microstructure consisting of nano-zones reinforced in the matrix of fully melted particles. The coating adhesion strength is noticed to be greatly affected by the melting state of agglomerates. Maximum adhesion strength of 42.39 MPa has been experimentally found out by selecting optimum levels of particle temperature and velocity. The enhanced bond strength of nano-YSZ coating may be attributed to higher interfacial toughness due to cracks being interrupted by adherent nano-zones.

Keywords: CeYSZ; nano-zones; spray diagnostics; adhesion; plasma spraying

1. Introduction

Increased operating temperatures and hence, improved performance of gas turbines or diesel engines can be realized by using thermal barrier coatings (TBCs) [1–6]. Plasma sprayed TBCs based on yttrium stabilized zirconia (YSZ) have been applied to hot section industrial components. Zirconium based ceramics are considered to be best suitable for TBC applications due to its low density, high hardness and low thermal conductivity [7–11]. The above properties are dependent on the microstructure of the ceramic system. Hence, it is imperative to have a control over the particle state in order to achieve reproducible microstructure and properties in coatings. It is evident from literature that both performance and characteristics of coatings are influenced by microstructure, which in turn, are affected by the particle state along with substrate and spray conditions [12]. Hence, controlling each parameter and evaluating its role in performance of coatings

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becomes difficult. Substrate and deposition conditions are relatively easier to control in comparison to the complex spray stream. Some uncontrollable factors like nozzle wear and gas flow stability make the process more difficult for assessment.

The important control parameters in plasma spraying are the flow rates of plasma and powder carrier gas, torch input power, dwell time and powder feed rate. There have been a few reports regarding the studies on structural, micro-structural, thermal and mechanical properties by controlling particle temperature and velocity [13–15]. However, optimum spray conditions which would yield required physical and mechanical properties have not been identified. Hence, a practical way of obtaining in-situ information from the individual in-flight coating particles provides the input for desired coating properties [16–18]. Amongst the parameters of utmost interest are the particle temperature and velocity distributions, size distribution of particles prior to the impact on the substrate. These parameters play an important role in enhancement of interfacial bond strength of nanostructured coatings as compared to conventional coatings. The increase in bond strength for the nanostructured coatings was approximately 1.8 times higher for atmospheric plasma spraying (APS) nano Al₂O₃–13 wt.% TiO₂ [19] and 2.4 times higher for high velocity oxy-fuel (HVOF)-sprayed nano TiO₂ [20]. The higher bond strength achieved may be attributed to higher interfacial toughness due to cracks being interrupted by strong adherent nano-zones [21]. The presence of dense nano-zones (bimodal distribution of microstructure reflected in our earlier work [22]) will have an effect on their mechanical properties and the microstructure which in turn depends on particle temperature and velocity. In this article, an attempt has been made to address the effect of controlling in-flight hot particle characteristics (monitored by CCD camera) on adhesion strength of as-sprayed CeO₂ doped YSZ coatings on Inconel 718 substrates.

2. Experimental details

2.1. Synthesis of nanostructured powders by sol-gel route

The nanostructured YSZ powders employed in this study were synthesized through sol-gel technique [23]. A water based solution of zirconium oxychloride and yttrium oxide was prepared in order to obtain 8 mol% YSZ. Precursor materials were taken according to the proper stoichiometric ratio and an excess amount of nitric acid was added to the solution. Final solution was homogenized by constant stirring at 100–120°C. After 5–6 h of constant stirring and heating, the translucent solution (with little amount of citric acid) was heated on a hot plate at about 200–250°C until it turned into a black viscous gel, which on continued heating burnt due to a vigorous exothermic reaction. Black ashes obtained after combustion were treated at 350°C in air for 1 h to eliminate the low temperature volatile residues and calcined at 600°C for 2 h to free the matrix from carbon, resulting in YSZ powder.

The transmission electron micrograph of as-synthesized YSZ powders by sol-gel technique is shown in Figure 1. The average grain size of the nanoparticles is on the order of 20–30 nm. The calcined YSZ and commercial CeO₂ powders were taken as the raw ingredients for the plasma spraying process and were mixed properly and heat treated at 1400°C.

2.2. Reconstitution of nano powders

Nano-sized powder of 10CeYSZ [90 wt.% YSZ (5.4 wt.% Y₂O₃–ZrO₂) + 10 wt.% CeO₂] was plasma sprayed on Inconel 718 substrates. The finely dispersed nanoparticles were agglomerated using spray-drying technique [24] to a size of ~6–10 µm as required for
plasma spraying. The agglomeration process was carried out in a Buchi B-290 (M/s BUCHI, Flawil, Switzerland) research model spray dryer. Spray-drying suspensions were prepared by mixing nano CeO$_2$ and nano-YSZ powders with 2 wt.% polyethylene glycol (PEG) binder and 1 wt.% ammonium citrate. Then the suspension was ball-milled for more than 24 h. The nano-CeYSZ slurry was attained via vigorous magnetic stirring for 30 min and heated up to 90°C. The preheating of solution assists in the slurry formation and in lowering the enthalpy needed during the drying process for moisture removal. The polymeric binder, PEG, in solution uses van der Waals forces to bind the nanoparticles together and forms spherical droplets during atomization. The suspension was spray-dried, and the granules were collected and sieved to a size of ~10 µm spherical agglomerates containing nanograins of size 20–30 nm as shown in Figure 2(a). Surface
morbidity of one agglomerated CeYSZ particle is shown in Figure 2(b). Nanocrystalline particles on the surface of CeYSZ agglomerate are clearly visible.

2.3. Development of coatings

The surface of the substrate was subjected to grit blasting to make the surface rough. In this grit blasting method, highly compressed air carrying alumina particles were bombarded on the surface to remove some material which made the surface rough. A uniform roughness of 6–8 µm was maintained in order to provide better adhesion at the interface. The coating process was carried out at CSIR-IMMT, Bhubaneswar, using an 80 kW plasma spray system supplied by M/s Metallization, UK. In this study, high purity argon and helium were used as primary and secondary plasmagen gas, respectively, at an outlet pressure of 4 kg/cm². A roughened Inconel 718 substrate of dimension 120 × 60 × 5 mm³ was fixed on the turn table and CeYSZ nanocomposite powders was sprayed by varying process parameters. The process parameters are listed in Table 1. Prior to top coat, NiCrCoAlY bond coats of thickness ~100 µm were applied on Inconel 718 substrates by HVOF (Hipojet 2700, M/s MEC, Jodhpur, India) by using set of process parameters given in Table 2. The number of passes was kept constant for each sample in order to make the thickness of all coatings (~250 µm including bond coat) within similar range.

| Parameter                              | Operating range     |
|----------------------------------------|---------------------|
| Operating power                        | 35–45 kW            |
| Current                                | 700–900 amps        |
| Primary plasmagen gas (argon) flow rate| 40–60 lpm           |
| Secondary plasmagen gas (hydrogen) flow rate | 0.5–2 lpm     |
| Carrier gas flow rate                  | 5 lpm               |
| Nozzle to substrate distance (stand-off distance) | 80 mm            |
| Powder feed rate                       | 25 g/min            |

| Parameter                              | Operating range     |
|----------------------------------------|---------------------|
| Oxygen pressure                        | 10 bar              |
| Oxygen flow rate                       | 265 lpm             |
| LPG pressure                           | 7 bar               |
| LPG flow rate                          | 70 lpm              |
| Air pressure                           | 5 bar               |
| Air flow rate                          | 700 lpm             |
| Carrier gas (nitrogen) pressure        | 6 bar               |
| Carrier gas flow rate                  | 6.5 lpm             |
| Air cap                                | 9.3 mm              |
2.4. Adhesion test
To evaluate the coating adhesion strength, universal testing machine (make: INSTRON 8801; M/s Instron India Pvt Ltd., Chennai, India) was used. The test was conducted by the pull-out method as per ASTM C633 standard using two cylindrical specimens. The face of one of the cylinders is coated by plasma spraying with the material under investigation. This coated face is glued with a resin HTK Ultra Bond 100 (M/s HTK, Hamburg, Germany) to the face of the other uncoated cylindrical specimen and kept in furnace at 150°C for approximately 1.5 hours for the setting of the glue. This uncoated face was sand blasted prior to gluing. The assembly of two cylinders is then subjected to gradual tensile load. The cross head speed is kept constant at 1 mm/min. The tensile strength, i.e. the coating adhesion strength is calculated by dividing the maximum load applied at the rupture (i.e. failure occurs only at the coating–substrate interface) by the cross-sectional area of the cylindrical specimen considered.

2.5. Online particle diagnostics
The coating properties are intimately linked to the properties of as-sprayed lamellae, which in turn depend on in-flight particle properties as well as substrate temperature during spraying. It is known that both performance and properties of coatings are influenced largely by the microstructure, which in turn is influenced by the particle state along with substrate and deposition conditions. Online diagnostics using SprayWatch 2i equipment were carried out at different spray conditions to measure the particle temperature and velocity. Primary gas flow (Ar) strongly influences the average particle velocity whereas secondary gas flow (H₂) and current strongly influence the average particle temperature [12]. These three parameters are varied to achieve adequate temperature and velocity of melted agglomerates. Distance of the camera from the spray gun was kept between 150 and 200 mm. Particle temperature determination is based on the two-color pyrometry and in-flight particle velocities are measured from the length of particle traces during known exposure times using a single high-speed CCD camera [25]. The average particle temperature is 2650 ± 50°C – which is below the melting point of YSZ [17] – and velocity prior to impact is 200 ± 50 m/sec.

3. Results and discussion
3.1. X-ray diffraction (XRD)
The XRD patterns of agglomerated CeYSZ composite powder, bulk YSZ, Nanocrystalline YSZ and the CeYSZ nanocomposite coatings are shown in Figure 3(a) and (b). The commercial bulk polycrystalline YSZ coating is taken as a standard to compare the change in XRD patterns of the nanocrystalline YSZ and CeYSZ nanocomposite coatings. The nanostructured coatings obtained from reconstituted YSZ synthesized by chemical technique show cubic phases of zirconia. Impurity phases of Y₂O₃ are hardly observed in the XRD pattern. However, the high intensity peak (111) shifts towards the lower 2θ due to the development of strain in the nano-YSZ coating. The nanocrystalline CeYSZ composite powder shows high intensity peaks of tetragonal YSZ phases and cubic CeO₂. When the nanocrystalline composite powders were taken for coating, the XRD pattern clearly reveals the presence of tetragonal zirconia phases. The pattern is well matched with the JCPDS File no. 30–1468 which corresponds to tetragonal YSZ and no peaks corresponding to Y₂O₃ are detected. It is also evident that no monoclinic phase of
zirconia exists in the nanocomposite coating. It indicates that no CeO$_2$ peaks appear in the pattern, which confirms that CeO$_2$ is in solid solution with ZrO$_2$ and does not form any cluster in the CeYSZ coating.

3.2. Adhesion test results

Adhesion strength for as-sprayed coatings with the variation of particle temperature and velocity is shown in Figures 4 and 5, keeping other process parameters constant. Based on
the present understanding, it can be achieved by fixing one of the three torch parameters. Of
the three significant torch parameters, primary gas flow (Ar) strongly influences the average
particle velocity whereas secondary gas flow (H_2) and current strongly influence the average
particle temperature. It is found that bond strength increases from 2550 ± 50°C to 2650 ± 50°C
and then decreases after 2700°C (~ melting point of feed stock). Similarly, it is maximum at
particle velocity of 240 m/sec and seems to attain minimum value at 220 m/sec (may be fully
melted) and 280 m/sec (may be un-melted). A series of coating are developed in the broad
range of temperature and velocity. The test results for the adhesion of the APS nano-YSZ-
coated substrate using Taguchi’s L_{16} orthogonal design along with the corresponding S/N
ratios are described elsewhere, where maximum adhesion strength is found to be 40.56 MPa
[26]. The improvement of adhesion strength compared to nano-YSZ coatings is attributed to
the compactness and uniform microstructure of as-sprayed coatings and formation of Ce-
diffusion layers within the splats, which enhances inter splat adhesive forces. The semi-melted
particles (nano-zones) and the substrate were adherent to each other for which no micro
cracks or gaps have been observed. Therefore, those cracks observed in conventional coating
may be arrest or interrupted in embedded dense nano-zones having high toughness. The
maximum adhesion strength of nano-CeYSZ nanocomposite coating is found to be 42.39
MPa at 40 kW torch input power corresponding to particle temperature of 2686°C and
velocity of 241.6 m/s.

3.3. Surface morphology analysis

The field emission scanning electron micrographs of YSZ-CeO_2 nanocomposite coatings
are shown in Figure 6, which represents bimodal microstructure consisting of dense and
smooth zones, indicating good molten state of particles and the rough and porous zones,
indicating unmolten or semi-molten state of particles (Figure 6(a) and (c)). The percentage
of nano-zones are less in case of coatings shown in Figure 6(a) than that in Figure 6(c),
which may be attributed to their corresponding particle temperature and velocity. At
temperature ~2550°C and velocity 280 m/sec, the particle residence time is less and not
molten and hence does not exhibit appreciable amount of adhesion, and the same holds good for high particle temperature and low velocity, i.e. particles become fully molten and nanostructure is lost. At higher magnification (Figure 6(b) and (d)), the micrographs show densely packed nanograins having average grain size of ~90–120 nm. The grains are very closely packed with development of distinct grain boundaries without having any voids and porous structure (Figure 6(d)). In Figure 6(b), the presence of grains and nano-zones on the surface is evident, but micro-pores are present, indicating the presence of some amount of unmolten particles.

4. Conclusions
This study indicates that successful deposition of nanocomposite CeYSZ powder by plasma spraying route is possible on Inconel 718 substrates. Particle temperature and velocity seem to be most significant parameter affecting adhesion in case of CeYSZ nanocomposite coatings. Optimum adhesion strength of 42.39 MPa has been experimentally found out at 40 kW torch input power corresponding to particle temperature of 2686°C and velocity of 241.6 m/sec. XRD pattern of nanocomposite coating clearly reveals the cubic phase transformation of tetragonal and monoclinic YSZ with a small percentage of tetragonal phases. Ce is in solid solution with ZrO$_2$ and helps in stabilizing ZrO$_2$ and does not cluster in as-sprayed nano-composite coating. Micrograph of surface reveals the average grain size to be in the range of ~90–120 nm. The grains are very closely packed with distinct grain boundaries. The grains

Figure 6. (a, b) Field emission scanning electron microscopy micrographs of YSZ-CeO$_2$ nanocomposite coatings at particle temperature $2550 \pm 50^\circ$C and particle velocity 280 m/sec, (c, d) at particle temperature $2650 \pm 50^\circ$C and particle velocity 240 m/sec.
are interconnected with tetragonal grain boundary junctions. In summary, the enhancement of adhesion strength may be attributed to compact structure and high toughness of embedded nano-zones.

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