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# Nanostructured YSZ thermal barrier coatings engineered to counteract sintering effects

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#### **Abstract**

Thermal spray zirconia–8 wt% yttria (YSZ) deposits have been employed as thermal barrier coatings (TBCs) in the hot sections of gas turbines. The use of nanostructured YSZ represents an alternative for improving the performance of these coatings. Despite some initial positive research results, there are still fundamental questions to be answered on the applicability of nanostructured YSZ coatings as TBCs. These questions are related to sintering effects, which could significantly increase the thermal diffusivity/conductivity and elastic modulus values of these types of coatings in high temperature environments. In this study, nanostructured and conventional YSZ coatings were heat-treated at 1400 °C for 1, 5 and 20 h. It was observed that the nanostructured coatings counteract sintering effects, due to the presence of a bimodal microstructure exhibiting regions with different sintering rates: (i) matrix (low rate) and (ii) nanozones (high rate). Important sintering-affected properties, like thermal diffusivity and elastic modulus were studied. The thermal diffusivity and elastic modulus values of the nanostructured YSZ coatings were significantly lower than those of conventional YSZ coatings, even after an exposure to a temperature of 1400 °C for 20 h. This study demonstrates that nanostructured YSZ coatings can be engineered to counteract sintering effects and exhibit significantly lower increases in thermal diffusivity and elastic modulus values in high temperature environments when compared to those of conventional YSZ coatings. Crown Copyright © 2007 Published by Elsevier B.V. All rights reserved.

Keywords: Thermal spray; Nanostructured ZrO<sub>2</sub>-8 wt% Y<sub>2</sub>O<sub>3</sub>; Thermal barrier coatings (TBCs); Elastic modulus; Thermal diffusivity; Heat treatment; Differential sintering

## 1. Introduction

# 1.1. Thermal barrier coatings (TBCs)

Thermal barrier coatings (TBCs) have been employed for many years to protect the metallic components (e.g., combustion cans, blades and vanes) of the hot sections of aerospace and land-based gas turbines against the high temperature environment. The state-of-the-art TBC system is currently formed by a metallic bond coat (e.g., CoNiCrAIY) and a zirconia–yttria (ZrO<sub>2</sub>–7–8 wt% Y<sub>2</sub>O<sub>3</sub>) (YSZ) top coat [1,2]. The typical thicknesses of TBCs vary between 100 and 500  $\mu m$ , and they can provide a major reduction in the surface temperature of the metallic components of up to 300 °C, when combined with the use of internal air cooling of the underlying metallic component. Due to this characteristic, TBCs allow gas turbine engines to operate at temperatures higher than that of the melting point

of the metallic components of turbines (superalloys), which is approximately 1300 °C. Therefore, TBCs enable an increase in the efficiency and performance, and a reduction in the pollution levels of these types of engines [1,2]. Ceramic coatings were first applied as TBCs during the 1960s in the nozzles of the X-15 rocket planes and they became a standard product for commercial gas turbines in the 1980s [1]. Air plasma spray (APS) and electron beam physical vapour deposition are the two main processing techniques used to deposit YSZ coatings today for TBC applications [2].

#### 1.2. Nanostructured materials and TBCs

Nanoscience and technology offer the potential for significant advances in the performance of new and established materials based on improvements in physical and mechanical properties resulting from reducing the grain size by factors from 100 to 1000 times when compared to current engineering materials. Nanostructured materials exhibit grain (particle) sizes that are less than 100 nm in at least one dimension [3]. In addition to

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research in bulk samples, the study of nanostructured materials has also been extended to the area of surfaces and coatings, including thermal spray coatings [4]. The possibility of engineering coatings with superior wear resistance and more durable TBCs when compared to the conventional thermal spray coatings currently available opens a wide range of research and industrial application opportunities.

Initial studies on nanostructured air plasma sprayed YSZ coatings have shown that it is paramount to carefully control the spray parameters to avoid the complete melting of the nanostructured YSZ agglomerates in the plasma jet to preserve and embed part of the nanostructure of the agglomerates into the coating microstructure. Those coatings were produced from microscopic porous spray-dried particles formed via the agglomeration of individual nanosized YSZ particles. The semi-molten agglomerates, once embedded in the coating microstructure, created a bimodal feature, which consisted of a structure formed by the resolidification of agglomerates that had been fully molten in the spray jet combined with zones resulting from the incorporation of semi-molten material. By controlling the amount of previously molten and porous semi-molten particles embedded in the coating microstructure, it was possible to change considerably the mechanical response of the coating. Therefore, this bimodal microstructure affected the mechanical behaviour of the coating [5–7]. For example, under scratch testing monitored via acoustic emission (AE), it was observed that conventional YSZ coatings exhibited a larger number of AE events when compared to those of nanostructured YSZ coatings [8]. It was also observed that on average, the transversal load during scratch testing exerted by the nanostructured coating that exhibited the highest amount of previously semi-molten porous nanoagglomerates embedded in the coating microstructure, was significantly lower than that of the conventional YSZ coatings [8]. Therefore it was concluded that the nanostructured coatings exhibited improved compliance characteristics.

More recently, thermal shock tests were carried out for air plasma sprayed nanostructured YSZ coatings produced from agglomerated powders. Liang and Ding evaluated the thermal shock resistance of nano and conventional YSZ coatings by heating them in a furnace for 30 min at a series of temperatures up to 1300 °C, followed by subsequent cooling (dropping) in cool water for 10 min. For the thermal shock tests carried out at temperatures from 1000 to 1300 °C, the number of cycles to failure of the nano YSZ coatings was approximately 2-3 times higher than that of the conventional coatings [9]. Wang et al. also evaluated the thermal shock resistance of nano and conventional (fused and crushed powder) TBCs. The coatings were heated to 1200 °C for 5 min in a furnace and quenched in water at room temperature. The number of cycles to failure of the nanostructured YSZ coating was 2-4 times higher than that of the conventional coating [10]. These results also demonstrate the higher compliance capabilities of the nanostructured YSZ coatings.

These studies are encouraging; however, there is a skepticism in the thermal spray scientific community about the applicability of these coatings as TBCs. It is hypothesized that these nanostructured YSZ coatings would exhibit sintering (densi-

fication) rates much superior to those of conventional YSZ coatings once exposed to the high temperature environment of gas turbines. These high densification rates would increase the thermal diffusivity/conductivity and elastic modulus values (coating stiffening) of the nanostructured YSZ coatings to above critical levels, thereby impeding the application of this type of coating in a TBC system or leading to its premature failure.

The objective of this work is to show that it is possible to engineer novel air plasma spray coating microstructures from nanoagglomerated YSZ powders that can counteract sintering (densification) effects, which will impede the significant increase of thermal diffusivity/conductivity and elastic modulus values in high temperature environments, keeping them at levels even lower than those of conventional YSZ coatings.

# 2. Experimental procedure

### 2.1. Feedstock powders

The nanostructured YSZ ( $ZrO_2-7$  wt%  $Y_2O_3$ ) (Nanox S4007, Inframat Corporation, Farmington, CT, USA) powder was produced by the manufacturer via spray-drying by agglomerating individual nanosized YSZ into microscopic agglomerates, suitable for being fed and thermally sprayed using conventional thermal spray powder feeders. The nanostructured YSZ agglomerated powder received from the manufacturer exhibited a nominal particle size distribution ranging from approximately 15 to 150  $\mu$ m. Sieving was employed to remove smaller particles from the initial size distribution to produce a distribution containing coarser particles. The 15–150  $\mu$ m powder was sieved using a 53  $\mu$ m (Mesh 270) USA Standard Testing Sieve and sieving equipment (Alpine Augsburg Vacuum Sifter, Germany) in to order to try to obtain a particle size range of approximately 50–150  $\mu$ m [11].

The conventional YSZ ( $ZrO_2$ –8 wt%  $Y_2O_3$ ) (Metco 204B-NS, Sulzer Metco, Westbury, NY, USA) powder had been spray-dried and plasma-densified forming the so-called hollow spherical powder (HOSP). According to the manufacturer, this powder exhibited a nominal particle size distribution varying from 45 to 75  $\mu$ m. Because this powder is widely used worldwide as feedstock for the production of TBCs, it is considered as representative of currently used standard conventional YSZ material employed for TBC applications.

The particle size distribution of both powders was evaluated by a laser diffraction particle size analyzer (Beckman Coulter LS 13320, Beckman Coulter, Miami, FL, USA). The nanostructural and microstructural characteristics of the nanostructured YSZ powder were evaluated via scanning electron microscopy (SEM).

### 2.2. Thermal spraying and deposition efficiency (DE)

The nanostructured YSZ powder was thermally sprayed using an Ar/H<sub>2</sub> APS torch (F4-MB, Sulzer Metco, Westbury, NY, USA). The conventional YSZ powder was also air plasma sprayed (Ar/H<sub>2</sub>), however, a different torch (9-MB (GH nozzle), Sulzer Metco, Westbury, NY, USA) was employed. The

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