

Stabilize Consequences of Y₂O₃ in Zirconia Thermal Barrier Coatings (TBC)

¹MUHAMMAD FAROOQ, ²SHAHZAD ALAM, ³SHAHZAD NASEEM,
⁴SALEEM FAROOQ SHAUKAT* AND ⁵ROBINA FAROOQ

¹*Institute of Chemical Engineering and Technology, University of the Punjab, Lahore-Pakistan*

²*Pakistan Institute of Minerals and Advanced Engineering Materials, PCSIR Laboratories,
Lahore-Pakistan*

³*Center for Solid State Physics, University of the Punjab, Lahore-Pakistan*

⁴*Department of Physics, COMSATS IIT, Lahore, Pakistan*

⁵*Department of Chemical Engineering, COMSATS IIT, Lahore, Pakistan
saleem@ciitlahore.edu.pk**

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Summary: The accumulation of cubic stabilizing oxides is a pre-requisite for the use of Zirconia as a main voter in thermal barrier coating. These can be added in ample amounts to form a partially stabilized Zirconia or to form a fully stabilized Zirconia. Zirconia yttria (ZrO₂Y₂O₃) coating deposited by plasma spray method is widely used in industry as a thermal barrier coating (TBC). Development of narrative and innovative ceramic materials, which have brought about significant hi-tech change, predominately by Y₂O₃ for the accumulation of varying amounts of cubic stabilizing oxide. This paper is a study on the effect of stabilizer on performance of ZrO₂ thermal barrier coatings. For experimentation, Y₂O₃ complete characterization was done with ZrO₂Y₂O₃ coated samples to optimize the micro structural, mechanical properties and characterization, using the latest techniques. It was observed that porosity content in all the coated samples was not very high. However the porosity content was uniformly distributed and pore size was small. It has been revealed that, in case of small porosity content, hardness values of thermal barrier coating with stabilizing effect of yttria were not very high.

Key Words: Thermal barrier coatings, bond coat, microstructure, hardness profile, scanning electron microscope

Introduction

Knowledge steps forward in numerous domains of contemporary civilization is eventually reliant on the stuff science and the engineering society to envision the narrative materials with extra ordinary grouping of their physical and mechanical properties. [1] The starting point of thermal spraying dates back to the early 1900s and the contraption of a metalizing procedure by Heimann are normally acknowledged as the rendezvous of the technology birth [2]. To begin with, the process had been used mainly for declaration of corrosion resistant zinc coatings, followed afterward by the spraying of durable metals. Thermal spraying processes form by melting the consumable substances into droplets and impinging droplets on the substrate. The mechanism of bonding to surface in thermal spraying is the same as plating, both mechanical interlocking and atomic interaction, with the shear strength around 7MPa. Plasma spraying process from one of the familiar thermal spraying process produces 1650 °C heats for melting powders and the surface temperature of the substrate exceeds 150°C. Plasma spraying process is thus more suitable for spraying ceramics on metals. Thermal barrier coatings (ceramic coatings) are being used for preventing the parts from thermal shocks and for preventing the material properties from the

heat treatment effect produced by elevated temperature when they are in process. [1].

Hi-tech advancement in numerous domains of social order is ultimately dependent on the material science and the ability of the engineering community to conceive novel materials with extra ordinary combination of their physical and mechanical properties. [1, 3]

For the duration of thermal cycling, the bond coat should not experience considerable plastic strain. The outer zirconium oxide/yttrium oxide (ZrO₂-Y₂O₃) system base ceramic layer can be applied by two techniques: air plasma spraying of powders (TBC-APS, this technique is used in current study) or vapor condensation at electric beam evaporation of ceramic pellets (TBC-EB). Ceramic coating overhaul life depends on Y₂O₃ content. However, one should keep in mind that the coating service life depends not only on its chemical concentration but also on its structure. The adhesive strength at the ceramic layer/bond coat crossing point depends on deposition modus operandi. [4-6]. Optical Microscopy, Scanning Electron Microscope, Surface Profile-meter and Vicker's hardness test techniques have been extensively used in this research work for characterizing the coating system.

*To whom all correspondence should be addressed.

Results and Discussion

Microstructures

Microscopic images obtained, when the hot mount samples were observed under the Leica Image Analyzer. Images have been taken at 50X, 100X, 200X and 500X. Most of the images taken were of the cross-section of samples, so that an image of the complete Thermal Barrier Coating system may be obtained.

Fig. 1 is a microstructure of base metal, bond coat (Ni-5%Al) and the zirconia top coat stabilized with 8% Y_2O_3 . It also shows a microstructure of the cross-sectional scrutiny of the coating system. The base metal can be seen to have an equi-axed grain size. Three equally spaced Vicker's indents in the base metal and the coating can be seen. The TBC coating consists of the bond coat and the $ZrO_2.Y_2O_3$ top coat. The top coat can be seen to contain large amounts of porosity. The top coat porosity can be premeditated in more detail. Porosity seems to be more or less often scattered throughout the top coat. Size of the porosity across the coating is seen to vary. This can be attributed to "particle pluck out" which has occurred in several regions of the coating. Particle pluck out is the result of pressure on top coat during hot mounting. Percentage porosity recorded for this sample was also very high as compared with the other samples. The thin white bond coat can be seen in between the base metal and top coat. Vickers hardness indents are also visible and porosity can also be seen

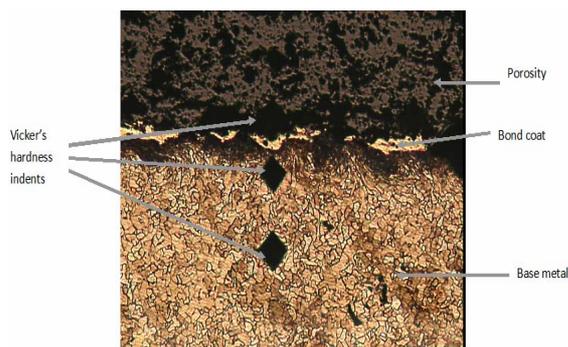


Fig. 1: Microscopic image showing the base metal, bond coat and top coat.

Fig. 2 shows archetypal Plasma sprayed zirconia yttria ceramic thermal barrier coating showing delamination problem due to excessive set down thickness. The existence of porosity in a thermally sprayed coating is to be anticipated.

Zirconia (ZrO_2) based ceramics have a thermal expansion coefficient of $11-13 \times 10^{-6} K^{-1}$ and a thermal conductivity of about 2.3 W/ (m.K) at 1000°C for a fully dense material; this can be further reduced by introducing porosity [7].

It can clearly be seen in both the microscopic images (Fig. 2 and 3) that there has been plastic deformation in the base metal in the region close to the coating. There is also validation of change in grain size of base metal in the coating region. The change in grain size is the result of sample being over heated during the coating process.

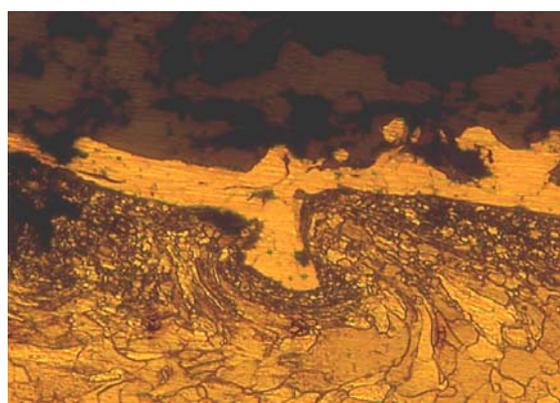


Fig. 2: Image showing deformation and change in grain size in base metal (200X).

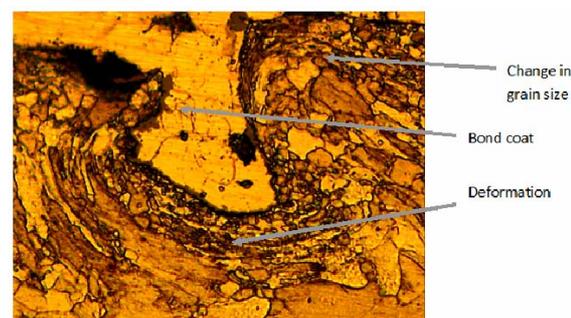


Fig. 3: Detailed view of the deformation caused in the base metal (500X).

It is alleged that the differences in porosity levels between the two types of coatings can be attributed to the behavior of the powders during thermal spraying. Typically Thermal Barrier Coatings can have up to 20% porosity which assists in lowering thermal conductivity of the coating. Often oxide inclusion can also be misinterpreted for porosity. The coating's porosity is a function of the material, plasma spray parameters and process conditions. Open porosity in as-sprayed deposits can

be produced in the range of 1-5% when the spray process is optimized. The higher porosity in as-sprayed zirconia-based materials can be endorsed, in part, to melting point differences of the alloys and the consequent effects on solidification [8].

Plasma sprayed coatings (as well as free-forms) are built-up by the impingement and solidification of molten droplets deposited in successive layers. Each layer consists of several lamella (thin layers), with each lamella approximately 3-10 microns thick, 60-180 microns in diameter and typically containing columnar grains 0.1-0.3 microns. The solidification of these lamellae is reliant upon the particle size, velocity, temperature, substrate surface state of affairs and physical properties of the molten material.

The formation and phase of each lamella depends on the cooling and solidification rates experienced during solidification. The cooling rate, in turn, depends on material properties such as the melting point, density and specific heat, and on the thermal contact between the lamella and previously deposited layer [9].

As a result of their unique microstructure, these coatings can endow with valuable mechanical, thermal and chemical properties to the components they are shielding. The coatings are less prone to catastrophic brittle failure, are able to withstand high thermal gradients. This quasi-layered process also provides tremendous flexibility in producing the desired thickness or surface texture required for the application. In as-sprayed coatings, some properties are inferior (e.g., mechanical properties) to those of bulk processed materials. However, in many cases, the flexibility of the plasma process compensate for this inferiority. When material properties similar to those of bulk processed ceramics are needed, the as-sprayed ceramics can be heat treated to reduce porosity by sintering. The mechanical properties of bulk ceramic materials are strongly influenced by the porosity. Similarly, the strength for as-sprayed ceramic deposits is related to the contact area between lamella which in fact produces porosity [9].

Bond coats practical using the APS spray method, undergo a slight internal oxidation at the time of deposition due to the deposition in atmospheric oxygen. This accounts for the presence of oxides and also porosity in the final microstructure. Porosity is present due to the characteristic lamellar structure of the TBC.

Fig. 4 shows top view of NiAl lamellar structure. Upon high temperature oxygen exposure,

Al present in the bond coats forms an exceedingly protective oxide scale throughout the thickness of the bond coat, commonly referred to as the thermally grown oxide (TGO) at the TBC-bond coat interface. Bond coats are also accountable for improving the thermo-mechanical compatibility between the metallic substrate and the ceramic topcoat.

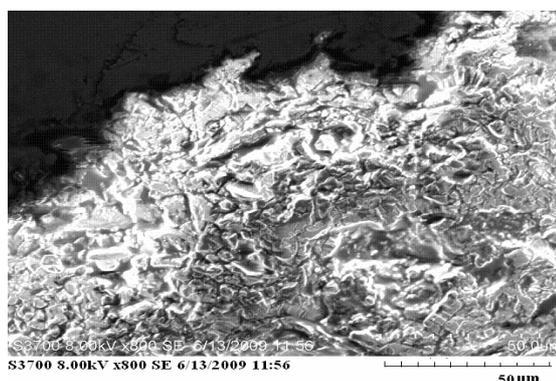


Fig. 4: Top View of NiAl showing lamellar structure.

Figure 5 is the SEM micrograph of zirconia yttria that was deposited in the present study. Also there are particles (liquid droplets of zirconia yttria coating) which cooled as they traveled through the air and by the time they were actually deposited on the substrate, they were solidified and so they could not be incorporated in the actual coating. Also it is possible that since these particles are traveling through air, they may have interacted with the oxygen and may have formed oxides. These oxides could not get incorporated in the actual coating.

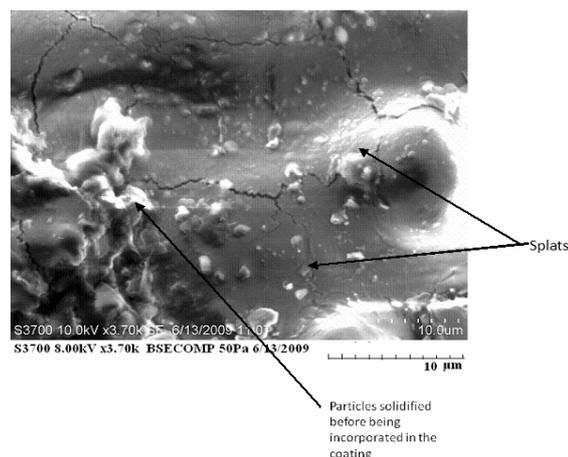


Fig. 5: SEM micrograph of Zirconia Yttria.

Particles like those mentioned above increase the surface roughness of thermally sprayed coatings. Sometimes an amplified surface roughness

can be harmful to the efficiency of the coating performance.

The characteristic lamellar structure (layers of splats deposited one over the other) is like flattened grains if seen closely and may be seen to flow in the direction of the substrate (Fig. 5). The structure is anisotropic, with physical properties being different parallel to substrate (longitudinal) than across the coating thickness (transverse). Strength in the longitudinal direction can be 5 to 10 times that of the transverse direction [9].

Experimental

Coupons of medium carbon steel (dimensions 12.5x 25mm) cut out from a medium carbon rolled steel sheet were chosen for this particular TBCs. Samples after chemical cleaning in CCl_4 solution were grit blasted with steel grit # 25 with right angle on the coupons and chemically cleaned with following process: The coupons were cleaned in distilled water and by mixture of 50% CCl_4 + 50% acetone followed by ultrasonic cleaner at optimum temperature of 60°C. Coupons were again rinsed in distilled water and dried with compressed air to ensure removal of all aqueous medium from the coupons.

The plasma coating system used was the 9th series Sulzer Metco, Air Plasma System (APS). This 80kVA system consists of a powder feeder, heat exchanger and a manual control unit to control the various parameters of coating. Before coating the system the powder was placed in oven at 70°C for about 30 minute in order to remove any moisture from the powder.

Metco 450 NS powder as coated on the mild steel coupon as a bond coat because of the NiO-ZrO role is not affecting the stability of Zirconia [10] and Zirconia Yttria as a thermal barrier coating. The coating parameters followed for depositing bond coat are specified in the Table-1.

Following the plasma spraying process and once the coating of all samples was completed, the coating quality was checked.

The first step involves microscopic assessment of the coatings where coating quality depends on the spraying parameters plus powder eminence and sample prepared. Metallography was carried out in accordance with ASTM standard E1920 - 03(2008).[10] Smaller sized coupons of dimensions 12.5mm x 25mm were cut out from each

of the coated coupons with the help of diamond blade speed of 10 rpm; moving from coating to substrate to avoid coating damage.[11].

Table-1: Coating Parameters for Deposition of Bond Coat and TBC.

Parameters	Specification for Bond Coat	Specification for Zirconia Yttria
Ar flow rate	90scfh	90scfh
Ar pressure	75psi	75psi
H ₂ pressure	50 psi	50 psi
H ₂ flow rate	15scfh	15scfh
Current	500 A	600 A
Carrier pressure	60 psi	60 psi
Carrier flow rate	13.5 scfh	13.5 scfh
Spray rate	9 lb/h	6 lb/h
Spray distance	5.5"	2.5"

Cross section of samples was Hot Mounted in hot mounting press by phenolic resin at 150°C with applied pressure of 1200 daN for the setting time of 15 minutes. And the grinding was performed by the use of SiC abrasive (particle size 320 μm , 240 μm , 180 μm) for grinding with water as lubricant. Diamond paste was used for rough polishing (particle size 6 μm) and fine polishing (particle size 3 μm). Oil was used as lubricant.

Microscopic images were obtained and observed on the Leica Image Analyzer. Images were taken at 50X, 100X, 200X and 500X. Both the cross-section and top surface of the coating were observed by the specially prepared mounts accordingly. Coating thickness was also determined on an optical microscope at a magnification of 100X using a micrometer scale. The number of divisions that sheltered the coating was counted, coating thickness was determined, i.e. 20 μm thickness of bond coat and 600 μm thickness of TBC.

Coating's hardness was characterized by micro Vicker's hardness tester at 500g with 50 μm intervals starting from substrate to coating; following standards: ASTM E384 (Vol. 03.01).[7] A hardness profile was generated and represented in a table using the results obtained.

The SEM imaging was performed using a Hitachi S3700N scanning electron microscope. Since the samples were mounted and was made conductive by using liquid conductive tape; to be left for around 24 hours for the tape to dry.

Surface roughness measurements were performed on the diamond tip used in Surf Corder 1700 α has a radius of 2 μm . The cut-off width is usually 0.8mm where the total stylus travel is usually 20 to 60 times the cut off width with the electronic

circuitry continuously averaging the readings over the set cut-off width. In the present study a diamond stylus was placed on the sample and was electronically dragged over the surface. While the roughness values were measured, special care was taken to avoid any sort of vibration within the environs of the instrument as that could escort to erroneous results.

Conclusion

An extensive research has been carried out in the deposition of zirconia stabilized with Yttria (thermal barrier coatings) with Ni-5%Al bond coat using plasma spray technique. It was observed that porosity content in all the coated samples was not very high. However the porosity content was uniformly distributed and pore size was small. It has been revealed that, in case of small porosity content, hardness values of thermal barrier coating with stabilizing effect of yttria were not very high. Moreover, the phase change in coating affects the hardness values of the overall coating.

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