# **GT2011-45\* (** MECHANICAL PROPERTIES OF TITANIA-DOPED YTTRIA STABILIZED ZIRCONIA (TIYSZ) FOR USE AS THERMAL BARRIER COATING (TBC)

M. Kibsey, J. Romualdez, X. Huang High Temperature Materials Research Department of Mechanical and Aerospace Engineering Carleton University 1125 Colonel By Drive Ottawa, ON, Canada

### ABSTRACT

Representative samples of Yttria Stabilized Zirconia (7YSZ) codoped with varying concentrations of TiO<sub>2</sub> were fabricated using plasma spraying. Samples were sintered in order to minimize porosity and to simulate the bulk material properties. After sintering, porosity levels of less than 1.25% were achieved. Both as-sprayed and sintered samples with 5, 10 and 15 wt% TiO<sub>2</sub> addition levels were microstructurally characterized using SEM, XRD and optical image analysis methods. Vickers hardness, Young's modulus, and fracture toughness were measured using nano and macroindentation methods. Microstructural analysis revealed that sintering of the TiO<sub>2</sub> doped samples was required to achieve a homogeneous composition distribution, with TiO<sub>2</sub> predominantly residing in solid solution within the ZrO<sub>2</sub> matrix. Sintering for 325 hours at 1200°C resulted in sufficient diffusion of TiO<sub>2</sub> into the 7YSZ. The addition of TiO<sub>2</sub> stabilized more tetragonal phase as revealed by XRD measurement. Sintering also showed significant improvements in fracture toughness in all co-doped samples. Fracture toughness values calculated using load-independent equations provided a clear trend in fracture toughness improvement with TiO<sub>2</sub> addition. Ferroelastic toughening of the tetragonal phase was believed to have played an effect. There was also a reduction in monoclinic phase content with  $TiO_2$  addition, which may have limited microcrack formation and consequently increased the fracture toughness. With the addition of 10 wt%  $TiO_2$ , the fracture toughness was improved by over 50%; however, this improvement started to decline at 15 wt% TiO<sub>2</sub> addition. Volumetric porosity measurements also revealed significant improvements in fracture toughness with respect to lowering the porosity content as observed in all sintered samples.

# **1.0 INTRODUCTION**

The present state-of-the-art in advanced gas turbine engine design requires turbine inlet temperatures in excess of 1300°C to optimize engine efficiency. However, the use of conventional high-temperature single crystal superalloys for 1<sup>st</sup> stage turbine blade and vane segments is limited due to their propensity for incipient melting when exposed to temperatures in this range. To prevent component failure and to extend service life, critical turbine components are almost always protected by ceramic coatings known as Thermal Barrier Coatings (TBCs).

One such ceramic used for TBCs is zirconium dioxide (ZrO<sub>2</sub>). Upon heating zirconia to typical turbine inlet temperatures, the material undergoes successive phase transformations, passing from monoclinic (*m*) to tetragonal (*t*) to cubic fluorite (*c*) phases. The  $m \leftrightarrow t$  transformation induces a 3-5% volume change, which can lead to cracking and brittle fracture in service [1]. In order to circumvent this phase change, yttria (Y<sub>2</sub>O<sub>3</sub>) is added as a dopant to stabilize the

R. Kearsey. Q. Yang Structures and Materials Performance Laboratory National Research Council of Canada, Institute for Aerospace Research 1200 Montreal Road

Building M13 Ottawa ON, Canada

zirconia and fully or partially retain the tetragonal phase to lower temperatures. Due to the high fracture toughness, thermal shock resistance and ionic conductivity of yttria stabilized zirconia, it is also used for oxygen sensors and solid oxide fuel cells, in addition to thermal barrier coatings [2]. Yttrium is an oversized trivalent cation and its charge dictates that two  $Y^{3+}$  cations produce one oxygen vacancy. The presence of oxygen vacancies in partially stabilized YSZ decreases tetragonality and leads to the formation of nontransformable tetragonal t' phase that is resistant to the transformation into m phase [3]. However, after repeated thermal exposure to extreme engine heating and cooling cycles, the metastable t' zirconia eventually undergoes equilibrium phase decomposition and results in the formation of m phase. Although higher concentration of Y<sub>2</sub>O<sub>3</sub> can fully stabilize the cubic phase, it has been found that adding 7 wt% yttria to zirconia (7YSZ), a partially stabilized zirconia, is the optimal concentration required to extend component service life and maximize the number of cycles until failure of the TBC [4].

The highest values of fracture toughness occur in partiallystabilized YSZ, containing concentrations of dopants that allow partial retention of the tetragonal phase. There are several mechanisms to account for the toughening effect. A process known as transformation toughening is one such mechanism [5]. Transformation toughening occurs when the tensile strains focussed at crack tips cause the crystal structure to undergo a local  $t \rightarrow m$ transformation. The accompanying volumetric expansion at the crack tip promotes crack closure, which hinders any further crack propagation. The ability of transformation toughening to limit crack propagation gives the transformable *t*-phase a high fracture toughness value. However, the benefits of transformation toughening are limited as the  $t \rightarrow m$  transformation only occurs readily at low temperatures. Thus, transformation toughening has little effect on toughness related properties during high temperature exposure at peak turbine power demand. Although the non-transformable t' phase is deficient in transformation toughening, it is preferred for use in thermal barrier coatings because the  $t \rightarrow m$  transformation during thermal cycling ultimately compromises the coating's integrity [5].

Ferroelastic toughening is another toughening mechanism employed in YSZ ceramics. Ferroelastic crystals are those in which the crystal structure can occupy two or more different orientations, and these orientations can be interchanged by the application of a mechanical stress [6]. The tetragonal phase in zirconia ceramics is ferroelastic because it can occupy three different orientations, at 90° intervals. When a stress is applied in a suitable crystallographic direction, the stress can cause the tetragonal cell to reorient in that direction. This results in the elongation of one of the *a* unit cell parameters into the characteristic *c* parameter. Consequently, the previous c cell parameter shortens to compensate. If a crack exists in a particular YSZ coating, ferroelastic toughening can hinder possible crack growth. Instead of propagating, the crack causes a stress concentration at its tip, which can reorient the tetragonal lattice in such a way that the elongated side of the tetragonal cell closes up the crack and hinders propagation [5].

An effective strategy for toughening zirconia ceramics involves stabilizing the tetragonal phase to a) avoid transformation into the mphase, which causes degradation due to volume change and b) avoid transformation into the c phase, because ferroelastic toughening cannot occur without tetragonality [7]. It is hypothesized that these toughening criteria are met by the addition of titania as a co-dopant. Ti4+ is an undersized tetravalent dopant. Tetravalent dopants have little effect on the oxygen vacancies in the microstructure. This is because tetravalent dopants have the same valency charge as the zirconium Zr<sup>4+</sup> cation. Thus, the tetravalent dopants do not cause vacancies in order to maintain electroneutrality [8]. By not creating oxygen vacancies, titania compensates for the negative effects of the yttria dopant, whose oxygen vacancies decrease tetragonality and increase oxygen diffusion. Undersized tetravalent dopants, such as Ti<sup>4+</sup>, have a smaller atomic radius than Zr<sup>4+</sup> and occupy less space in the crystal lattice. The smaller dopants produce tensile stresses in the lattice, which stabilize the t phase and destabilize the c phase [7,3]. For these reasons, titania was selected as a potential co-dopant for 7YSZ.

The objective of this study is to analyze the mechanical properties of plasma sprayed titania-doped 7YSZ (TiYSZ) with the intent of applying this material in TBCs. In order to simulate the bulk properties of the material, a higher density was favoured. For this reason, all test samples were sintered in order to minimize porosity. The bulk density, hardness, Young's modulus, fracture toughness and volumetric porosity will be assessed herein.

# 2.0 MATERIALS AND EXPERIMENTAL PROCEDURE 2.1 Sample Preparation

In order to observe the effect of increased titania content, three different concentrations of titania were combined with 7YSZ: 5 wt%, 10 wt%, and 15 wt%. These will be referred to as 5TiYSZ, 10TiYSZ and 15TiYSZ. Undoped 7YSZ samples (7.5 wt%  $Y_2O_3$ -Zr $O_2$ ) were also prepared to provide a basis for comparison.

TABLE I FOWDERS USED FOR FLASIMA SPRATING					
	Composition	Powder size	Trade	Supplier	
		distribution	Name		
		(µm)			
Coarse	92.5 wt% ZrO2	106±45	Al -	Praxair	
7YSZ	7.5 wt% Y <sub>2</sub> O <sub>3</sub>		1075	Canada	
Fine	92.5 wt% ZrO <sub>2</sub>	45±5	ZrO-	Praxair	
7YSZ	7.5 wt% Y <sub>2</sub> O <sub>3</sub>		271-3	Canada	
TiO <sub>2</sub>	TiO <sub>2</sub>	45±10	TiO-114	Praxair	
				Canada	

TABLE 1 POWDERS USED FOR PLASMA SPRAYING

TABLE 2 SPRAY	PARAMETERS FOR	PLASMA SPRAYING

Argon	0%	Total Flow Rate	250 slm
Nitrogen	75%	Powder Feed Rate	~50 g/m
Hydrogen	25%	Carrier Gas Flow Rate	12 slm
Current 250 Amps		Nozzle Size	3/8 in
Distance of Plasma Gun from Substrate 150 mm		Duration of Coating Run	7 min.

The powders were all manufactured by Praxair and sprayed on to a mild steel substrate using a Mettech Axial III plasma spray system, manufactured by Northwest Mettech Corporation (Vancouver, Canada). Before being loaded into the Axiall III Powder Feeder (Thermach Inc. AT-1200HP Powder Feeder), all powder mixtures were baked for 30 minutes to remove any moisture that could cause clumping during the spraying process. The powders were mixed using a ball mill (Fritsch GmbH Planetary Mono Mill Pulverisette 6), using settings that would mix the powders without further particle size reduction. To remove the substrate after spraying, the strips of ceramic were soaked in 25% nitric acid and distilled water for 2 hours to dissolve the majority of the carbon steel. Any remaining metal substrate was removed using 120 grit sandpaper. Two sets of samples were produced, one with coarse 7YSZ and the other with fine 7YSZ. A portion of the first set was sintered for 100 hours at 1100°C. This was to determine if the sintering time and temperature were sufficient to produce dense and homogeneous microstructure. The other portion was then sintered for 325 hours at 1200°C, which was found to be more adequate for material densification. Half of the second sample set was sintered at 1200°C for 325 hours and the other half was left in the "as-sprayed" condition (unsintered).

TABLE 3 FINAL COMPOSITION OF FINE-POWDER TITANIA-DOPED 7YSZ SAMPLES

Sample	wt% TiO <sub>2</sub>	wt% $Y_2O_3$	wt% ZrO <sub>2</sub>
7YSZ	0	7.5	92.5
5TiYSZ	5	7.125	87.875
10TiYSZ	10	6.75	83.25
15TiYSZ	15	6.375	78.625

The samples for microstructural analysis were cold mounted in a transparent Hysol epoxy resin. The mounted samples were prepared using successive grit sandpaper, ranging from 180, 240, 320, 400 to 600 on a standard circular platform. After grinding, the samples were ultrasonically cleaned for 30 minutes to remove any accumulated grinding debris. The samples were polished with 9  $\mu$ m, 6  $\mu$ m, 3  $\mu$ m, and 1  $\mu$ m diamond suspension and a 0.05  $\mu$ m alumina suspension final polish. Polishing was done using TEXMET 2000 and TEXMET 1500 polishing pads for coarse ( $\geq 6 \ \mu$ m) and fine polishing (< 6  $\mu$ m), respectively.

# 2.2 Etching Procedures and Grain Boundary Observation

Some of the samples were etched in order to examine porosities and grain growth. The etchant used was a solution of 2 parts HF (38-40%), 1 part HNO<sub>3</sub> (38-40%) and 2 parts HCl (48-50%). Representative samples of 5TiYSZ, 10TiYSZ and 15TiYSZ were submerged in the etchant for 5 minutes, then removed and rinsed with ethyl alcohol and distilled water. The etched samples were then carbon-coated and observed under the Tescan Vega-II XMU VPSEM scanning electron microscope (SEM). Carbon-coating is a standard procedure that deposits a conductive film over the sample's surface, which allows the SEM's electron beam to disperse freely after coming in contact with the surface. Without a carbon coating, surface charging would occur and the images produced by the SEM would display uncharacteristically light and dark regions.

# 2.3 Fracture Toughness Measurements Using Indentation Methods

It is known that determining the fracture toughness ( $K_{1C}$ ) of a material through indentation methods is very uncertain. In fact, the use of indentations is not considered a standard method for determining the fracture toughness for design purposes due to the inherent number of factors that affect the results. These factors include the residual stresses left on the sample surface after preparation, residual stresses left from the indenter, the variability of apparent crack lengths depending on the quality of sample imaging and the different crack shapes (which can be Palmqvist or radialmedian type cracks). The results of an indentation method can also depend on the applied force. Consequently, the indentation method for determining  $K_{1C}$  should be used only for the qualitative comparison of samples generated using similar procedure [9]. The values presented in this study are meant to show trends, while standard tests, such as surface crack in flexure (SCF), single-edge

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precracked beam (SEPB), or chevron notch in bending (CNB), were carried out according to ASTM C 1421-99 standards prior to material's use in service [10].

There is also much debate over how to mathematically relate the parameters of an indentation (such as crack geometry, indentation load, Hardness and Young's modulus) to obtain an accurate value for the fracture toughness. In order to examine the validity of various  $K_{1C}$  formulas, Clément [11] performed indentation tests with a range of applied loads and compared the results using seven different empirical formulas. These seven formulas are as follows [12,13,14,15,16,17,18]:

$$K_{1C} = 0.0154(E/H_v)^{\frac{1}{2}} \left( P/c^{\frac{3}{2}} \right)$$
(1)

$$K_{1C} = 0.0095(E/H_v)^{\frac{2}{3}} \left( P/c^{\frac{3}{2}} \right)$$
<sup>(2)</sup>

$$K_{1C} = 0.028 \left( H_v a^{\frac{1}{2}} \right) (E/H_v)^{\frac{1}{2}} (c/a)^{-1.5}$$
<sup>(3)</sup>

$$K_{1C} = 0.0303 \left( H_{\nu} a^{\frac{1}{2}} \right) (E/H_{\nu})^{\frac{2}{5}} \log(8.4 \ a/c)$$
<sup>(4)</sup>

$$K_{1C} = 0.015 (E/H_v)^{\frac{2}{3}} \left( P/c^{\frac{3}{2}} \right) \left( \frac{1}{a} \right)^{-1/2}$$
(5)

$$K_{1C} = 0.0495 \left( H_{\nu} a^{\frac{1}{2}} \right) (E/H_{\nu})^{\frac{2}{5}} \left( \frac{c}{a} \right)^{\left( \left( \frac{c}{18a} \right) - 1.51 \right)}$$
(6)

$$K_{1C} = 0.0782 \left( H_v a^{\frac{1}{2}} \right) (E/H_v)^{\frac{2}{5}} \left( \frac{c}{a} \right)^{-1.56}$$
(7)

where *E* is Young's modulus,  $H_V$  is Vickers hardness and *P* is the applied load during indentation. The parameters *a* and *c* are taken from a Vickers indentation, where *a* is the indent half-diagonal and *c* is the crack length (as shown in Fig. 1). Note that Equations 1, 2 and 5 depend on the load *P*, while Equations 3, 4, 6 and 7 do not. The effect of the indentation load on the fracture toughness equations will be further discussed.



FIG. 1 VICKERS INDENTATION CRACK GEOMETRY MEASUREMENTS

A Vickers-Armstrong Ltd. macro indenter was used with a load of 3 kg in this study. The produced indentations were examined using an Olympus PMG3 optical microscope at 10X magnification, which allowed the indent diagonals and cracks to be measured using the ImageTool software. It was observed that the cracks produced from the indentation were often not linear, but were branched and randomly broken. In a previous study [19], it was shown that measuring the linear crack length (directly from the indent centre to the crack tip) or measuring the non-linear length of the crack (by following the crack path) had little effect on the overall trends produced in the fracture toughness results. It was noticed that the fracture toughness was slightly lower based on the non-linear crack lengths, due to longer reported cracks. In order to accurately present the length of indentation cracks, the non-linear cracks were measured in this study.

The fracture toughness of partially yttria-stabilized zirconia (PSZ) ceramics should lie in the range of 3.0 to 15 MPa m<sup>1/2</sup> [20]. In order to compute  $K_{IC}$ , the Young's modulus, hardness, indentation load and crack geometry were also determined in this study.

#### 2.4 Hardness

The hardness of the specimens was found using the CSM Nanoindentation Tester with a Berkovich indenter, which employed the concept of Depth-Sensing Indentation. The nano-indenter of a known geometry steadily applied a load at the material surface, until a maximum load was reached. The device then proceeded to reduce the load. A force over displacement graph was produced for the loading and unloading cycle, from which the hardness and the Young's modulus could be calculated. The indentation hardness is defined as

$$H = \frac{P_{max}}{A} \tag{8}$$

where  $P_{max}$  is the maximum load applied during the indentation and A is the projected area of the hardness indentation [21]. For each sample, a series of 5 indents were made using a 100 mN load. Additional indentations were made if significant scatter was observed in the measured hardness results.

#### 2.5 Young's Modulus

As with hardness, the CSM Nano-indentation tester was used to obtain the Young's modulus. Assuming that the unloading sequence is purely elastic, the reduced Young's modulus can be determined from [22]

$$E_{reduced} = \frac{\pi^{1/2}}{2} \cdot \frac{S}{a^{1/2}}$$
(9)

where *S* is the stiffness at maximum loading (determined from the unloading cycle) and *a* is the contact area between the indenter and the material surface at maximum loading. The value of *a* is evaluated using the contact depth  $h_c$  and from the known geometry of the indenter. The contact depth  $h_c$  can be estimated using the Oliver and Pharr method [21]:

$$h_c = h_p - \theta \cdot \frac{F_{max}}{S} \tag{10}$$



FIG. 2 (A) SCHEMATIC OF THE INDENTATION TESTING FOR AN IDEAL CONICAL INDENTER AND (B) THE INDENTATION LOAD-DISPLACEMENT CURVE [22]

The values of  $h_p$  and  $F_{max}$  are depicted in Fig. 2. The value of angle  $\theta$  is 0.72 for the Berkovich indenter. During indentation, both the indenter and the specimen undergo elastic deformation. The reduced Young's modulus includes both of these deformations. To account for the elasticity of the indenter, the following relation applies:

$$\frac{1}{E} = \frac{(1 - \gamma_i^2)}{E_i} + \frac{(1 - \gamma_s^2)}{E_s}$$
(11)

where  $\gamma_i$  and  $\gamma_s$  are the Poisson's ratios of the indenter and the specimen. Knowing the parameters for the indenter, the specimen's Young's modulus,  $E_s$ , can be found. Furthermore, due to the nature of the nano-indentation technique, the modulus value that is found is skewed by the porosity of the sample. Mackenzie's equation [23] can be used to find the Young's modulus of non-porous material. Note that Mackenzie's equation is not generally used for indentation techniques. The values produced are only used to observe trends.

$$E = E_o \cdot (1 - 1.9P + 0.9P^2) \tag{12}$$

*P* is the volume fraction porosity that is found using image analysis described below, and  $E_o$  is the Young's modulus of non-porous material [22]. Rearranging the equation allows  $E_o$  to be found based on the measured *E*.

# 2.5 Bulk Density

The bulk density of the ceramic samples was measured in order to ascertain the effectiveness of the selected sintering process, and also to verify whether the mechanical properties are affected by the density of the materials. The bulk density was found using Archimedes' theorem, which states that [3]

$$\rho_{bulk} = \frac{w_{dry}}{w_{dry} - w_{wet}} \rho_{liquid} \tag{13}$$

where  $\rho_{bulk}$  is the bulk density of the sample,  $w_{dry}$  is the dry weight of the sample,  $\rho_{liquid}$  is the density of the suspending liquid and  $w_{wet}$  is the weight of the sample suspended in the liquid. All weight measurements were made on a digital scale with an accuracy of  $\pm 0.0001$  g. Each sample was first weighed dry, and then submerged into a beaker of distilled water while being suspended in a small hanging basket. The added weight of the sample in the water was taken as  $w_{wet}$ . The density of distilled water  $\rho_{liquid}$  is known, thus the bulk density could be calculated. In order to account for the uptake of water in porous ceramic samples, a standard submersion time of 30 seconds was used.

#### 2.6 Volumetric Porosity

The porosity of the material can affect the K<sub>1C</sub> of the material, given that pores and internal cracks can act as stress concentrators that initiate crack propagation [8]. To determine the extent to which porosity affects the K<sub>1C</sub>, the porosity was measured using a combination of two methods: a visual image analysis and a bulk density method. In the image analysis method, the polished samples were photographed twice at 5X, 10X and 20X magnifications. The resulting digital images were subjected to black and white threshold processing, so that all pores appeared as black and the solid ceramic material appeared as white. The measured percentage of black pixels was inferred as the areal fraction porosity. However, given the linearity of the spraying process, it was reasonable to assume that the pores were not evenly shaped in all directions. Rather, it was suspected that the pores would have a flattened shape due to the high speed impacts of particles onto the substrate during the spraving process. To assess the three-dimensional shape of the pores, additional samples were mounted and polished in the transverse direction to provide a cross-sectional view of the sprayed ceramic.

The bulk density method for determining porosity involves comparing the bulk density of the samples with the theoretical density of non-porous samples.

$$Vol\% = \frac{\rho_{theoretical} - \rho_{measured}}{\rho_{theoretical}}$$
(14)

where  $\rho_{theoretical}$  is the theoretical density of a non-porous material and  $\rho_{measured}$  is the measured bulk density from Archimedes' buoyancy technique [22]. The theoretical density of each sample was calculated by combining the theoretical densities of the three ceramic oxides being used:  $ZrO_2$  (5.89 g/cm<sup>3</sup>),  $Y_2O_3$  (5.01 g/cm<sup>3</sup>) and  $TiO_2$  (4.26 g/cm<sup>3</sup>) [24]. Knowing the weight percent of each oxide, the theoretical density of the samples could be calculated as follows:

$$\rho_{sample} = \frac{100\%}{\left(\frac{wt\%_{TiO_2}}{\rho_{TiO_2}}\right) + \left(\frac{wt\%_{Y_2O_3}}{\rho_{Y_2O_3}}\right) + \left(\frac{wt\%_{ZrO_2}}{\rho_{ZrO_2}}\right)}$$
(15)

The results of the two methods were compared. The data from the method showing the least scatter was retained in order to correct the Young's modulus to account for porosity in the measurements.

# 3.0 RESULTS AND DISCUSSION 3.1 Bulk density

Upon comparing the fine- and coarse-sized powder samples, it was noticed immediately that the bulk density was much higher in the former. This is demonstrated in Fig. 3, where there is a significant increase in bulk density with the use of the finer 7YSZ powders with a diameter within the range of  $45\pm5$  µm prior to being plasma sprayed. This allowed for a more close-packed structure of the powder particles and hence for more rapid diffusion during spraying and sintering. Due to their higher density, only the fine powder samples were tested for mechanical properties. This approach was chosen in order to observe the bulk properties of the material.



# FIG. 3 BULK DENSITIES OF CERAMIC SAMPLES

#### 3.2 Effect of Sintering on Microstructure and Porosity

Effective sintering of the samples allows full diffusion of the titania into the 7YSZ structure to form a homogeneous solid and to impart a tetragonal stabilizing effect. Therefore, proper sintering is important to ensure potential fracture toughness improvement through ferroelastic toughening of the tetragonal phase. As shown in Fig.4, the 7YSZ reference sample and the titania-doped 15TiYSZ sample both underwent consolidation and grain growth, as the grains are visibly larger after sintering.

Contrary to the hypothesis, the cross-sectional pores were not flattened or elongated from the spraying process. A comparison between the top and cross-sectional porosities in Fig. 5 shows that pores in both orientations are equally misshapen.

The average volumetric porosity was reduced in all samples after sintering (Fig. 6). This is due to the filling of pores to reduce overall surface energy during sintering, which is consistent with the observation shown in the microstructures after sintering (Fig. 4). Although there was a visible drop in porosity between the as-sprayed and sintered samples using the image threshold method, the trends shown between samples with different TiO<sub>2</sub> composition are less obvious. In addition, as the image analysis was being carried out, it was noted that very small variations in the darkness threshold caused large fluctuations in the recorded ratio of black and white pixels. Consequently, there was a large degree of subjectivity involved in data collection, and the porosity results were scattered. Conversely,



(a) 7YSZ, finer powder, as-sprayed



(c) 15TiYSZ, finer powder, as sprayed

# FIG. 4 GRAIN STRUCTURE OF FINE POWDER 7YSZ AND 15TIYSZ

the bulk density results were consistent and generally did not match those from the image threshold method as shown in Fig. 6. In light of this, the porosity results from the bulk density method were used in the calculation of the Young's modulus for non-porosity material.



FIG. 5 IMAGES OF 7YSZ (1200°C-325HRS) USED FOR POROSITY CALCULATIONS, (A) TOP VIEW, (B) CROSS-SECTIONAL VIEW

# 3.3 Effect of Titania Concentration on Phase Content

Using x ray diffraction (XRD), the *m*, *t*, *c* phase and rutile (TiO<sub>2</sub>) content of the sintered titania-doped 7YSZ samples is summarized in Fig. 7. The addition of TiO<sub>2</sub> to 7YSZ has resulted in an increase in *t*-phase while at the same time reducing the amount of *m* phase and *c* phase. Very little TiO<sub>2</sub> was detected, indicating that sintering was effective at placing the TiO<sub>2</sub> in solid solution. This finding correlates with previous studies, in which it was found that TiO<sub>2</sub> could be doped in yttria partially-stabilized zirconia up to 20 mol% [25]. However, XRD techniques may not be suitable for detecting dopant concentrations below 5%. Thus, full solid solution may not have been achieved. These composition issues will be examined further.

#### 3.4 Young's Modulus and Hardness

The hardness and Young's modulus results obtained from the nanoindentation test are given in Table 4. The average volumetric



(b) 7YSZ, finer powder, sintered at 1200°C, 325hrs







#### FIG. 6 A COMPARISON BETWEEN THE BULK DENSITY METHOD AND THE IMAGE THRESHOLD METHOD FOR DETERMINING THE POROSITY

porosity is also given in this table. Young's modulus is corrected for non-porous materials based on the average porosity value.

The hardness and Young's modulus were both higher after sintering, which is explained by an associated decrease in average porosity after sintering as shown in Fig. 6. Furthermore, there was a slight decrease in hardness with the addition of 5 and 10 wt% titania. TiO<sub>2</sub> has a Vickers hardness of approximately 6 GPa at a 100 gm load, while tetragonal PSZ has a hardness of 15 GPa under the same loading scheme [26]. Thus, titania alone has a lower hardness than yttria-stabilized zirconia, so the addition of titania in the samples should cause a decrease in hardness when TiO<sub>2</sub> is not diffused into the 7YSZ structure. After sintering, however, TiO<sub>2</sub> co-doped 7YSZ showed higher hardness values and this was believed to be the result of increased *t* phase (and reduced *m* phase) in the TiYSZ samples.



FIG. 7 XRD PATTERNS OF (A) 5TIYSZ AND (B) 10TIYSZ (AS SPRAYED) AND (C) 7YSZ, (D) 5TIYSZ, (E) 10TIYSZ, AND (F) 15TIYSZ (SINTERED)

TABLE 4 MECHANICAL	PROPERTIES OF I	BALL-MILLED SAMPI	ES FROM NANOIN	DENTATION TESTING

	Sample	Hardness	Measured Young's Modulus	Volumetric Porosity	Young's Modulus for Non-Porous Material (from Eqn 12)
Condition		(GPa)	(GPa)	(%)	(GPa)
As-Sprayed	7YSZ	$8.6 \pm 1.5$	91 ± 8	1.00	93
	5TiYSZ	$5.7 \pm 1.8$	$100 \pm 12$	1.56	104
	10TiYSZ	6.0 ± 1.3	$87 \pm 11$	2.59	92
	15TiYSZ	$9.8 \pm 1.5$	123 ± 7	4.82	136
Sintered	7YSZ	$12.5 \pm 1.6$	$185 \pm 11$	0.59	187
(1200°C, 325 hrs)	5TiYSZ	$15.5 \pm 2.7$	180 ± 13	1.23	184
	10TiYSZ	14.9 ± 1.2	$185 \pm 16$	0.82	188
	15TiYSZ	$13.4 \pm 1.6$	$181 \pm 10$	0.76	183



g) 10TiYSZ Fine Powder, Sintered 325 Hours @ 1200°C

FIG. 9 INDENTATIONS OF AS-SPRAYED AND SINTERED SAMPLES



(A) LOAD DEPENDENT EQUATIONS

#### (B) LOAD INDEPENDENT EQUATIONS

FIG. 10 FRACTURE TOUGHNESS OF THE FINE POWDER SAMPLES



# FIG. 8 MACROINDENTATION IN 5TIYSZ AS-SPRAYED, SHOWING CRUMBLING AND FRACTURE

These results are comparable to previous research by Schaedler et al. [7].

The Young's modulus results in Table 4 fluctuated within a two standard-deviation range, which made it difficult to observe any trends with the addition of  $TiO_2$ . The only observation seemed to be the slight reduction in Young's modulus for sintered samples with  $TiO_2$  addition.

# 3.5 Fracture Toughness

A series of 5 indentations were made with a 3kg load in each of the fine powder samples. It must be noted that samples with higher porosity, such as the 5TiYSZ in the as-sprayed condition (Fig. 8), did not show linear cracks from the indentations, but rather showed signs of crumbling and larger depression at the center. These irregular cracks made it difficult to obtain correct measurements of crack geometry. It is for this reason that repeat indentations were made, and the five most proportioned indentations were chosen for measurements. For sintered samples, the crack geometry was much more regular and linear, as shown in Fig. 9, although five indentations were also made for consistency. A summary of the a and c measurements is given in Table 5.

TABLE 5 AVERAGE CRACK GEOMETRY MEASUREMENTS USED FOR FRACTURE TOUGHNESS CALCULATIONS (µm)

Condition	Sample	a	с	a/c ratio
As-sprayed	7YSZ	38.28	75.15	0.5094
	5TiYSZ	59.06	116.70	0.5061
	10TiYSZ	57.11	108.73	0.5253
	15TiYSZ	58.48	130.47	0.4483
Sintered (1200°C				
325hrs)	7YSZ	44.64	78.41	0.5694
	5TiYSZ	47.50	70.91	0.6699
	10TiYSZ	52.96	75.44	0.7020
	15TiYSZ	52.43	76.67	0.6839

The fracture toughness values were calculated using Eqn. 1 through 7 and the results are given in Fig. 10. The presentations of the results are divided into load dependent and load independent equations.

Considering that the same crack measurement values were used for both Fig. 10 (A) and (B), the trends displayed are very different. The load-dependent equations 1, 2 and 5 use a ratio  $\frac{P}{c}$  (load over the crack length), assuming that crack length would vary linearly with the indentation load. In contrast, the load-independent equations 3, 4, 6 and 7 employ a ratio  $\frac{c}{a}$  (the crack length over the diagonal length of the indentation). Given that material's fracture toughness should not depend on the applied load, equations that are load-independent will provide a better estimate of the fracture toughness based purely on crack geometry. Fig. 10 (A) also showed large discrepancies between the results of equations 1 and 2, and equation 5. Using the loaddependent equations, the improvement of fracture toughness from sintering was apparent, while the effect of TiO<sub>2</sub> addition in samples after sintering was not observed in Fig. 10 (A).

Using load-independent equations, the fracture toughness values shown in Fig. 10 (B) suggest that  $TiO_2$  addition in sintered samples increases fracture toughness over the undoped 7YSZ. This trend was

apparent in the four different equations, and also correlates with findings by Schaedler [7]. For the as-sprayed samples, the fracture toughness did not appear to be affected by  $TiO_2$  addition. Again, sintering improved the fracture toughness of all samples.

The increased fracture toughness in  $\text{TiO}_2$  doped 7YSZ samples was believed to be as a result of increased ferroelastic toughening. Ferroelastic toughening occurs when tetragonal phase domains are reoriented by the application of stress at a crack tip. The reorientation and elongation of tetragonal lattice parameters can close up a crack tip, which has a toughening effect [6]. It is believed that the addition of TiO<sub>2</sub> increases the tetragonality (*c/a* ratio) of zirconia which in turn enhances the ferroelasticity, as previously described [7]. Further study focused on measuring changes in lattice parameters is underway to confirm the modification to tetragonality due to TiO<sub>2</sub> addition.

The XRD results in Figure 7 also show that the addition of titania to 7YSZ produced a slight reduction in the m and c phases and stabilized the t phase. The fracture toughness varies for different zirconia phases (monoclinic, tetragonal or cubic) that are present in the crystal structure of the ceramic. When grains of m phase form among other grains of t phase and c phase, the accompanying volume change during phase transformation causes microcracks to form along grain boundaries. The microcracks allow intergranular crack propagation with minimal energy. The fracture toughness of samples containing higher concentrations of m phase suffers as a result. Conversely, in the absence of the m phase, the t and c phases will undergo transgranular crack propagation, resulting in a higher fracture toughness [19]. In addition, transformable regions of tetragonal phase are additionally toughened by the transformation toughening phenomenon, in which the tensile strains at a crack tip cause a spontaneous  $t \rightarrow m$  transformation that result in crack closure due to the volume expansion [1,5]. In summary, the increased tetragonality and slightly reduced m phase in the TiO<sub>2</sub> doped 7YSZ are likely the reasons for any fracture toughness increases observed.

Although toughening by the addition of  $TiO_2$  was observed for all three samples, shown in Fig. 10 (B), it seemed that addition of 15 wt%  $TiO_2$  did not offer further improvement to the toughness values. The reason for this trend is uncertain at present; as such, supplementary samples with 7.5 wt% and 12.5 wt% of  $TiO_2$  are being evaluated. In addition, the lattice parameters of all samples are being studied to confirm the presence of ferroelastic toughening.

#### 3.6 Effect of Porosity on Fracture Toughness

The average volumetric porosities of the as-sprayed samples were significantly higher than the sintered samples, as shown in Fig. 6. The addition of TiO2 to 7YSZ also influenced the occurrence of porosity in the as-sprayed and sintered samples. Fig. 11 displays the volumetric porosities of various samples along with the corresponding fracture toughness values (averaged from load-independent results). The higher porosity in the as-sprayed samples translated to lower fracture toughness, while the sintered samples with lower density have higher fracture toughness so clearly related, it becomes difficult to determine the true influence of TiO<sub>2</sub> addition without the influence of porosity. In order to ascertain the effect of TiO<sub>2</sub> content on fracture toughness, a further study should be conducted with specimens of constant volumetric porosity.

As a design consideration, it has been shown [27] that the thermal conductivity of YSZ materials decreases as porosity increases. For thermal barrier purposes, it would be favorable to have the lower thermal conductivity associated with high porosity. Care must therefore be taken to ensure that the necessary fracture toughness is not sacrificed as a result of the high porosity. More focused research would be required to determine an optimal balance between the thermal and mechanical implications of increasing porosity.

#### CONCLUSIONS

In this study, the microstructure and mechanical properties of  $TiO_2$  doped 7YSZ were studied. Specimens of  $TiO_2$ -doped YSZ were



FIG. 11 VOLUMETRIC POROSITY COMPARED TO FRACTURE TOUGHNESS

created by plasma spraying. The microstructure analysis showed that only after sintering, the  $TiO_2$  doped sample displayed more homogeneous distribution of  $TiO_2$  in zirconia matrix. In the assprayed state, solid solution was not obtained as individual  $TiO_2$  particles were observed.

Sintering of the specimens after spraying also resulted in a significant decrease in porosity and an associated increase in hardness and fracture toughness. The  $TiO_2$  doped samples showed improved fracture toughness, but there may exist a limit of  $TiO_2$  addition beyond which further addition is no longer beneficial. The fracture toughness increased with  $TiO_2$  as a result of increased tetragonality, which improved the effect of ferroelastic toughening. Better stabilization of the non-transformable *t* phase may also have played a role.

When using indentation methods, the semi-empirical formulas incorporating load as a variable produced an ambiguous trend, due to the use of crack length without the indentation diagonal length. The load-independent formulas produced a clear, logical trend by employing a ratio of crack length to indentation diagonal length. Despite a wide variation in fracture toughness values calculated using different methods, a general trend was observed in which the addition of TiO<sub>2</sub> increased the fracture toughness of 7YSZ. For this reason, and due to the favorable thermal conductivity observed by [28], TiO<sub>2</sub> doped 7YSZ shows great potential for use in future TBC systems. Future studies may focus on analyzing the properties of TiYSZ applied to the full TBC system, including the interactions between the substrate, bond coat and top coat layers.

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