Effect of Gd content on mechanical properties and erosion durability of sub-stoichiometric
 $\text{Gd}_2\text{Zr}_2\text{O}_7$

Michael P. Schmitt^{a,b}, Jamesa L. Stokes^{a,b}, Brenna L. Gorin^{a,b}, Amarendra K. Rai^c, Dongming
Zhu^d, Timothy J. Eden^e, and Douglas E. Wolfe^{a,b,e,†}

^a Department of Materials Science and Engineering, The Pennsylvania State University,
University Park, PA 16802, USA

^b The Applied Research Laboratory, The Pennsylvania State University, University Park, PA
16802, USA

^c UES Inc. 4401 Dayton Xenia Road, Dayton, OH 45432, USA

^d NASA Glenn Research Center, Cleveland, OH 44135, USA

^e Department of Engineering Science and Mechanics, The Pennsylvania State University,
University Park, PA 16802, USA

[†] Corresponding author. Email address: dew125@arl.psu.edu Telephone: 1-814-865-0316

Abstract

Advanced thermal barrier coating materials are necessary to improve the efficiency of next-generation gas turbine engines. As such, different TBC chemistries must be developed with enhanced temperature stability above that of 7YSZ (~1200°C) while maintaining thermal and mechanical reliability. The present study investigates the effect of rare-earth content on the mechanical properties of ZrO_2 TBCs. Various cubic compositions in the $\text{ZrO-GdO}_{1.5}$ system were investigated in the form of monolithic pellets and coatings with stoichiometric GZO

serving as reference. The fracture toughness and erosion durability were evaluated, and it was found that fracture toughness decreased with increasing rare-earth content, 15.66 mol% $\text{GdO}_{1.5}$ yielding $1.25 \text{ MPa m}^{1/2}$, compared to $1.04 \text{ MPa m}^{1/2}$ for GZO (50 mol% $\text{GdO}_{1.5}$). It was observed that the erosion performance of the coatings was much more sensitive to the changes in mechanical properties than the bulk specimens and showed a 125% increase through the fluorite region to GZO whereas the dense pellets only exhibited a 33% increase in erosion behavior. These results indicate that cubic ZrO_2 phase with reduced rare-earth content show promise as TBC materials with improved durability over GZO as well as temperature stability in this region of the phase diagram.

Keywords: Thermal barrier coating, GZO, $\text{Gd}_2\text{Zr}_2\text{O}_7$, erosion, mechanical properties

1. Introduction

As the push continues to enable higher operating temperatures of gas turbine engines, the thermomechanical requirements for the thermal barrier coatings employed to protect these engines become more extreme. The current state-of-the-art TBC top coat material, 7 wt.% yttria stabilized zirconia (7YSZ), has high durability and relatively low thermal conductivity but exhibits instability beyond approximately 1200°C, where after prolonged periods of operation, the t' phase will destabilize into equilibrium cubic and tetragonal phases [1,2]. On cooling, the resulting tetragonal to monoclinic phase change is accompanied by a volumetric expansion of ~5%, which can cause stresses in the coating, leading to eventual spallation and failure.

The rare-earth pyrochlore zirconate phases ($\text{RE}_2\text{Zr}_2\text{O}_7$) have been studied as a possible replacement for 7YSZ [3,4]. The rare-earth pyrochlores possess an ordered defect fluorite structure, with a RE atom substituting for one Zr atom at every other site as well as ordered oxygen vacancies. Due to the high number of oxygen vacancies, this structure has a very low thermal conductivity while being stable to 1500°C in the case of $\text{Gd}_2\text{Zr}_2\text{O}_7$ (GZO). Unfortunately, the pyrochlore phases exhibit poor erosion durability due to their reduced fracture toughness [1] ($\sim 1.0 \text{ MPa m}^{1/2}$) compared to 7YSZ, thereby precluding the adoption of pyrochlore phases materials for many TBC applications.

In the $\text{ZrO-GdO}_{1.5}$ system [5], it is shown that the fluorite structure has a large range of thermal stability, with many compositions being stable until melting temperature. The phase stability of the fluorite structure shows that mixtures in this region of the phase diagram are potentially useful for TBC application. However, the erosion durability and mechanical properties of coatings of rare-earth doped cubic zirconia phases has yet to be investigated or fully

understood. Zhang *et al.* [6] proposed initially that incorporation of excess ZrO_2 with respect to the $\text{Nd}_2\text{Zr}_2\text{O}_7$ pyrochlore results in a contraction of the lattice and attributes the toughening to a compressive stress caused by that lattice contraction. This explanation is unlikely, as the excess ZrO_2 is in solid solution and is directly incorporated in the lattice (and residual stress scans were not shown to confirm stresses).

The same group then investigated ytterbia stabilized zirconia (YbSZ) and $\text{Gd}_2\text{Zr}_2\text{O}_7$ mixtures [7] and again show an increase in toughness with decreasing total RE content. The mixtures with >15 mol% YbSZ showed a tetragonal phase, hence the increase in toughness, however in the single phase region (<15 mol% YbSZ), the increase in toughness cannot be attributed to the formation of a ferroelastic tetragonal phase [8,9]. The proposed mechanism is an increase in the lattice cohesive energy which results in a larger fracture energy, though this is difficult to understand given that the Yb-O bond is significantly weaker than the Gd-O bond (388 kJ/mol vs. 766 kJ/mol [10]) and thus doesn't correlate with the increased toughness of the Yb-doped single phase materials. Similar behavior was also observed by the same authors for non-stoichiometric GZO where excess ZrO_2 yielded improved toughness [11]. Additionally, the cohesive energy generally dictates the stable (lowest energy) polymorph but does not directly relate to the mechanical properties. Zhang *et al.* [12] fabricated mixtures of YSZ and GZO and indentation measurements indicated that increasing the YSZ content yielded an increase in toughness (while maintaining a single disordered fluorite phase). They proposed that the basis of the observed increase in toughness with increasing YSZ content, i.e. decreasing rare earth content, was due to crack tilting and twisting caused by differences in thermal expansion between YSZ and the secondary phases. However, their results for the GZO-YSZ composites show no secondary phases, and nor are secondary phases likely as t' YSZ (comparable to YSZ)

and GZO react to form a single fluorite phase [13]. Furthermore, the CTE differences between YSZ (11 ppm/°C) and GZO (11 ppm/°C) are quite small [14], particularly at elevated temperatures. It is therefore likely that a different mechanism is occurring.

It is evident that non-stoichiometric pyrochlore and fluorite phases can possess modified mechanical properties. This study aims to investigate the mechanical properties and erosion durability of pressed pellets of cubic phase in the ZrO-GdO_{1.5} system ($\text{Gd}_x\text{Zr}_{1-x}\text{O}_{2-1/2x}$, $0.1 < x < 0.5$) as possible replacements for stoichiometric GZO. Coatings of the same compositions were also fabricated to elucidate the effects of changes in bulk mechanical properties on coating erosion durability and to assess the feasibility of these compositions.

2. Experimental Procedure

2.54 cm × 2.54 cm. polycrystalline $\alpha\text{-Al}_2\text{O}_3$ coupons (99.5%, CoorsTek Inc.) were used as substrates. Coatings were deposited onto substrates using electron beam-physical vapor deposition (EB-PVD) and co-evaporation of t' Low-k YSZ ($\text{ZrO}_2: 2\text{Y}_2\text{O}_3 + 1\text{Yb}_2\text{O}_3 + 1\text{Gd}_2\text{O}_3$, Trans-Tech Inc.) and GZO ($\text{Gd}_2\text{Zr}_2\text{O}_7$, Trans-Tech Inc.) ingot feedstock with 4.93 cm diameters. A source-substrate distance of 30.48 cm was maintained while substrates rotated at 7 rpm on a 5.08 cm diameter mandrel. Substrates were arranged in three rows on the mandrel, as shown in Figure 1. Row 1 substrates were positioned directly above the t' Low-k ingot and Row 3 substrates were positioned directly above the GZO ingot, with Row 2 substrates positioned in the middle. Rotation through the vapor clouds provided coatings with varying rare-earth content based on their positions on the mandrel. Depositions using only a single ingot were performed to yield monolithic coatings which served as a reference for the co-evaporated coatings. Prior to the deposition of the co-evaporated and monolithic GZO coatings, a ~ 25 μm diffusion barrier layer of t' Low-k was deposited on top of the substrate to prevent interaction between the

substrates and coatings. Row 1, Row 2, and Row 3 compositions are referred to as C1, C2, and C3 in this study.

The synthesis of the bulk ceramic powders was carried out using a solid state reaction method. ZrO_2 (99+%, Alfa Aesar, Thermo Fisher Scientific) and Gd_2O_3 (99.5%, HEFA Rare Earth Canada, Co. Ltd.) were used as starting powders. The two powders were mixed in respective weight ratios in ethanol with 7 mm cylindrical YSZ media for 24 hours, dried overnight, then calcined at 1300°C for 24 hours. After calcination, the resulting powders were then ball milled again in ethanol with 2 mm YSZ spherical media for 24 hours. Once dried, the powders were uniaxially pressed into 25.4 mm diameter pellets at 19.67 MPa before cold isostatic pressing (CIP) at 200 MPa with no hold. The pellets were then sintered at 1600°C for 15 hours to obtain dense samples. The Archimedes method was used to determine the density of the pellets.

Particle erosion was performed using an in-house erosion rig. Coatings and pellets were weighed and mounted into the sample holder with a 1.27 cm mask. The initial sample mass was measured and the samples were exposed to successive increments of 5 g of 240 grit ($50\text{ }\mu\text{m}$) $\alpha\text{-Al}_2\text{O}_3$ at a feed rate of $\sim 2\text{ g/min}$ and a velocity of 100 m/s with incidence angles of 90° . After each increment, the samples were weighed again to measure mass loss until a total of 50 grams of erodent exposure occurred. Mass loss was then plotted as a function of erodent exposure with the coatings were eroded for a total of 10 data points and the erosion rate calculated as the slope of the linear portion of the graph. A more extensive description of the erosion set-up is detailed elsewhere [15].

Longitudinal and shear sound wave velocities (V_L and V_S) of the pellet samples were measured using the ultrasonic pulse/echo method in order to determine the elastic modulus (E), shear modulus (G) and Poisson's ratio (ν) as follows:

$$E = \frac{\rho V_S^2 (3V_L^2 - 4V_S^2)}{V_L^2 - V_S^2} \quad (1)$$

$$G = \rho V_S^2 \quad (2)$$

$$\nu = \frac{V_L^2 - V_S^2}{2V_L^2 - 2V_S^2} \quad (3)$$

The modulus measurements are the effective modulus of the bulk pellet, based on composition and morphology. Because dense pellets were fabricated and thus microstructure should have minimal impact on the measurements, the measured modulus is deemed to be an accurate representation of the intrinsic modulus of the compositions. Vickers Hardness indentation (LECO M-400-G1 Hardness Tester, ASTM E384) was used to determine the hardness (H) and the indentation fracture resistance (K_{ifr}) of the pellet samples at 1 kg. The fracture toughnesses and hardnesses are calculated as

$$K_{ifr} = \alpha \sqrt{\frac{E}{H} \frac{P}{c^{\frac{3}{2}}}} \quad (4)$$

$$H = \frac{1.844 P}{d^2} \quad (5)$$

respectively, where P is the applied load, c is the crack length measured from the center of the indent, and d is the average width of the indent (measured as the average of the two diagonals). 1.844 is a geometrical factor implemented when using a square pyramidal indenter tip and α is a constant, typically valued at 0.018 ± 0.004 . Only indents with four good cracks were used, where ideal cracking is characterized by no outliers in length (e.g. extremely short or long cracks), no porosity interference, no bifurcation, no angular crack path, and no chipping from lateral cracks. The crack length was averaged for each indent and the standard deviation is from a minimum of

four total indents. For comparison to literature values, the interfacial toughness (Γ) was calculated as

$$\Gamma = \frac{K_{ifr}^2}{E} \quad (6)$$

The utility of the indentation technique for measurement of fracture toughness has been debated in the literature [16,17]. Quinn *et al.* [16] point out a variety of flaws for using the indentation technique to measure fracture toughness, with perhaps the most obvious discrepancy being a critical crack does not occur (e.g. the crack is arrested). In addition, the authors point out that no single indentation equation can be applied to a variety of ceramics and with good agreement and that the dimensionless coefficient is baseless scaling factor. In contrast, Marshall *et al.* argue that indentation is a useful technique if the correct precautions are taken and that many of the assertions against indentation were indeed mentioned in the original literature describing the technique. Both of these viewpoints have merit. The use of a somewhat arbitrary dimensional factors is disconcerting, however, when comparing like materials within a class (as in this paper), the potential error shrinks dramatically and nearly disappears as the materials behave and fail in a similar manner. Therefore, though the overall magnitude of the results may be questionable, the difference between materials and ‘ranking’ is likely quite accurate. Furthermore, the utility of the indentation technique is unmatched when investigating small samples made of small batch chemistries or specimens.

Scanning electron microscopy (FEI Quanta 200 ESEM) was used to characterize the morphology of the coatings and pellets, as well as to image the Vickers Hardness indents. Using SEM, energy dispersive spectroscopy (EDS) was carried out in order to obtain the chemical compositions of the coatings. X-ray diffraction (XRD) (PANalytical XPert Pro MPD) and the

ICDD Crystallographic Database (Jade 10) were used to characterize the crystallography in all the samples.

3. Results and Discussion

3.1 Pellets

Dense pellets were fabricated across the fluorite region as shown in the $\text{ZrO}_2\text{-GdO}_{1.5}$ phase diagram modified from [2] and provided in Figure 2 with the compositions, lattice parameters, and densities provided in Table 1. The X-Ray diffraction patterns of the pressed pellets are provided in Figure 3 and the C1 – C3 pellets each exhibit the fluorite structure with the GZO pellet also exhibiting some superstructure peaks indicative of the pyrochlore phase. A leftward shift was observed with increasing Gd content, as expected based on the addition of the larger Gd which act to expand the lattice and correlates well to the whole pattern fit lattice parameters provided in Table 1. The densities of the pellets are all 97-98% dense, and thus a very low amount of porosity is present. Since the porosity was consistent across pellets and overall small in magnitude, the mechanical properties reflect the compositional variation and not the changes in porosity or morphology.

The mechanical properties are provided in Table 2 along with those of t' YSZ from Watanabe *et al.* [18] for reference. In general, as rare earth content increases and approaches the pyrochlore, the elastic modulus, shear, and bulk moduli increase while Poisson's ratio decreases slightly. The results are appropriate, given the modulus of YSZ is typically reported at around 210 GPa [3] while GZO is typically around 240 GPa [19]. In contrast, the hardness appears to decrease with increasing Gd content, following an inverse trend with the elastic modulus. The increase in modulus does not appear to be linear and is indeed saturated by the C3 composition. The reason for this increase is not obvious, as the Zr-O bond enthalpy (766 kJ/mol) is similar to

that of Gd-O (715 kJ/mol) [10], and so the average bond strength should not increase in the solid solution. Increasing the rare earth content does result in a substantial increase in the oxygen vacancy content, though it is unknown if there is a linkage between elastic modulus and oxygen vacancy content. One feasible explanation could be that the increase in oxygen vacancy concentration helps further satisfy the desired 7-fold coordination environment for the Zr^{4+} cation which in turn results in stronger bonding and a higher modulus. It is not known if the overall expansion of the lattice would negate this effect and this will be investigated in the future with high resolution diffraction studies combined with Rietveld refinements to look at atomic positions and bond lengths as a function of rare earth content.

The indentation fracture resistance is provided in Table 2 with a typical indent and cracks used for measurement provided in Figure 4. The indentation fracture resistance appears to decrease with increasing Gd content, showing an inverse trend with respect to the modulus and agreeing well with the hardness. The influence of rare earth content on toughness in fluorite and pyrochlore phase zirconia has largely been overlooked in the literature, with the few studies investigating rare earth content showing similar results but with no clear explanation [6,7,11,12]. One factor which hasn't been discussed is the effect of oxygen vacancies. As rare earth content increases, the charge compensating oxygen vacancies increase according to:

and thus these compositions can contain high concentrations of vacancies. The commensurate increase in vacancy content could perhaps explain the reduction in fracture resistance. The literature has shown that annihilation of vacancies via Ta^{5+} and Nb^{5+} doping in tetragonal zirconia can improve toughness [20] indicating the sensitivity of this material in the ferroelastic regime, though this is not active in the fluorite regime. For the fluorite phase, experiments on

gadolinia doped ceria for fuel cell applications showed that decreasing oxygen partial pressure and increasing vacancy content yielded lower fracture stresses and a change in failure from transgranular to intergranular [21]. The reason for this transition is unclear, though it is possible a similar mechanism occurs in zirconia as rare earth content and vacancy content increase. Another indicator that vacancies and ordering play a role is a study on stoichiometric pyrochlore zirconate by Wang *et al.* [22] where Gd was replaced by equal parts of the smaller Sc (e.g. $\text{Gd}_{2-x}\text{Sc}_x\text{Zr}_2\text{O}_7$). In this study, the fracture resistance increased significantly when approaching the order-disorder fluorite boundary. In the most basic sense, the fracture of brittle ceramics can be explained through Griffith's failure criterion:

$$\sigma_{crit} = \sqrt{\beta \frac{E \gamma}{\pi a}} \quad (8)$$

Where σ_{crit} is the critical stress required to propagate a flaw of length $2a$, and E and γ are the Young's modulus and surface energy, respectively. β relates to the loading conditions (plane stress or plane strain) and is typically near unity. Interestingly, based on Griffith's equation, the observed increase in the elastic modulus should presumably increase the fracture toughness, indicating that the surface energy term is decreasing (and at a more substantial rate than the increase in E). As the γ term becomes smaller, less energy is required to form the new surfaces and thus lower stresses are required to propagate a crack. It is possible that the increase in oxygen vacancy content produces lower surface energies, though these effects have not been well studied in the rare earth - zirconia system to the authors' knowledge. Another explanation could be that the slightly lower bond enthalpy of the Gd-O bond results in easier cleavage. It is noted that the change in the K_{ifr} and Γ values for the fluorite zirconates are still much lower than that of YSZ from Watanabe *et al.* [18], however, this paper seeks to quantify and understand the cause of these changes and further, to determine their effect on the change in erosion durability.

The erosion rates of the pellets are provided in Figure 5. There is an overall increase of nearly 40% in the erosion rate when transitioning from the 15.66 mol% $\text{GdO}_{1.5}$ C1 composition to the 41.88 mol% $\text{GdO}_{1.5}$ C3 composition. As expected, the erosion rate trends inversely with the fracture resistance and increases with increasing Gd content, reaching an apparent asymptote at the pyrochlore composition. Based on the surface energy argument, the onset of the asymptote at C3 could perhaps be attributed to the onset of order-disorder and changes in the local energy, as the C3 composition is close to the order-disorder boundary of the pyrochlore phase [23]. These results suggest that in terms of erosion durability, low rare earth content fluorite phases may be ideal. The literature has shown that thermal conductivity is minimized by around 20 mol% $\text{REO}_{1.5}$ and that further increasing the rare earth content does not provide a substantial benefit to the thermal conductivity [24,25]. Thus, low rare earth fluorite compositions would provide better toughness than pyrochlores and with the similar phase stability and thermal conductivity. The drawback is a lower source of reactant species for CMAS precipitation and a possible reduction in the sintering resistance.

3.2 Coatings

To better understand the advantages of lower rare earth fluorite phase materials and the influence of microstructural effects, coatings were fabricated with compositions provided in Table 1. The as-deposited surface images and polished cross sections of the co-evaporated coatings from C1 – C3 are provided in Figure 6. The C1 coating exhibits a standard columnar morphology where the columns grow continuously from the substrate to the surface. With increasing gadolinia content, the columns appear to grow wider and with more frequent branching and renucleation, as shown in Figure 6a-b. These observations correlate well with the surface images, which show the typical A-frame morphology and an increase in column size

from C1 to C2 as shown in Figure 6d-e. For the C3 sample in Figure 6f, many smaller nuclei are present, correlating with the observed increase in column branching and re-nucleation in the cross sectional image. This is attributed to a lower temperature near the back of the mandrel which favors renucleation. Importantly, though branched, many of the columns still appear larger than those of C1. Porosity was maintained from 8.4 – 11.2% in the coatings, indicating only small changes as a function of position and gadolinia concentration.

X-ray diffraction patterns of the as-deposited coatings are provided in Figure 7 and the coatings each exhibit a fluorite phase show a leftward shift from C1 to GZO, correlating to an increase in the lattice parameters provided Table 1. The coatings are more textured than the pellets, with the C1 coating exhibiting severe texture in the (220). This texture decreases as the Gd content increases from C1 to C3. The (220) plane has a larger surface energy than the (111) plane in FCC crystals, therefore suggesting adatom mobility decreased with increasing gadolinia content. This correlates to the increase in the amount of branching and renucleation observed in the C2 and C3 coatings with higher Gd content. The apparent increase in column width may be therefore be related to the change in the preferred texture as well as changes in temperature and deposition rate. Larger columns in GZO coatings processed under identical conditions to these coatings has been observed by the authors previously [13] and confirms GZO coatings tend to have larger columns at these parameters.

The erosion results for the co-evaporated coatings are provided in Figure 8 as a function of total rare earth content. The erosion rate of the C1 samples is increased by ~5X compared to pure t' Low-k, correlating to the transition from the ferroelastic toughening in the t' phase to the cubic phase which exhibits no intrinsic toughening mechanism. As expected, additional increases in the gadolinia content yields a further increase in the erosion rate until reaching the

pyrochlore composition, whose erosion rate is nearly an order of magnitude larger than t' Low-k. The erosion rates again appear to approach an asymptote at approximately the pyrochlore composition similar to the behavior observed in the pellets. Unlike the pellets however, the increase in erosion rate is much more substantial in the coatings. When transitioning from the C1 coating to the C3 coating there is a 78% increase in the erosion rate compared to the 33% increase observed in the pellets. The pyrochlore composition in the coating shows a 125% increase from C1, indicating that the small changes in fracture resistance are magnified when in coating form.

4. Conclusions

This paper investigated the effect of rare earth concentration on mechanical properties and erosion durability of zirconia-gadolinia solid solutions in the fluorite regime for bulk and coating specimens. It was observed that fluorite compositions have a larger fracture resistance and lower elastic modulus than pyrochlore compositions, and that fracture resistance decreases with increasing Gd content while the moduli increase with increasing Gd content. These results indicate that lower rare earth compositions in the fluorite phase have better mechanical properties than the higher rare earth pyrochlore phase in the zirconia-gadolinia system. Since the bond strengths of these two materials are quite similar, it is suggested that vacancies and ordering play a role in the fracture energy. Coatings of the same compositions were also deposited and the erosion behavior followed the same trends, with an asymptote near the pyrochlore composition. The coatings were shown to be much more sensitive to the changes in mechanical properties than the bulk specimens indicating small improvements in the fracture resistance can have large improvements in erosion durability. Overall, these results suggest that low Gd content fluorite phase coatings have potential for low thermal conductivity, high stability

coatings with improved mechanical performance over GZO pyrochlores with the primary drawback of a lack of CMAS resistance.

Future studies will investigate the hyper-stoichiometric zirconia-gadolinia fluorite region to determine if the asymptotic behavior at the pyrochlore composition is in fact a maxima/minima in modulus and fracture resistance. In addition, the zirconia-lanthana system will be explored to test if the introduction of stronger bonding lanthana to zirconia will exhibit the same trends.

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Table 1 Mol% of zirconia and gadolinia in each composition as measured via EDS, lattice parameter and theoretical density for each composition as calculated from XRD pattern fitting, and bulk density from Archimedes method. A t' phase composition is included for comparison.

	C1	C2	C3	GZO
Mol % ZrO ₂	84.34%	68.42%	58.12%	50%
Mol % GdO _{1.5}	15.66%	31.58%	41.88%	50%
Pellet Lattice Parameter (Å)	5.156	5.195	5.233	5.268
Coating Lattice Parameter (Å)	5.142	5.169	5.214	5.266
Theoretical Density (g/cm ³)	6.414	6.709	6.839	6.950
Measured Density (g/cm ³)	6.248 (97%)	6.476 (97%)	6.709 (98%)	6.779 (98%)

Table 2 Elastic properties, hardness, fracture resistance, and interfacial toughness of C1—GZO pellets, as well as a t' phase YSZ pellet from Watanabe *et al.* [18]for reference.

Sample	Poisson's Ratio	Elastic Modulus (GPa)	Shear Modulus (GPa)	Hardness (GPa)	K _{ifr} (MPa√m)	Interface Toughness (J/m ²)
C1 Pellet	0.30	208.03	69.34	14.89±0.32	1.25±0.14	7.5±9.42×10 ⁻²
C2 Pellet	0.29	225.58	75.19	13.79±0.79	1.14±0.11	5.8±5.36×10 ⁻²
C3 Pellet	0.27	246.00	82.00	12.87±0.96	1.06±0.08	4.6±2.6×10 ⁻²
GZO Pellet	0.22	248.19	82.73	11.75±0.32	1.03±0.02	4.3±1.61×10 ⁻³
t' YSZ [18]	--	180	--	--	3.0	50

List of Figure Captions

- Fig. 1** Schematic of the co-evaporation set-up. Rotation through both vapor clouds provided coatings with varying rare-earth content as a function of the position on the mandrel.
- Fig. 2** Modified phase diagram of $\text{ZrO}_2\text{-GdO}_{1.5}$ system from [2], with compositions synthesized in this study shown by the diamonds. A t' phase composition is included for comparison.
- Fig. 3** X-ray diffraction patterns of the pellets, showing peak shifting indicative of increasing rare-earth content. The GZO pellet exhibits superstructure peaks, which indicate that some ordering has occurred.
- Fig. 4** SEM image of a typical indent produced by a 1 kg load.
- Fig. 5** Erosion data for C1 – GZO pellets, with pellet erosion rate plotted as a function of rare-earth content. Erosion rates are calculated as mass loss (g) over mass of erodent exposure (kg) and tended to increase with increasing rare-earth content with a potential asymptote or maxima near the pyrochlore region.
- Fig. 6** Cross sectional images of as deposited coatings from a) C1 b) C2 and c) C3 and surface images of d) C1, e) C2 and f) C3.
- Fig. 7** X-ray diffraction patterns of as deposited coatings. The C1—C3 coatings tend to be textured in the (220) and the leftward shift is present due to the increase Gd content.
- Fig. 8** Erosion data for C1 – GZO coatings, with pellet erosion rate plotted as a function of $\text{GdO}_{1.5}$. A t' Low-k coating was eroded with the samples for comparison, which has been plotted as a function of its total rare-earth content ($\sim 7.5\% \text{ REO}_{1.5}$). The difference in erosion rate between compositions is much higher than the pellets indicating a much higher sensitivity of the coating microstructure.

◆ t' ◆ C1 ◆ C2 ◆ C3 ◆ GZO