Journal of the European Ceramic Society 36 (2016) 357–364

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Electrophoretic deposition of multilayered (cubic and tetragonal stabilized) zirconia ceramics for adapted crack deflection

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ARTICLE INFO

Article history:
Received 3 April 2015
Received in revised form 13 August 2015
Accepted 15 August 2015
Available online 29 August 2015

Keywords:
Electrophoretic deposition
Yttria stabilized zirconia
Transformation toughening
Multilayer
Crack deflection

ABSTRACT

The electrophoretic deposition process was used to produce multi-layered ceramics consisting of alternating layers of fully stabilized cubic zirconia and partially stabilized tetragonal zirconia to make use of their different mechanical behaviour, investigating the possibility to deflect advancing cracks at the interfaces of the different layers. This crack deflection is apparently impacted by a toughening mechanism only found in the tetragonal stabilized zirconia polymorph and is characterized by the stress induced transformation of the metastable tetragonal phase into the monoclinic one, which is accompanied by a volume increase resulting in a closing mechanism for advancing cracks.

While improving the electrophoretic deposition process, we investigated the transformation toughening mechanism at the layer interfaces and their effect on crack propagation. Investigations involved a combination of different imaging methods, including light microscopy, white light interferometry, atomic force microscopy, scanning electron microscopy, energy dispersive X-ray spectroscopy and Raman spectroscopy.

1. Introduction

Zirconia (ZrO_2) exists in three different polymorphs: monoclinic, tetragonal and cubic. The monoclinic crystal structure represents the stable modification at temperatures up to 1173 °C, while the other two represent high temperature modifications (tetragonal: 1173–2370 °C, cubic: >2370 °C). The high temperature modifications can be stabilized at low temperature conditions by certain oxides such as MgO, Y_2O_3, CaO, HfO_2 and Ce_2O_3 [1].

In engineering applications, the partially stabilized, tetragonal modification became well known in 1975 by the work of Garvie et al. who discussed zirconia as "ceramic steel" [2].

The high mechanical toughness and crack resistance of the tetragonal stabilized zirconia is due to a unique mechanism, which is known as transformation toughening [3]. Transformation toughening can be triggered for example at crack tips by high tensile mechanical stresses resulting in the transformation of the tetragonal into the monoclinic polymorph. In this regard, we have shown previously [4], that sectioning and grinding can possibly introduce surface related transformations in unknown quantities, which possibly can be reversed by annealing the material to temperatures above 1173 °C as the transformation from the tetragonal polymorph to the monoclinic one is diffusionless and therefore favoured. The corresponding volume increase acts against further crack growth, by closing advancing cracks due to the developing compressive residual stress field, and decreasing the tensile stresses felt at the crack tip. This is the principal mechanism responsible for the relatively high toughness of tetragonal partially stabilized zirconia ceramics.

In addition, zirconia ceramics exhibit good corrosion resistance, high temperature ionic conductivity and good biocompatibility, making them useful in applications such as solid oxide fuel cells (SOFC), cutting tools, thermal coatings and biomedical appliances [5–7]. A high specific weight and limitations in shaping complex structures recently increased interest in coating techniques [8]. Thermal spraying and physical vapour deposition (PVD/EBPVD) as well as sol–gel techniques are well established methods to produce zirconia layers [9,10].

Another approach, electrophoretic deposition (EPD), has attracted attention due to its versatility and ability to efficiently combine different materials in unique shapes and structures [11,12]. Electrophoretic deposition is generally characterized by

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http://dx.doi.org/10.1016/j.jeurceramsoc.2015.08.022
0955-2219/

Table 1
Powder and suspension data.

		3YSZ	8YSZ
Raw powder composition		5.22 wt% Y_2O_3 for 3YSZ,	13.60 wt% Y_2O_3 for 8YSZ
Specific surface		14.8 m^2/g	13.5 m^2/g
Crystallite size		26 nm	23 nm
Suspension 1	Composition	20 g/100 ml EtOH (pH adjusted with acetic acid*)	
	pH***	6.35	5.78
	Conductivity	48.5 $\mu S\,cm^{-1}$	211 $\mu S\,cm^{-1}$
Suspension 2	Composition	99 g/100 ml EtOH (pH adjusted with benzoic acid**	
	pH***	4.3	4.15
	Conductivity	53.8 $\mu S\,cm^{-1}$	67.6 $\mu S\,cm^{-1}$

* Carl Roth GmbH & Co. KG, Karlsruhe, Germany.
** Sigma–Aldrich, St. Louis, USA.
*** Non aqueous.

electric field induced migration of particles suspended in a liquid towards an electrode and subsequent aggregation/deposition at the electrode site. We have applied EPD to both zirconia and alumina ceramics demonstrating the possibility for the deposition of defined microstructures [13,14]. With fibrinogen as an intermediate phase, 3D shaping of alumina ceramics was also possible [13,14].

Previously, we have successfully deposited alternating layers of zirconia doped with different amounts of yttria (tetragonal, 3 mol% and cubic, 8 mol%) [15,16]. This layering of alternating tetragonal and cubic zirconia layers allows establishing structures with relevant engineering properties, combining increased mechanical toughness (tetragonal zirconia) with high ionic conductivity (cubic zirconia) and adapted thermal conductivity, which is most useful in applications like solid oxide fuel cells and thermal barrier coatings [17]. Similarly, biomedical and engineering applications [18,19] can benefit from such a layered structure, allowing tailored crack-deflection due to differences in mechanical properties (especially the layer specific fracture toughness) and the innate transformation toughening in tetragonal zirconia [16]. Nevertheless, it is well known, that layered samples of different materials, even differently stabilized zirconia polymorphs, will possibly exhibit residual stresses due to differences of the coefficient of thermal expansion (CTE) which impacts the sintered material during the cooling process [20]. These two mechanisms together allow deflecting cracks at internal interfaces, thus increasing the length of the crack path and the energy necessary for crack growth. This can result in an improved lifetime of the constructs depending on the mode of application.

In this work, we investigated the crack deflection behaviour, the toughening mechanisms and the hardness in structures made of alternating layers of cubic and tetragonal zirconia using indentation techniques coupled with scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), atomic force microscopy (AFM), white light interferometry and Raman spectroscopy.

2. Experimental procedures

2.1. Ceramic EPD processing

Partially stabilized tetragonal (3 mol% Y_2O_3, termed 3YSZ) and fully stabilized cubic (8 mol% Y_2O_3, termed 8YSZ) zirconia nanoscale powders from Tosoh (Shunan, Japan) were used to prepare two different suspensions according to Table 1. The conductivity and the pH of the suspensions were measured with a redox meter PCE-PHD 1 (PCE Inst., GmbH, Meschede, Germany). Due to the autoprotolysis of ethanol, the measured pH values represent a measure of the hydrogen ion concentration in this non-aqueous system. Suspension 1 needed constant stirring, while suspension 2 was much more stable and only needed to be stirred for several minutes. After stirring, all suspensions were ultrasonicated for approximately 3 min using a micro-ultrasonic cell disruptor (Kontes, Vineland, United States of America) and were used in either the manual or the automatic EPD setup with electrode orientations according to Fig. 1a and b. The automated EPD setup was custom made using parts and software from Fischertechnik GmbH (Waldachtal, Germany). Aluminium electrodes were used in both the manual (electrode distance: 25 mm) and automated setup (electrode distance: 30 mm). The EPD process of the multilayered samples was carried out at a constant DC voltage of 15 V for the 3YSZ layers and of 10 V for the 8YSZ layers. 3YSZ and 8YSZ layers were deposited consecutively with a fixed deposition time of 30 min for each layer for the manual setup, whereas for the automated setup it was varied between 5, 2.5 and 1 min to achieve specimens differing in the thickness of their layers. The electrodes with the deposited multi-layered ceramic were air-dried for several hours, followed by careful removal of the deposited ceramic.

The specimens were sintered at 1450 °C for 3 h in a VITA Zyrcomat oven (Vita Zahnfabrik, Bad Saeckingen, Germany) followed by sectioning and were ground with SiC paper and fine polished using diamond suspensions. Finally, the specimens were annealed at the sintering temperature to reverse the tetragonal/monoclinic transformation induced by the grinding/polishing procedure and to better visualize the grain structure.

As a result, multilayered samples of alternating tetragonal and cubic phases with a clearly defined interface were produced [15,16]. The manual vertical setup resulted in several multilayered specimens with layers of significantly varying thicknesses. Whereas the automated horizontal setup allowed a much more homogeneous layer deposition along the sample, obtaining three different samples with 15, 31 and 75 layers and mean layer thicknesses of approximately 125 μm (15 layers), 55 μm (31 layers) and 20 μm (75 layers).

2.2. Vickers indentation

Single Vickers indents were placed on the polished and annealed cross-sections of the samples with 125 μm thick layers. They were used to investigate crack growth and crack deflection in the interface region of 3YSZ and 8YSZ layers and to map the hardness over the cross-section of the layer structure. For the crack growth and crack deflection investigations, Vickers indentations (HV 5/12 s) were placed in either the 3YSZ or the 8YSZ layer in the direct vicinity of the adjacent layer using a Zwick 3212 microindenter (Zwick, Ulm, Germany). The distance of the centre of the indents to the layer interface was approximately 50 μm. Additionally, for hardness mapping, an array of 210 indents (array dimension: 21 × 10 indents, indent spacing: 50 μm, HV 0.2/12 s) was introduced across the layer structures of all three sample types. The hardness profiles were analysed using image data from a Leitz DMRM microscope