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ScienceDirect
Journal of the European Ceramic Society 32 (2012) 299–306
www.elsevier.com/locate/jeurceramsoc

Structural characterization of bulk $ZrTiO_4$ and its potential for thermal shock applications

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Received 1 June 2011; received in revised form 1 August 2011; accepted 4 August 2011
Available online 7 September 2011

Abstract

Zirconium titanate, $ZrTiO_4$, is a well known compound in the field of electroceramics. Furthermore, it shows a large potential as structural material for thermal shock resistance applications, since it presents crystallographic anisotropy in thermal expansion. However, there is no information in the current literature about its thermomechanical behaviour. In this work, single phase zirconium titanate bulk materials have been prepared from well dispersed ZrO_2 and TiO_2 mixed suspensions, combining reaction and conventional sintering processes. The crystal structures of $ZrTiO_4$ have been studied by the Rietveld method for bulk samples. The structural evolution upon the cooling rate has been unravel, as the *b*-axis strongly decreases for slow cooled samples when compared to quenched materials. For the first time apparent Young's modulus (≈130 GPa) and Vickers hardness (≈8 GPa) values of a fully dense single phase zirconium titanate material have been evaluated and its potential for thermal shock applications has been analysed in comparison with other thermal shock resistant materials.

Keywords: A. Suspensions; B. X-ray methods; C. Mechanical properties; D. Zirconium titanate; E. Structural applications

1. Introduction

In general, compounds displaying anisotropic thermal expansion are good candidates to form low thermal expansion materials,[1] which are frequently used in the field of structural applications involving thermal shocks.

Aluminium titanate[2,3] is one of the compounds most widely used as a constituent of low thermal expansion materials. However, aluminium titanate decomposes into Al_2O_3 and TiO_2 at temperatures between 1073 and 1553 K, typical range of temperatures where oxides are used for structural applications. Moreover, low thermal expansion of aluminium titanate materials is always associated to extremely low values of fracture strength (≈20 MPa at 298 K).[4] For these reasons, it is necessary to search other compounds with crystallographic anisotropy in thermal expansion to overcome the current limitations of the available materials and to enlarge the range of thermal shock resistant ceramics.

Zirconium titanate, $ZrTiO_4$, is a well known compound in the field of electroceramics, where it has been used in dielectric resonators and materials for telecommunications.[5–10] In spite of its large potential as structural material for thermal shock resistance applications, since it shows anisotropic thermal expansion ($\alpha_{a298-1073K} = 8.0 \times 10^{-6}\,K^{-1}$, $\alpha_{b298-1073K} = 10.0 \times 10^{-6}\,K^{-1}$, $\alpha_{c298-1073K} = 6.2 \times 10^{-6}\,K^{-1}$, P*bcn* setting),[11] there is no information in the current literature about its thermomechanical behaviour. In particular, it is not known whether its crystalline thermal expansion anisotropy will originate sufficient thermal stresses in $ZrTiO_4$ bulk materials as to develop microcracked microstructures as occurs in the typical low thermal expansion thermal shock resistant materials.

Zirconium titanate is an intermediate compound in the binary system ZrO_2–TiO_2.[12–14] Several authors have studied this system to establish the equilibrium phases.[13,15,16] McHale and Roth heated samples of $ZrTiO_4$ at $T \approx 1273$ K around 4 months and they concluded that the stable compound of the binary system ZrO_2–TiO_2 at room temperature was $ZrTi_2O_6$.[15] Other authors

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doi:10.1016/j.jeurceramsoc.2011.08.004

studied the influence of cooling rate in the lattice parameters of zirconium titanate at room temperature.[5,11,13,17,18] Some authors proposed two phases to explain the differences in lattice parameters due to different cooling rates.[13,18] However, other study[19] reported an important change in the *b* lattice parameter (P*bcn* setting) as function of the cooling rate, after sintering, that it was assigned to local ordering of the Ti, Zr-cations for slow cooling treatments.

The synthesis of $ZrTiO_4$ has been reported by several methods including sol-gel,[8,20–23] co-precipitation,[24,25] mechanochemical processing[26] and solid state reaction.[12,13,15,16,27] These methods have been used to make powders or small pieces of $ZrTiO_4$. However, structural applications require bulk materials, so it is necessary to combine synthesis and processing methods which allow the preparation of zirconium titanate 3D-shaped materials.[28,29]

This work deals with the fabrication of single phase $ZrTiO_4$ bulk materials by solid state reaction of ZrO_2 and TiO_2. The final goal is to determine the basic thermomechanical properties to evaluate the true possibilities of $ZrTiO_4$ as a constituent of thermal shock resistance materials. In order to do so, the Vickers hardness and the apparent Young's modulus values of isostatic pressed bodies sintered at 1773 K for 12 h are reported and discussed.

2. Experimental

Commercial m-ZrO_2 (TZ-0, Tosoh Tokyo, Japan) and anatase-TiO_2 (808, Merck, Darmstadt, Germany) were used as starting powders. Both powders have average particle diameters of 0.3 μm and the specific surface areas are 14 m^2/g for m-ZrO_2 and 9 m^2/g for TiO_2.

Particle size distribution was determined with a laser diffraction analyser (Mastersizer S, Malvern, Worcestershire, UK), and the specific surface area was measured by the N_2 adsorption method (Monosorb Surface Area Analyzer MS13, Quantachrome Co., Boynton Beach, Florida, USA). Colloidal stability of m-ZrO_2 (Z) and TiO_2 (T) suspensions was determined through zeta potential measurements by the laser Doppler electrophoresis technique (Zetasizer NanoZS, Malvern, Worcestershire, UK). Suspensions were prepared to a solids content of 0.01 wt.% by mixing with an ultrasonic probe (UP 400 S, Hielscher, Stuttgart, Germany) for 2 min in a solution of KCl 10^{-2} M to maintain a constant ionic strength. Slurries were stirred for 20 h prior to measurements in order to reach surface equilibrium. A polyacrylic-based dispersant (Dolapix CE64, Zschimmer-Schwarz, Lahnstein, Germany) was used as the dispersing aid. The influence of the polyelectrolyte concentration on the zeta potential was also investigated. Concentrated aqueous suspensions of m-ZrO_2 (Z) and TiO_2 (T) were prepared separately. Solid contents were 40 vol.% (≈80 wt.%) for Z and 45 vol.% (≈76 wt.%) for T. Both slurries were prepared by adding the powder to the proper amount of deionised water containing polyacrylic-based dispersant (Dolapix CE64) to a total concentration of 0.8 wt.% on a dry solids basis, and further mixing with a high shear mixer (L2R, Silverson, Chesham, UK). Then, they were ball milled for 24 h using alumina jar and balls. The as-prepared one component slurries were mixed to relative molar ratio of 1 in order to obtain Z + T suspension. The resulting mixture was ball milled during one additional hour to assure uniform mixing. Details of the preparation procedure are given in a previous work.[28]

For rheological characterisation of the suspensions a rotational rheometer (RS50 Thermo, Thermo-Haake, Karlsruhe, Germany) with a double cone/plate geometry was used. Flow curves were performed by changing shear rate between 0 and 1000 s^{-1} for 5 min for the up and down ramps. Dwell time at the maximum rate was 1 min. Temperature was maintained constant at 298 K. All suspensions were prepared and measured at least three times and representative curves are given.

Z + T green bodies were shaped into plates (≈70 mm × 70 mm × 10 mm) by slip casting the Z + T suspension in plaster moulds and dried in air for 48 h. Green and sintered densities were determined by Archimedes' method, using mercury and deionised water, respectively. Open porosity was determined in sintered samples immersing samples in boiled deionised water and heating it up to boiling point during 2 h.

Constant heating rate (CHR, heating and cooling rates 5 K/min) experiments up to 1973 K were performed in a differential dilatometer with alumina rod (DI24, Adamel Lhomargy, Brie, France). From the derivatives of the shrinkage-temperature curves two temperatures (1210 and 1450 K) were selected to prepare quenched specimens to determine the crystalline phases present at both temperatures during the reaction sintering process. The experimental procedure to obtain the quenched specimens consisted in heating at 5 K/min to the final temperature (dwell time 1 min) in an electrical furnace, and quenching in air stream using an electric fan. This cooling method assures cooling times from the treatment temperature to 1073 K of less than 1 min for the small (≈5 mm × 5 mm × 5 mm) specimens used. From the phase analysis of the quenched specimens and the shrinkage curves, the selected temperature to sinter Z + T green compacts was 1773 K. Higher temperatures were observed to lead to liquid formation in the material. Specimens were fabricated by treating the green compacts at 1773 K using different dwell times (2, 8 and 12 h).

Since it was not possible to get dense materials directly by the single-step reaction sintering process described above, conventional sintering of green compacts of already reacted ZT powders was investigated. ZT specimens were obtained after sintering the Z + T green compacts at 1773 K for 2 h, attrition milling (Y_2O_3-stabilized ZrO_2, diameter 3 mm: YTZ Grinding Media, Tosoh Co, Tokyo, Japan) the sintered compacts during 4 h, drying and sieving the resulting powder using 37 μm mesh diameter, further compactation of the sieved powders by isostatic pressing at 200 MPa and finally sintering the ZT pressed compacts at 1773 K during 12 h. Conventional sintering process was performed with heating rate of 5 K/min and cooling rate of 5 K/min to 1373 K and then 2 K/min to room temperature.

Quenched specimens were characterised as pieces by X-ray diffraction (XRD) (D8 Advance, Bruker, Karlsruhe, Germany). The obtained XRD patterns were analysed using the diffraction files of $ZrTiO_4$ (PDF: 00-034-0415), a-TiO_2 (PDF: