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Sintering properties and thermal depletion of boron in zirconia–zirconium diboride conductive ceramic

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Abstract

Zirconium diboride (ZrB_2) as an ultrahigh temperature ceramic (UHTC) with excellent electrical conductivity is a potential candidate for harsh-environment devices. Fabrication of ZrB_2-based materials however involves processing in the active oxidation regime ($T > 1200$ K) leading to depletion of boron. We report a simple technique to prevent degradation during pressureless sintering of zirconia-matrix composites of ZrB_2. The composites prepared using this method reach the percolation threshold at ~10 wt% ZrB_2 and metal-like conductivity (~10^5 S/m) at 25 wt% ZrB_2 in agreement with the general effective media theory. The improved mechanical properties are also discussed in terms of various toughening mechanisms.

Keywords: A. Sintering; B. Composites; C. Electrical conductivity; E. Functional applications

1. Introduction

Yttria tetragonal zirconia polycrystal, subsequently known as Y-TZP, exhibit exceptional mechanical properties amongst the family of stabilised and partially stabilised zirconia ceramics [1]. In recent years many studies have focused not only on the improvement of toughness and strength of zirconia-based ceramics, but also on enhancing zirconia matrix's electrical conductivity to cater for applications in the semiconductor industries [2]. One possible approach is to introduce hard and electro-conductive particulate such as zirconium diboride (ZrB_2) into the ceramic body to produce ceramic matrix composites (CMC) characterized by having high conductivity, improved hardness and toughness [3].

The main challenge with the use of such electro-conductive particles in zirconia CMC is to preserve the conductive ZrB_2 phase and at the same time retain the tetragonal phase stability of the host matrix. The sintering of transition metal borides, in particular is difficult because of their highly covalent nature and low grain boundary diffusion rate resulting in poor sinterability at relatively low temperatures [4]. On the other hand, at high temperatures ($T > 1000$ K), boron is rapidly depleted in the form of volatile B_2O_3 [5]. Transition from passive to active oxidation kinetics in subsequent stages ($T > 1200$ K) not only hinders a complete densification [6] but also significantly reduces the electrical conductivity [7] of the ceramic matrix. In the case of ZrB_2, the remaining zirconium further oxidizes into the an inferior monoclinic zirconia (as opposed to the tetragonal phase which is essential for effective transformation toughening to take place [8]) and ultimately leads to microcrack-induced fractures [9].

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Previous studies have explored a variety of processing techniques to eliminate or attenuate the degradation of ZrB_2-based materials. Hot isostatic pressing (HIP) [10–12] and spark plasma sintering (SPS) [13–15] have been most commonly utilized to obtain nearly dense samples, although both methods suffer from a number of limitations with respect to size, geometry and cost of the fabricated components. More recently, pressureless sintering as a more versatile technique has also been reported, albeit often with addition of sintering aids such as $MoSi_2$ [16], SiC [17], B_4C [18], VC [19] and carbon [20]. Without such additives, even at high relative densities, mechanical properties have been found to significantly deteriorate due to excessive grain growth [21].

Among a few studies which have also investigated electrical properties, the effort to fully retain the metal-like conductivity of ZrB_2 in a tetragonal zirconia CMCs even by processing in inert gas [22] or vacuum [23,24] has not been successful regardless of the sintering technique. Overall, the measured values appear to be insufficient for certain purposes such as electrical discharge machining (EDM) or plasma cutting of Y-TZP based CMCs containing ZrB_2 particles for which resistivity should not exceed 100 Ω cm [25]. Furthermore, ZrB_2 because of its metal-like conductivity may enable a wider range of applications if there is found to be an effective way to prevent its thermal degradation during processing. These include specialized devices for high-radiation environments such as outer space, ultrahigh-temperature electrodes for ion propulsion systems as well as corrosion-resistant sensors in reactors.

With regard to electronic or sensing applications, realizing conductive composites in a high-κ dielectric matrix such as that of an oxide [26,27] may lead to the development of functional high performance devices simply by selectively protecting a ZrB_2 substrate against thermal depletion of boron. A yttria-stabilized zirconia (YSZ) matrix is especially of interest because of its large number of established applications which can further benefit from integration with conductive CMCs. For example, superb corrosion, thermal shock and wear resistance of YSZ along with its high melting point can greatly contribute to the durability of thermal barriers in gas and jet turbines [28]. In addition to its favorable structural properties, YSZ owing to its excellent ionic conductivity [29] is also commonly used as solid electrolyte in electrochemical devices such as oxygen sensors [30,31] as well as solid oxide fuel cells (SOFCs) [32].

Here, we report a new fabrication technique based on pressureless sintering using which YSZ–ZrB_2 CMCs without any significant boron depletion can be produced. The mechanical properties of these new CMCs well exceed the limits of YSZ monolith while their electrical conductivity reach $\sim 10^5$ S/m at 25 wt% ZrB_2, in agreement with the general effective media (GEM) theory.

2. Experimental procedures

2.1. Sample preparation

Various amounts (5–50 wt%) of high purity ZrB_2 (Wako, Japan) were mixed with 3 mol% yttria stabilized zirconia (~15% monoclinic as-received, Kyoritsu, Japan) through wet milling using zirconia beads and ethanol as the mixing media. The slurries were then dried at 60 °C in a standard box oven for 24 h after which the resulting agglomerates were crushed and sieved through a 212 micron mesh sieve. YSZ–ZrB_2 composite bodies were prepared by uniaxial pressing at 0.3 MPa followed by cold isostatic pressing at 200 MPa. Green samples were finally sintered in argon atmosphere (flow rate: 2 L/min) while buried under a layer of ZrB_2 power bed as oxidation barrier. Sintering temperatures varied from 1300 °C to 1550 °C with 1 h of holding time and a constant ramp rate of 5 °C/min for both heating and cooling. All sintered samples were polished to 1 micron surface finish prior to characterization.

2.2. Mechanical properties

The bulk densities of sintered samples were measured using a common water immersion technique through retrofitting an electronic balance with a density determination kit from Mettler Toledo, Switzerland. The Young's moduli were determined for sintered rectangular bars ($32 \times 13 \times 6$ mm) via a resonance frequency technique on a Grindosonic MK5 (Belgium) according to ASTM standards (E1876-97). Hardness and fracture toughness were measured at least 5 times using the micro-indentation results and the equation developed by Niihara et al. [33] The indentation force was maintained at 98.1 N (10 kg) for a loading time of 10 s.

2.3. Electrical properties

The electrical resistivity of monoliths as well as composites was measured using a Keithley 3706 DMM. The four-point probe setup consisted of four equally spaced ($s = 1.5875$ mm) tungsten metal tips with finite radius. A high impedance electrical current I was supplied to the outermost probes while the voltage V was measured between the two inner probes to determine the electrical resistivity ρ using the equation $\rho = 2\pi s(V/I)$. At least 50 readings were taken for each sample from which the average was calculated. The electrical conductivity σ was then calculated as the reciprocal of ρ.

2.4. Phase identification

Major phases present in the monoliths as well as the YSZ–ZrB_2 composites were studied by a Shimadzu (Japan) X-ray diffractometer at room temperature with a Cu-Kα ($\lambda = 1.54056$ Å) radiation source. The scan speed and step were 0.5°/min and 0.02°, respectively. Quantitative analyses to survey relative phase contents were based on the strongest reflections from (111) and $(11\bar{1})$ lattice planes in tetragonal and monoclinic zirconia, respectively, while for ZrB_2, (101) was the main indicator. Fractions of monoclinic phase in both monolithic and composite samples were determined after the protocol by Toraya et al. [34]