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Processing of alumina–zirconia composites by surface modification route with enhanced hardness and wear resistance

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Abstract

Zirconia toughened alumina (ZTA) materials are frequently used in mechanical engineering and biomedical applications due to their enhanced toughness, strength and wear resistance compared to monolithic alumina. In this study, a submicron size alumina powder was modified *via* wet chemical route: the alumina particles surface was coated with zirconium chloride, to yield 10 vol% zirconia by subsequent thermal treatment. From this powder, several ZTA materials were produced by slip casting, sintered at different temperatures from 1475 to 1575 °C. In all materials, a full characterization of their mechanical properties, microstructure and phase composition was carried out, together with wear tests carried out in a linear-reciprocating mode using a Y-TZP ball counterpart under environmental conditions.

The results show low wear at sintering temperatures below 1525 °C and high wear at higher sintering temperatures, which can be well correlated to the hardness, microstructure and phase evolution. The microstructure of the materials is initially extremely homogeneous and fine grained. The grain size increases moderately both for the zirconia and alumina components with the sintering temperatures considered. The grain shape of alumina gradually changes from isometric to elongated. Up to 1525 °C, the size of zirconia grains stays below 400 nm. The zirconia transformability was evaluated and it was observed that the zirconia dispersion remains vastly untransformable up to that sintering temperature. In this condition, the alumina matrix is under compressive hydrostatic stress and fracture resistance is moderate. At higher sintering temperatures, grain growth induces higher zirconia transformability and fracture resistance but at the expense of hardness and wear resistance. The simultaneous evolution of tabular morphology in matrix grains also contributes to toughness but facilitates grain breakout and disruption of the surface during final machining and under tribological load.

Keywords: B. Microstructure-final; C. Mechanical properties; C. Wear resistance; Al_2O_3–ZrO_2

1. Introduction

Technical ceramics such as alumina and zirconia find increasing applicability in industrial and biomedical fields. Fully dense, high-purity alumina presents good strength, outstanding hardness and wear resistance. However, its relatively low fracture toughness compared as for example to zirconia may cause catastrophic failure in service. Zirconia was originally referred to as *ceramic steel* by Garvie et al. [1] because of its three allotropes and its particular transformation-toughening mechanism. In addition, its Young modulus and thermal expansion coefficient are similar to those of steel [2,3]. Zirconia combines high strength and fracture toughness with good wear resistance, being most of its mechanical properties a consequence of the phase transformation toughening that increases the crack propagation resistance [4–8]. Nevertheless, in the biomedical field zirconia applicability is limited by its *in vivo* stability (related to its resistance to low hydrothermal degradation [9,10]) and its low thermal conductivity (related to the thermally induced crack formation [11,12]) which make it inadvisable for tribological applications.

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Given the properties of monolithic alumina and zirconia, extensive investigations have been devoted to develop adequate composite ceramics based on this biphasic system. In particular, zirconia-toughened alumina (ZTA) composites consist of an alumina matrix, which provides high strength and hardness, with a fine dispersion of zirconia particles exerting a toughening effect thanks to their transformation toughening mechanism [13,14]. ZTA composites find nowadays application in many fields: cutting tools, bearings, biomaterials for orthopedic and dental implants, thermal and corrosion-resistant coatings. This wide field of applications is possible thanks to their high hardness, chemical inertness, high melting points and the ability to retain the mechanical strength at elevated temperature. Furthermore, most of these applications require excellent wear behavior, but usually ZTA composites present lower wear resistance and hardness than alumina [12–14].

Currently, a number of attempts have been made to optimize the mechanical properties of ZTA composites, in particular the wear resistance by controlling the microstructure and composition. For instance, He et al. [15] reported that zirconia fine grains increase the load at which mild to severe wear transition occurs, thus improving the wear resistance. The matrix grain size also plays a key role, since decreasing the grain size increases the wear transition load [15]. In spite of such findings, the development of new processing routes that improve the wear resistance and hardness of ZTA composites without deteriorating their outstanding strength and toughness is still the subject of extensive research.

In this paper, ZTA composite materials have been produced by a surface modification route, providing *in situ* crystallization of ultra-fine zirconia grains on the alumina surface. This method is an effective alternative to the mixing and milling approach, since it allows producing a highly homogeneous composite with a good distribution of zirconia particles inside the alumina matrix [16,17], which is one of the key requirements to achieve a good wear resistance [18].

In a previous work [17], the surface modification method was applied to the processing of ZTA composites containing different amounts of zirconia (from 5 to 20 vol%). Green samples were prepared by slip casting and then pressurelessly sintered. A preliminary mechanical characterization, based on Vickers hardness and fracture threshold (K_{I0}) data, attested the better behavior of the sample containing 10 vol% zirconia.

On the ground of these results, the current work focuses on the overall mechanical behavior including the wear resistance of the ZTA with a 10 vol% zirconia. The aim has been assessing the effectiveness of the surface coating route in the manufacturing of ZTA composite and evaluate its mechanical properties and reliability, validating the process as an alternative to the conventional mixing and milling route.

2. Experimental

2.1. Powder synthesis and sintering

Alumina–10 vol% zirconia (which will be referred to as 10ZTA) powder was prepared starting from commercial α-alumina (APA 0.5, Ceralox, USA, S_{BET}=8 m^2 g^{-1}, average particle size 0.3 μm, according to the manufacturer' specification). A well-dispersed aqueous suspension of this alumina powder was mixed with an aqueous solution of zirconium chloride (Sigma Aldrich, purity > 99.5%) and then spray dried. The powder was calcined at 600 °C for 1 h to decompose the synthesis by-products (mainly chlorides) and to induce the crystallization of tetragonal zirconia on the alumina surface [19]. The water suspension at 60 wt% solid loading was attrition milled for about 12 h, by using 3Y-TZP (Tosoh corporation) milling balls. The dispersed slurry was then degassed at 200 mbar for 3 h cast into porous molds and dried in humidity-controlled chamber for about 1 week. The slip cast green bodies were pressureless sintered between 1475 °C and 1575 °C, for 2 h, at heating/cooling rate of 2 °C/min.

2.2. Physical and microstructural characterization

The sintered density was determined by the Archimedes method and related to the theoretical density (TD). A TD of 4.18 g/cm^3 was calculated assuming that zirconia was fully tetragonal (6.05 g/cm^3) after sintering. The microstructural characterization of the sintered bodies was carried out by Scanning Electron Microscopy (Carl Zeiss SEM DSM982 Gemini, Germany) on polished and thermally etched surfaces. Polishing was performed down to 1 μm with diamond paste, and thermal etching was carried out at 1300 °C, for 10 min, in air.

2.3. Phase composition

The phase composition of the zirconia was determined in polished surfaces and in fracture faces using X-ray diffraction (XRD) in Bragg–Brentano configuration (Bruker D8, Germany) in the 27–33° 2θ-scale. The intensities of the monoclinic (−111) and (111) peaks as well as of the tetragonal (101) peak were integrated and volumetric content of monoclinic was calculated with the equation from Toraya et al. [20].

2.4. Mechanical characterization

Sample preparation for the mechanical tests was performed following a standardized procedure. After removing the grout by grinding, the 10ZTA plates were lapped with 15 μm diamond suspension and polished with 15 μm, 6 μm and 1 μm diamond suspension on both sides (Struers Rotopol, Denmark). Each plate was cut into 7 bars of 4 mm width and 1.5 mm thickness. The sides were ground and edges were bevelled with a 40 μm diamond disk and polished to a 15 μm finish to remove cutting grooves and edged defects. The remaining parts were kept for hardness testing and XRD. The 4-pt bending strength (σ_{4pt}) of 10 bars of 10ZTA was determined in a setup with 20 mm outer and 10 mm inner span at a crosshead speed of 0.5 mm/min (Zwick, Germany). The Vickers hardness HV_{10} (Bareiss, Germany, 5 indents) and microhardness $HV_{0.1}$ (Fischer, Germany, 12 indents) were determined and the indentation modulus E_{IND} was calculated