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Densification and characterization of spark plasma sintered ZrC–ZrO_2 composites

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ABSTRACT

ZrC based composites alloyed by nanosized tetragonal 3 mol% yttria stabilized zirconia were produced with spark plasma sintering to $>98\%$ of the theoretical density by sintering at 1900 °C under pressure of 50 MPa for 10 min. The volume fraction of stabilized zirconia varied from 25 to 40 vol% in the precursor powder blend. Room temperature hardness and modulus of elasticity of the compacts were in the range reported earlier for similar materials densified by pressureless sintering, while indentation fracture toughness was around 7 MPa $m^{1/2}$. Structural analysis indicated formation of oxycarbides of various stoichiometries.

1. Introduction

Zirconium carbide (ZrC) is one of the ultra-high temperature materials (melting point is about 3530 °C) commercially adopted in tool bits for cutting tools and can be suitable for many other applications such as crucibles, re-entry vehicles, jet engines or supersonic vehicles where low density and high-temperature load-bearing capability constitute the most important requirements [1,2]. Due to the presence of metallic bonding, ZrC has thermal and electrical conductivity that is comparable to the zirconium metal. High hardness ($\sim$25 GPa) and modulus ($\sim$390 GPa) combined with a relatively low density (6.63 g cm^{-3}) makes this material particularly attractive for tribological applications. Zirconium carbide was densified to 98% of relative density by conventional hot pressing at 2300 °C applied for 60 min under the pressure of 40 MPa [3]. However, low sinterability of powders and poor fracture toughness of bulks ($\leq$4 MPa $m^{1/2}$) limit the wide application of ceramics based on ZrC. One of the promising approaches for improving sinterability and material reliability includes the use of sintering additives. For example, the use of molybdenum as a binder agent for liquid-phase sintering of ZrC–Mo cermets has resulted in mechanically enhanced bulk materials [4,5]. The addition of zirconium diboride was reported to enhance the densification of ZrC-based composites of low porosity level (2–4%) [6]. Silvestroni et al. observed formation of binary phases of ZrC–$MoSi_2$ and ternary phases of ZrC–HfC–$MoSi_2$ and ZrC–ZrB_2–$MoSi_2$ [6]. New phases such as (Zr, Hf)C solid solutions, SiC and Zr–Mo–Si secondary phases were detected after a heat treatment at 1900–1950 °C in 60 min. The room temperature mechanical properties of these materials were comparable to properties of ZrC bulks produced by the pressure-assisted technique. Fracture toughness values in the range of 3.5–4.0 MPa $m^{1/2}$ give no evidence of significant toughening in the composites. In [7], yttria stabilized zirconium dioxide was tested as sintering additive for zirconium carbide consolidation. The mixtures of ZrC with 20–40 wt% ZrO_2 were sintered to near theoretical density at temperatures $\geq$2000 °C and dwell time $\geq$1 h. The final microstructure consisted of a dispersed zirconia in continuous oxycarbide matrix. Zirconium carbide exhibits a rock salt structure ($Fm-3m$ space group), in which the oxygen can either be incorporated into the vacant sites or be partially substituted by carbon. It is believed that formation of defective oxycarbides enhances the diffusion and densification in carbide matrix [7,8]. Formation of ZrC_xO_y compounds in the ZrC–ZrO_2 system at temperatures around 2000 °C was outlined in [9] and maximum solubility of oxygen in zirconium carbide at this temperature was found not to exceed 15 at%. The composites of ZrC_xO_y–ZrO_2 sintered at 1800–2000 °C in an argon atmosphere in a graphite tube furnace possessed a four-point bending strength of 220–320 MPa and a fracture toughness of 4–5.8 MPa $m^{1/2}$ [7]. The moderately high fracture toughness of 5.8 MPa $m^{1/2}$ was associated with the presence of tetragonal

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zirconia, which induced toughening through residual stresses and possible transformation of zirconia grains.

Utilization of zirconia (ZrO_2) as a ceramic sintering additive has been extensively studied for the last few decades [10–13]. Moreover, among oxide ceramics, tetragonal zirconia polycrystals (TZP) have an excellent combination of strength and toughness, wear resistance, as well as high chemical and corrosion resistance [10]. Due to the stress-induced martensitic phase transformation of the metastable tetragonal phase to the monoclinic polymorph ($t \rightarrow m$), zirconia is expected to increase the fracture toughness of composites [14,15]. Factors controlling the transformation include the size, charge and amount of stabilizer cations [14,15]; the grain size and grain size distribution [12,16]; residual stresses [17]; temperature; oxygen vacancy concentration; thermal expansion anisotropy of the t-ZrO_2; and microstructural constraints imposed by inert non-transforming phases [15–19]. The tetragonal phase of ZrO_2 can generally be stabilized by dopants; and yttria (Y_2O_3) is one of the most commonly adopted ones. For example, optimal mechanical properties and electrical conductivity of ZrO_2–40 vol% WC composites were found for zirconia, which was stabilized with 2 and/or 3 mol% Y_2O_3 [11,20,21]. The presumed successful incorporation of stabilized tetragonal zirconia is expected to increase the fracture toughness of ceramic composites, as well as to improve material performance at tribological conditions. The processing parameters influence zirconia polymorphism and, therefore, the recent developments have focused on technologies that allow retaining tetragonal zirconia after sintering for possible phase transformation toughening of the material containing t-ZrO_2 [10,21–23].

With field-assisted sintering, also known as spark plasma sintering (SPS) or pulsed electric current sintering, which employs a pulsed DC current, it is possible to consolidate powders to full density much faster and at lower temperatures than with traditional methods such as pressureless sintering and hot pressing [21–23]. In particular, the SPS method has potential to maintain the nano and submicrostructure in nanopowder-based materials after consolidation [22]. The present study focuses on (i) densification behavior of the ZrC–ZrO_2 composite system by spark plasma sintering; and (ii) mechanical characterization of the sintered bulks.

2. Experimental procedure

2.1. Materials and processing

Commercially available zirconium carbide (ZrC) powder (particle size around 3.5 μm; Strategic Metal Investments Ltd., Canada) was mixed with 25 and 40 vol% partially 3 mol% yttria stabilized tetragonal zirconia (t-ZrO_2) nanopowder of 99% purity (average primary particle size 30 nm and agglomerate size about 0.2 μm; Tosoh, Japan). The blend was milled in a planetary ball milling device (Fritsch, Pulverisette 6 classic) with ZrO_2 balls (∅ 10 mm) and a ball-to-powder ratio of 4:1 for 6 h at 300 rpm in ethanol.

Spark plasma sintering (FCT HPD 25-2 GmbH with vertically positioned pyrometer for temperature control) was performed in vacuum at 1600–1900 °C. A pulsed electric current with pulse duration of 10 ms and pause time of 5 ms was applied throughout all sintering cycles. The powder blend was poured into a cylindrical graphite die with an inner diameter of 20 mm and sintered for 10 min. The heating rate was set at 100 °C/min up to the sintering temperature and the cooling rate was ~200 °C/min. The relatively low heating rate was applied since a high heating rate can cause temperature gradients and subsequently sintering inhomogeneity, leading to non-uniform microstructural and mechanical properties of the sintered parts [3,21,22]. ZrC–YTZ composites were densified by means of a solid state sintering, which is a common procedure for producing high temperature ceramics and composites. Densification at the solid state is controlled by diffusion and a large part of the densification in SPS occurs already during heating. Slow heating rate enhances the densification. The applied pressure of 50 MPa was adjusted to the powder at room temperature and kept constant throughout the experiment. The load was applied at the beginning of the sintering process because high green density is favorable for better densification rate by reducing the pores prior to the densification during heating. Graphite papers were employed to separate the powder from the graphite die/punch set-up.

2.2. Material characterization

Specimen density was measured by means of Archimedes′ method with distilled water as an immersing medium. The bulk Vickers hardness was estimated with Indentec 5030 SKV at the load of 98.1 N applied for 15 s according to ISO 6507. Modulus of elasticity was measured with the indentation technique as described in [25] according to EN ISO 14577 (ZHU Zwicki-Line Z2.5). The indentation fracture toughness (IFT) was calculated by resorting to the both Palmqvist and Median crack systems [26]. The surface cracks initiated by the indent were measured with SEM microscopy (TM Hitachi 1000, Japan). A large load of 50 kg on the indenter was applied to drive the well-distinguished surface cracks and mitigate any surface effects. The reported hardness and fracture toughness constitute the mean and standard deviation values of 10 indentations.

The microstructure of the polished samples was examined by means of Scanning Electron Microscopy (SEM, Hitachi S-4700, Japan). The chemical compositions of the powder mixtures and bulk samples were analyzed with the help of X-ray diffraction analysis (XRD, Philips PW3830 X-ray Generator, 4 kW, Cu-Anode) using CuK_α radiation at the accelerating voltage of 40 kV and a filament current of 30 mA with a scan step size of 0.02° and a count time of 0.4 s at each step. X-ray diffraction was applied for phase identification and calculation of the relative monoclinic and tetragonal ZrO_2 phase content following the method of Toraya et al. [26]. The transformability of a ceramic is defined as the difference in m-ZrO_2 content detected from fractured and polished surfaces.

3. Results and discussion

3.1. Precursor powders

A survey of the yttria stabilized zirconia (YTZ) peaks indicates that in the precursor powder, zirconia was in its tetragonal polymorph and the powder blend mixed in ethanol showed insignificant t–m phase transformation (Fig. 1) during processing. The mixing of the carbide–oxide blend revealed no notable solid-state reactions between ZrC and YTZ; XRD investigation indicated the presence of tetragonal yttria stabilized zirconia and cubic zirconium carbide as the major phases in the precursor.

In essence, powder particles can be considered hierarchically structured agglomerates of nano-sized zirconia dispersed between and/or on the surface of zirconium carbides, Fig. 2. Therefore, bi-model pore size distribution is expected in the final product because the densification of agglomerates is easier than elimination of inter-agglomerate pores.

3.2. Densification

Near full densification of ZrC–ZrO_2 composite by means of pressureless sintering at temperatures higher than 2000 °C was