I O U R N A L O F

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Densification behavior of Y-TZP containing zirconium diboride composites

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In the present study, the densification behavior of yttria-stabilized tetragonal zirconia containing zirconium diboride (up to 50 wt%) composites was prepared by a pressureless sintering method in an argon atmosphere over the temperature range of 1350-1550 °C for one hour holding time were investigated. The influences of zirconium diboride additions in the zirconia matrix, as well as the sintering temperature, on the densification, phase stability and mechanical properties of sintered samples have been studied. The results showed that the tetragonal phase stability of the zirconia was affected by the addition of zirconium diboride, with large amounts of the monoclinic phase formed after sintering. This in turn has resulted in a decline in the relative density of the sintered samples and mechanical properties.

Key words: Y-TZP composites, Zirconium diboride, Sintering, Mechanical properties.

Introduction

Zirconia ceramics are attractive materials mainly due to their exceptionally high mechanical properties such as flexural strength and fracture toughness [1]. In particular, yttria-tetragonal zirconia polycrystals (Y-TZP) has been used in diverse applications ranging from household appliances such as knives, scissors and cutters to in aggressive/mechanical environments such as in chemical filters, piston rings, extrusion dies, cutting tool inserts, etc. [2].

The uniqueness of Y-TZP as compared to other monolithic materials is its microstructural ability to absorb energy from propagating crack, thus preventing further crack advancement. This phenomenon is known as transformation toughening [1]. In this mechanism, the energy absorbed by the zirconia matrix in the vicinity of the propagating crack is consumed by the tetragonal (t) grains to transform to the monoclinic (m) symmetry which is accompanied by \sim 3-4% volume expansion. As a result, the generated compressive stress generated resulting from the volume expansion and surrounding matrix constraint act to hinder crack propagation [3].

Due to the high hardness of tetragonal zirconia, shaping of the ceramic requires the use of diamond tools which can be expensive and the cutting process can be time consuming. In addition, the production of complicated shape ceramics by a diamond grinding route is almost impossible. In contrast, electrical discharge machining (EDM) has been widely employed in the metal cutting industry because of its low cost and the ability for intricate parts to be machined easily and with high accuracy. However, due to the high resistivity, zirconia-based ceramics would not be able to be machined via the EDM technique. Thus, in order to take advantage of EDM, various electro-conductive phases such as WC, TiC, TiCN, ZrB₂ and TiB₂ have been investigated [4-6]. One of the most interesting com-binations is the incorporation of zirconium diboride (ZrB₂) since it is a non-oxide ceramic with special properties such as high electrical conductivity and high hardness [7, 8].

The objective of the present study was to investigate the effect of adding varying amounts of ZrB_2 on the sintering properties of Y-TZP composites.

Experimental Procedures

The 3 mol% yttria-stabilized zirconia (Y-TZP) starting powder used in this study was manufactured by Kyoritsu Ltd., Japan according to the hydrolysis method and spray dried to obtain free-flowing ready-to press powder. The zirconium diboride used in this study was obtained from a commercial available powder (Wako, 99% purity). Varying amounts of ZrB₂ additions ranging from 5 to 30 wt% were prepared. The Y-TZP and ZrB₂ powders were mixed in 150 ml of ethanol via ultrasonification followed by ball milling for 1 hour. After the mixing, the wet slurry was dried, crushed and sieved into powder form. The composite powder obtained was uniaxially pressed at 2.5-3.0 MPa into circular discs

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(20 mm diameter and 3 mm thickness) and rectangular bars ($4 \times 13 \times 32$ mm) and subsequently cold isostatically pressed at 200 MPa (Riken Seiki, Japan). The compacted green samples were sintered at temperatures ranging from 1350-1550 °C, in a tube furnace with a ramp rate of 5 °Kminute⁻¹ and a soaking time of 1 hour in an argon atmosphere. Prior to testing, all sintered samples were polished to a 1 µm surface finish.

Phase analysis of the starting powders and sintered samples were carried out by X-ray diffraction (XRD) (Geiger-Flex, Rigaku Japan) under room temperature conditions using Cu-K α as the radiation source. The bulk density of the sintered bodies were obtained by a water immersion technique (Mettler Toledo, Switzerland). The Young's modulus (E) by sonic resonance was determined for rectangular samples using a commercial testing instrument (GrindoSonic: MK5 "Industrial", Belgium) [9]. The Vickers hardness (H_v) of sintered discs was determined using a pyramidal diamond indenter (Future Tech, Japan) with an applied load of 10 kg and for 10 seconds. At least five indentations were made for each sample and the average value recorded.

Results and Discussion

XRD analysis was carried out on all the sintered samples to study the effect of the sintering condition as well as incorporation of the ZrB₂ phase on the tetragonal phase stability of Y-TZP matrix. Fig. 1 summarizes the measured monoclinic content obtained from XRD profiles of all the sintered composites. Although both tetragonal and monoclinic phases were present in the as-received Y-TZP powder (Fig. 1), the XRD patterns of the sintered monolithic Y-TZP samples exhibited a fully tetragonal phase. In addition, increasing the sintering temperature did not affect the tetragonal phase stability since the sample sintered at a high temperature of 1550 °C contains 100% tetragonal phase. However, incorporation of the secondary ZrB₂ phase into the Y-TZP matrix and sintering in an inert atmosphere had a significant effect on the composition and especially on the tetragonal phase stability of the



Fig. 1. Monoclinic phase contents in Y-TZP/ZrB₂ composites sintered at different temperatures



Fig. 2. Optical micrograph revealing a network of micro and macro-cracks on the surface of the Y-TZP/50 wt% ZrB_2 composite sintered at 1550 °C.



Fig. 3. Effect of the sintering temperature and ZrB_2 content on the relative density of Y-TZP/ZrB₂ composites.

samples. The retained tetragonal phase in the Y-TZP/ ZrB₂ composites was found to decrease with increasing both the sintering temperature and Y-TZP/ZrB₂ ratio. Sintering at a temperature as high as 1550 °C resulted in the formation of large amounts (\sim 45%) of the monoclinic phase in the samples containing 35 and 50 wt% ZrB₂. This phase transformation was also accompanied by severe formation of micro and macro-crack networks on the surfaces as is typically shown in Fig. 2.

The relative density variations with sintering temperature for Y-TZP/ZrB₂ composites are shown in Fig. 3. Although the relative densities for all composites were lower than that for the monolithic sample, the plots revealed a rising trend for all composites with increasing sintering temperature. The results presented clearly indicate that the density increased with increasing sintering temperature and decreasing ZrB₂ content. Monolithic samples which were sintered above 1350 °C attained more than 98% of the theoretical density, while incorporation of the ZrB₂ compound hindered densification. The low relative density exhibited by the Y-TZP/ZrB₂ composites compared to monolithic



Fig. 4. Effect of the sintering temperature and ZrB₂ content on the Young's modulus of Y-TZP/ZrB₂ composites.



Fig. 5. Linear relationships exist between the Young's modulus and relative density of Y-TZP/ZrB₂ composites.

Y-TZP could be attributed to the presence of a large amount of the monoclinic phase in the structure.

The effect of ZrB₂ incorporation on the Young's modulus of composites sintered at temperatures ranging from 1300-1550 °C is shown in Fig. 4. The addition of ZrB₂ was not beneficial in enhancing the stiffness of Y-TZPs sintered at temperatures lower than 1500 °C. Fig. 4 also shows that a Young's modulus of more than 200 GPa could be achieved when monolithic Y-TZP samples are sintered at temperatures higher than 1350 °C. Similar to the density trend, the Young's modulus of all composites also increased gradually with an increment of the sintering temperature and attained a Young's modulus value of ~ 180 GPa when sintered at 1500 °C. The increase of the modulus values was not significant at lower temperatures (1300-1400 °C) whereas it showed a sharp increase when sintered at temperatures higher than 1450 °C, particularly for the 25 wt%, 35 wt% and 50 wt% ZrB₂ containing composites. Similar to the observation obtained from the densification behavior, the addition of ZrB2 resulted in a decrease in Young's modulus. The monolithic Y-TZP samples achieved a higher Young's modulus compared to the other composite samples sintered at 1300 °C.

Attempts to correlate the bulk density and Young's



Fig. 6. Effect of the sintering temperature and ZrB₂ content on the Vickers hardness of Y-TZP/ZrB₂ composites.

modulus revealed a linear trend (i.e the R-squared value for all the regression line varies between 0.9-0.94 which is almost equal to 1 indicating a linear correlation) exist between both properties as depicted in Fig. 5. The modulus of elasticity of the sintered Y-TZP body increased linearly up to a maximum of > 190 GPa with increasing relative density up to ~95%, regardless of the addition of ZrB₂. Thus, it can be inferred that the bulk density or porosity is an important parameter governing the stiffness of the Y-TZP based composites.

The Vickers hardness curves as a function of sintering temperature and ZrB_2 content are shown in Fig. 6. The graphs of the Vickers hardness of Y-TZP/ ZrB_2 composites varied in the same manner as for the relative density variation with sintering temperature (Fig. 3). In general, the results showed a negative effect of ZrB_2 additions on the hardness of the Y-TZP matrix mainly at sintering temperatures below 1450 °C.

The increase in hardness can be attributed to the increase in bulk density. For example, in the case of the Y-TZP/10 wt% ZrB₂ samples, sintering at 1300 °C resulted in a low relative density (90%) and consequently a low hardness value (5.5 GPa). However, when the sintering temperature was increased to 1450 °C, significant increases in the relative density (96%) and Vickers hardness (12 GPa) were obtained.

Conclusions

In the present research Y-TZP containing ZrB_2 composites were pressureless sintered in an argon atmosphere. The phase analysis of the sintered composites indicated that a phase transformation from the tetragonal symmetry to the monoclinic phase proceeded during cooling from the sintering temperature. This effect was more pronounced with increasing ZrB_2 content. The presence of the monoclinic phase in the structure resulted in a lower densification for the composite body and overall lower mechanical properties of the sintered composites. Nevertheless, it was found that the mechanical properties of the composites improved with increasing

sintering temperature. The study found that the addition of more than 25 wt% ZrB_2 was not beneficial in promoting densification of Y-TZP composites.

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