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Processing and properties of zirconia-toughened alumina ceramics

D S PATIL* and B C MUTSUDDY
Institute of Materials Processing, Michigan Technological University, Houghton, Michigan 49931, USA
* Present address: Laser and Plasma Technology Division, Bhabha Atomic Research Centre, Bombay 400085, India

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Abstract. Al_2O_3:ZrO_2 ceramics have been prepared from physically mixed pure oxide powders. The results indicate that careful processing of the starting powders and a two-stage sintering process can avoid expensive processing methods like hot pressing/hot isostatic pressing used for achieving high densification. The mechanical properties were measured and the resultant microstructure studied to explain the toughening behaviour of this material.

Keywords. Al_2O_3; ZrO_2; toughening; gas over pressure sintering.

1. Introduction

Alumina has been used more frequently than any other type of ceramic in structural applications. A lot of attention has also been given to improving the mechanical properties of this engineering ceramic. For improvement in the mechanical properties, toughness is one of the most important parameters. One way to improve the fracture toughness is the use of the phenomenon of transformation toughening, which is associated with ZrO_2-containing ceramics.

The concept of toughening alumina ceramics by dispersing zirconia particles in the matrix has been recognized in the last decade. The ceramic containing ZrO_2 can have relatively high value of fracture toughness. This has been attributed to a number of different mechanisms such as stress-induced tetragonal–monoclinic martensitic transformation (Lange 1982; Ruhle *et al* 1986), microcracking due to the stress set up in the matrix around ZrO_2 particles which have undergone martensitic transformation (Claussen *et al* 1982; Ruhle *et al* 1986) and crack deflection around the dispersed ZrO_2 particles.

In the zirconia-toughened alumina, retention of > 10 vol% metastable tetragonal ZrO_2 in the alumina matrix is the key to obtaining the increased room-temperature fracture toughness. However, to retain the metastable tetragonal ZrO_2 it is essential that ZrO_2 grain size be less than some critical size which is reported to be in the range of 0·5 to 0·8 μm (Lange and Green 1981; Green 1982; Heuer 1982; Lange 1982; Garvie 1984). Above this critical size, the ZrO_2 grains transform to the monoclinic form.

The high temperatures which are required for the densifications usually result in significant grain coarsening and growth of ZrO_2 particles above the critical size and therefore it is difficult to retain the desired zirconia volume concentration and phase form. Zirconia grain growth occurs at the elevated sintering temperatures of $> 1600°C$. To meet these requirements, numerous processing approaches have been investigated to achieve lower densification temperature and homogeneous distribution of ZrO_2 in the alumina matrix. The methods which are commonly used include attrition milling, colloidal processing, chemical vapour co-deposited alumina zirconia powders

with a surfactant, co-pyrolysed solutions, hydrothermal reaction of aluminium–zirconium alloys, hydrolysis of zirconium alkoxide in the presence of Al_2O_3 particles, polymer/powder flocculation and sol–gel processing. Leriche *et al* (1988) obtained 99·3% density after attrition milling for 6 h of a mix of two separate slips (of dispersed alumina and zirconia powders) showing same rheological behaviour and sintering in air at 1550°C for 2 h. They could get 100% density for the same samples after hot pressing at 1500°C for 15 min at 30 MPa. Mechanical property measurements were done on their samples by Orange *et al* (1988). For material containing 15 vol% ZrO_2 they obtained a fracture toughness (K_{IC}) value of 6 MPa $m^{1/2}$. For the hot-pressed sample of the same composition K_{IC} value was around 6–7 MPa $m^{1/2}$. Aksay *et al* (1983) started with colloidal suspension which was further milled for 16 h. Using filtration as a consolidation method and sintering at 1600°C in air for 2 h they obtained density > 98·5%. White *et al* (1988) started with 0·25 μm narrow-sized powders; suspension processing and sintering at 1500°C for 2 h led to a densification around 91–93%.

To avoid grain growth which occurs during pressureless sintering expensive processing like hot pressing/hot isostatic pressing (HIP) is required. However, it is highly desirable to produce structural ceramics with good mechanical properties by conventional processing technique, i.e. normal shaping and simple firing process without expensive processing techniques like hot pressing/hot isostatic pressing. This is particularly advantageous when complicated shapes are required to be made.

The objective of this study was to combine the effects of processing to achieve the high level of densification and fine zirconia phase retention to form toughened alumina–zirconia composites without using expensive high-temperature processing such as hot isostatic or hot pressing.

2. Experimental

The starting powder of Al_2O_3:ZrO_2 was made by mixing Alcoa Al6SG alumina with average particle size of 0·52 μm (Alcoa, Alumina Company of America, Pittsburgh) and Cerac ZrO_2 (monoclinic, −325 mesh) L-1041 (Cerac, Inc., Milwaukee) to get 15 vol% ZrO_2 in the mix. The mixture was rolled with ZrO_2 grinding media and isopropyl alcohol for 80 h. The slurry was dried under an IR lamp and the powder was sieved through the 100 mesh screen. The particle size of the ZrO_2 in the powder was examined under a JEOL JSM-820 scanning electron microscope (JEOL USA, Inc., Peabody, MA). The zirconia particle size distribution is shown in figure 1. From this figure it is clear that majority of the ZrO_2 particles are in the size range around 0·2 μm.

The powder was cold isostatically pressed into cylindrical pellets at a pressure of 276 MPa. The samples were sintered in normal air atmosphere at 1450°C for 90 min (heating and cooling rates of 200°C/h). The densities of the samples were measured by Archimedes method. The density was 4·150 g cm^{-3}, which is ~98% of the theoretical density (TD, 4·235 g cm^{-3}).

To enhance further densification, the samples were heat-treated in a graphite furnace. The samples were embedded in boron nitride powder and wrapped in molybdenum foils. The samples were then heated to 1450°C and 10·35 MPa argon gas over pressure was maintained for 2 h.

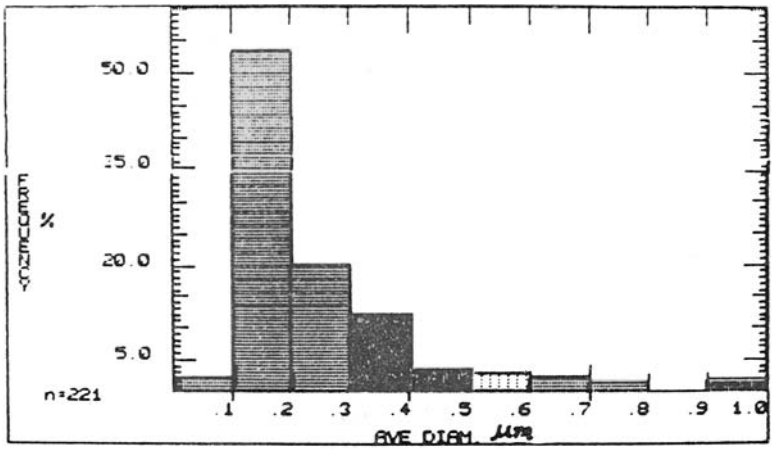

Figure 1. Zirconia particle sizing on the milled Al_2O_3:ZrO_2 powder.

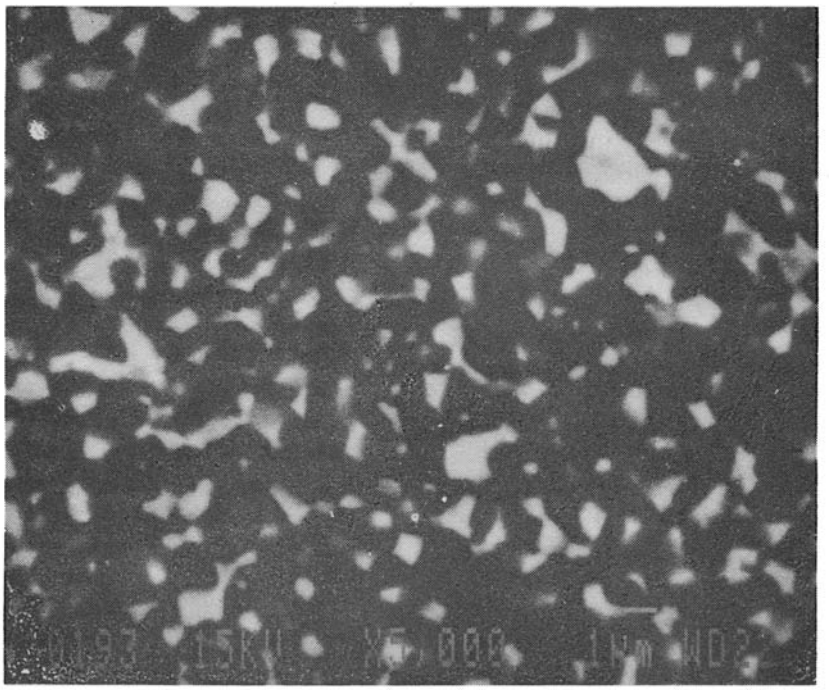

Figure 2. Polished section of sintered Al_2O_3:ZrO_2 (BEI).

The densities of the sintered samples were measured after the gas over pressure sintering. Specimens were cut from the sintered samples and the surfaces were polished to a 0·25 μm finish with diamond paste. The samples were chemically etched in 40% hydrofluoric acid (HF) for 2 min to reveal the microstructure. The polished and etched surface as examined under the scanning electron microscope is shown in figure 2. Zirconia particle sizing was done on the polished section and is shown in figure 3.

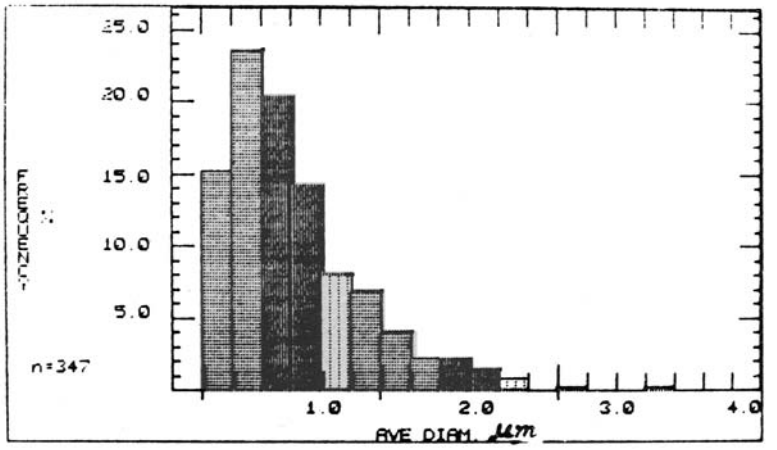

Figure 3. Zirconia particle size distribution on sintered and polished Al_2O_3:ZrO_2 surface.

The hardness, fracture toughness and elastic modulus of the polished samples were determined by indentation techniques (Anstis *et al* 1981; Marshall *et al* 1982). To produce well-developed microcracks ($c > 2a$), loads of 10–50 kg were applied depending upon the samples. Controlled flaws were introduced by Vickers diamond pyramid indenter with loads varying between 10 and 50 kg. The specimens were indented at a constant crosshead speed to the selected load and then slowly unloaded. Hardness values were obtained from these measurements. To calculate the toughness of the material it is essential to know its elastic modulus which has been calculated from the Knoop indentation on the sample. This technique of measuring hardness to modulus ratio is based on measurement of the elastic recovery in surface dimensions of Knoop indention.

3. Results and discussion

The density measurements on the samples after the gas over pressure sintering show that the density was 4·233 g/cm^{-3}. This indicates that the samples were sintered to near theoretical density (99·95% of TD). This also confirms that the samples were sintered to closed porosity state by normal air sintering and the gas over pressure sintering was helpful in eliminating the pores further to get full densification. Thus by careful processing of the starting powder (i.e. by making sure that ZrO_2 particles are fine and majority of them are within narrow size range) and a combination of air sintering and gas over pressure sintering, it should be possible to densify even complicated shapes of this material without the necessity of expensive processing methods.

The room-temperature hardness and fracture toughness values for this material (values reported here are the average of several measurements) are as follows: Hardness (GPa) 17·8, E/H 23·6, and fracture toughness (MPa m$^{1/2}$) 4·8.

The data can be explained in the light of the observed microstructure. Fine zirconia particles are retained after sintering as seen in figure 2. This is further clear from the zirconia particle size distribution on the sintered sample as shown in figure 3. These

fine zirconia particles are possibly in the tetragonal form. Presence of these fine zirconia particles gives rise to transformation toughening effects in the wake of the advancing crack and this must be the main contributing factor for the observed hardness and fracture toughness of this material.

4. Conclusions

It has been demonstrated that high-density zirconia-toughened alumina ceramics with good mechanical properties can be obtained by careful processing of the initial powder and a combination of air sintering and gas over pressure sintering. These results also indicate that material can be densified to high density without the necessity of expensive hot pressing/hot isostatic pressing.

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