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Duplex spinel–ZrO_2 ceramics

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Duplex spinel–ZrO_2 ceramic composites were produced by an emulsion–hot kerosene drying technique. The sintered duplex spinel–ZrO_2 ceramics which had the composition of 55 wt% Al_2O_3–20 wt% ZrO_2–25 wt% MgO, consisted of a spinel matrix, whose grain size was in the range of 1.5 to 2.0 μm, and uniformly dispersed zirconia agglomerates having grain sizes ranging from 1.0 to 2.0 μm. Zirconia agglomerates began to appear at a temperature of 1500 °C and the duplex spinel–ZrO_2 structure was formed with the weight ratio of Al_2O_3/MgO being within 1.67 to 2.20 and the amount of ZrO_2 addition being within 5 to 25 wt%. The relative density, fracture toughness, flexural strength, and critical temperature difference of the spinel–ZrO_2 composite were 97.8%, 1.98 $MPam^{0.5}$, 390 MPa, and 275 °C, respectively.

1. Introduction

ZTC is an abbreviation for zirconia-toughened ceramic that includes all ceramics whose toughness arises from the addition of zirconia to some other ceramic matrix such as Al_2O_3, mullite, Si_3N_4, spinel, cordierite, forsterite, MgO, and zircon [1–6]. Among the ZTC, zirconia toughened alumina composites are called ZTA. Microstructurally, ZTA can be divided into four groups [7, 8]: group I is alumina with dispersed unstabilized zirconia: group II is alumina with dispersed partially stabilized zirconia (PSZ): group III is alumina with PSZ agglomerates: and group IV is alumina–zirconia duplex structures. For the last few years we have studied the microstructures of ceramic composites in the Al_2O_3–ZrO_2–MgO system. It was found that cubic ZrO_2 agglomerates were well dispersed in a fine-grained spinel matrix by the emulsion–hot kerosene method and concluded that our duplex spinel–ZrO_2 ceramics were similar to group III in that agglomerated ZrO_2 grains were dispersed in a ceramic matrix. But there were two differences. One was the preparation process and the other was the zirconia form. The process that was used in the preparation of duplex spinel–ZrO_2 ceramics was an emulsion technique and the zirconia form in the agglomerates was cubic.

A microstructure which used a polycrystalline agglomerate of metastable zirconia in a matrix of fine-grained alumina (group III) was first described by Stevens and Evans [9]. As with all toughened ceramics, the toughening was a result of microcracking and stress-induced transformation toughening. The energy of the crack could be absorbed by the effective concentration of the zirconia particles in the agglomerates. They obtained alumina with PSZ agglomerates having a high toughness value, unusual for coarse-grained materials, but also found that it was difficult to control the agglomerate size together with a fine-grained matrix. The microstructure of toughened alumina consisted of a uniformly dispersed ZrO_2 phase in the size range 5 to 25 μm, with an occasional layer agglomerate (> 30 μm) being present.

In the present work duplex spinel–ZrO_2 composites were fabricated by the emulsion-hot kerosene drying method [10–12] to control ZrO_2 agglomerate size. The formation mechanism of the ZrO_2 agglomerates and the microstructure and properties of the duplex spinel–ZrO_2 ceramics were reported.

2. Experimental procedure

Starting materials included kerosene for the continuous oil phase: distilled water and aqueous $MgSO_4$. $Al_2(SO_4)_3$, and $ZrOCl_2$ (Junsei Chemical Co./Japan) solutions for the dispersed phase: and span 80 (Yakuri Chemical Co./Japan) as the emulsifying agent.

The experimental route is detailed in Fig. 1. Water-in-oil type emulsions were prepared by dissolving the span 80 in the kerosene at room temperature, followed by the dropwise addition of the aqueous phase while stirring. The amount of kerosene (oil phase) and span 80 in the emulsion were 40 and 2 vol%, respectively. When the mixture of these constituents were vigorously agitated at 6500 r.p.m. for 1 h, a stable emulsion was obtained. Droplet sizes of the emulsion were studied by optical microscopy.

Formation of solid particles was accomplished by dropwise addition of the emulsion to hot kerosene whilst stirring with a magnetic stirrer. The hot kerosene temperature in the bath was maintained between 165 and 175 °C. Precursor particles were recovered by filtration and further dried overnight at 110 °C, and then calcined at 1100 °C for 2 h to obtain oxide particles. The calcined powders mixed with methyl cellulose were pressed into bars at a pressure of 40 MPa in a steel die, followed by hydrostatic pressing at 207 MPa. The sintering of the compacts were carried out at 1650 °C for 4 h in air.

The microstructural characterization was made using X-ray diffraction (XRD) and scanning electron

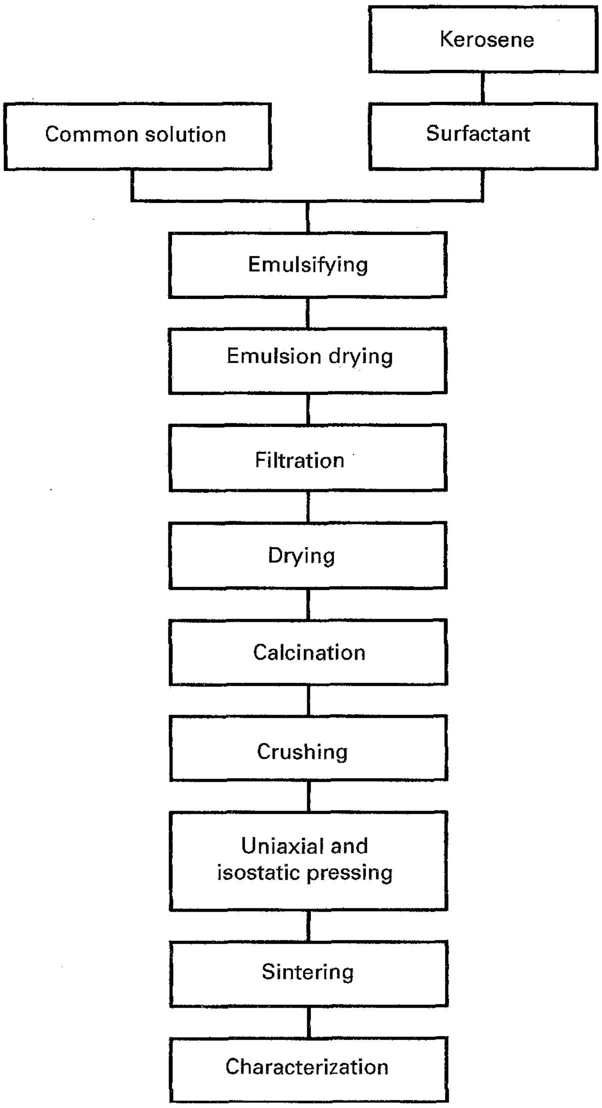

Figure 1 Experimental flow chart for the emulsion–hot kerosene drying method.

microscopy (SEM). The fracture toughness of the ceramic was measured using the indentation technique of Evans and Charles [13]. Finally the flexural strength of the bars was measured by the three-point bending method using an Instron tensile testing machine.

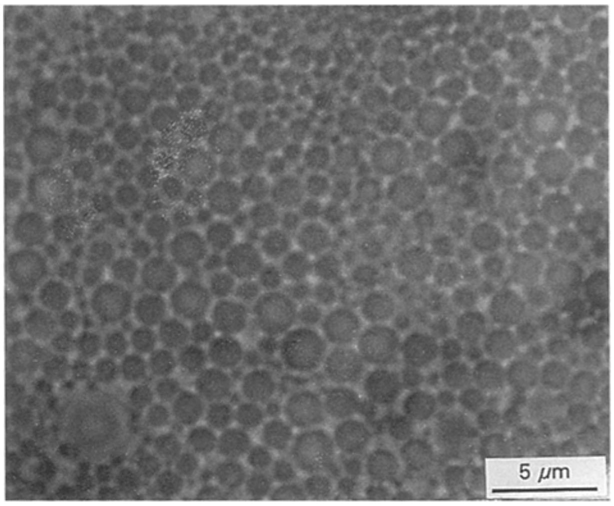

Figure 2 Optical micrograph of an emulsion droplet.

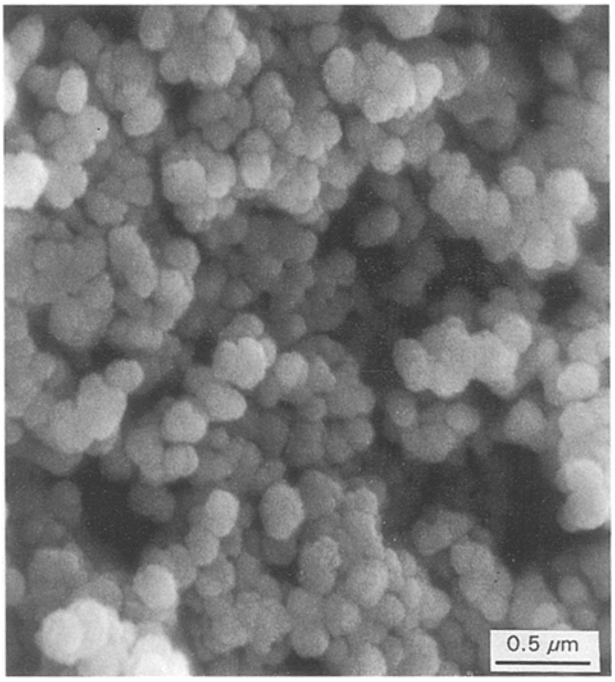

Figure 3 Scanning electron micrograph of spinel–ZrO$_2$ powders calcined at 1100 °C for 2 h.

3. Results and discussion

Fig. 2 shows the optical micrograph of a water-in-oil type emulsion. The droplet size of the emulsion was between 1 and 2 μm, and the emulsion was stable for 24 h. Inspection of the X-ray diffraction for the calcined powders indicated that the major phases were spinel and cubic zirconia, and the presence of a small amount of magnesia was detected. The calcined spinel–ZrO$_2$ powders had an average particle size of 0.2 μm and a narrow size distribution (Fig. 3).

As can be seen from the microstructure of the sintered spinel–ZrO$_2$ composites (Fig. 4), duplex spinel–ZrO$_2$ ceramics (55 wt % Al$_2$O$_3$–20 wt % ZrO$_2$–25 wt % MgO) consisted of a spinel matrix (1.5 to 2.0 μm) and uniformly distributed zirconia agglomerates (1.0 to 2.0 μm). For the sintering of ZTA, it was considered that zirconia particles could ripen by-coalescence or Ostwald ripening during the later stages of sintering. For coalescence, ZrO$_2$ particles grow as a result of being dragged together by migrating alumina grain boundaries. In this coalescence process, grain growth and the disappearance of small alumina grains caused particles to meet, coalesce, and thus form larger particles [7, 14]. In the duplex spinel–ZrO$_2$composites, ZrO$_2$ particles grew by coalescence during the later stages of sintering. But as there existed a small amount of excess MgO around the grain boundary of the ZrO$_2$ grains, these grains came together, coalesced, and formed ZrO$_2$ agglomerate, and not a ZrO$_2$ grain. The minimum temperature at which ZrO$_2$ agglomerates were formed was 1500 °C and at this stage zirconia agglomerates about 0.5 μm size, took shape by the coalescence of three or four small particles. In Fig. 5 the coalescence process that grew ZrO$_2$ particles could easily be seen by varying

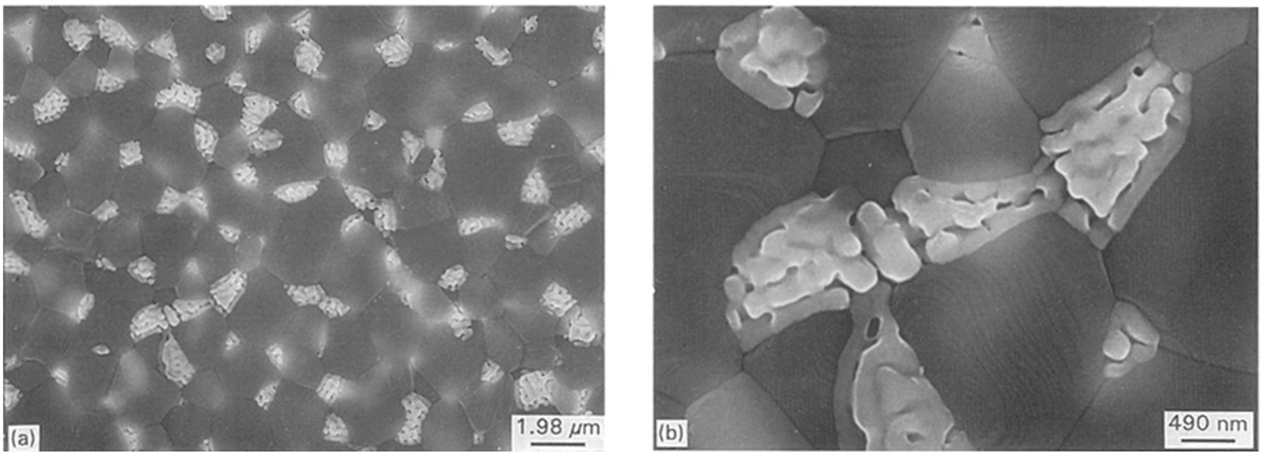

Figure 4 Scanning electron micrographs of a spinel–ZrO$_2$ composite sintered at 1650 °C for 4 h: (a) ×4400 and (b) ×17600.

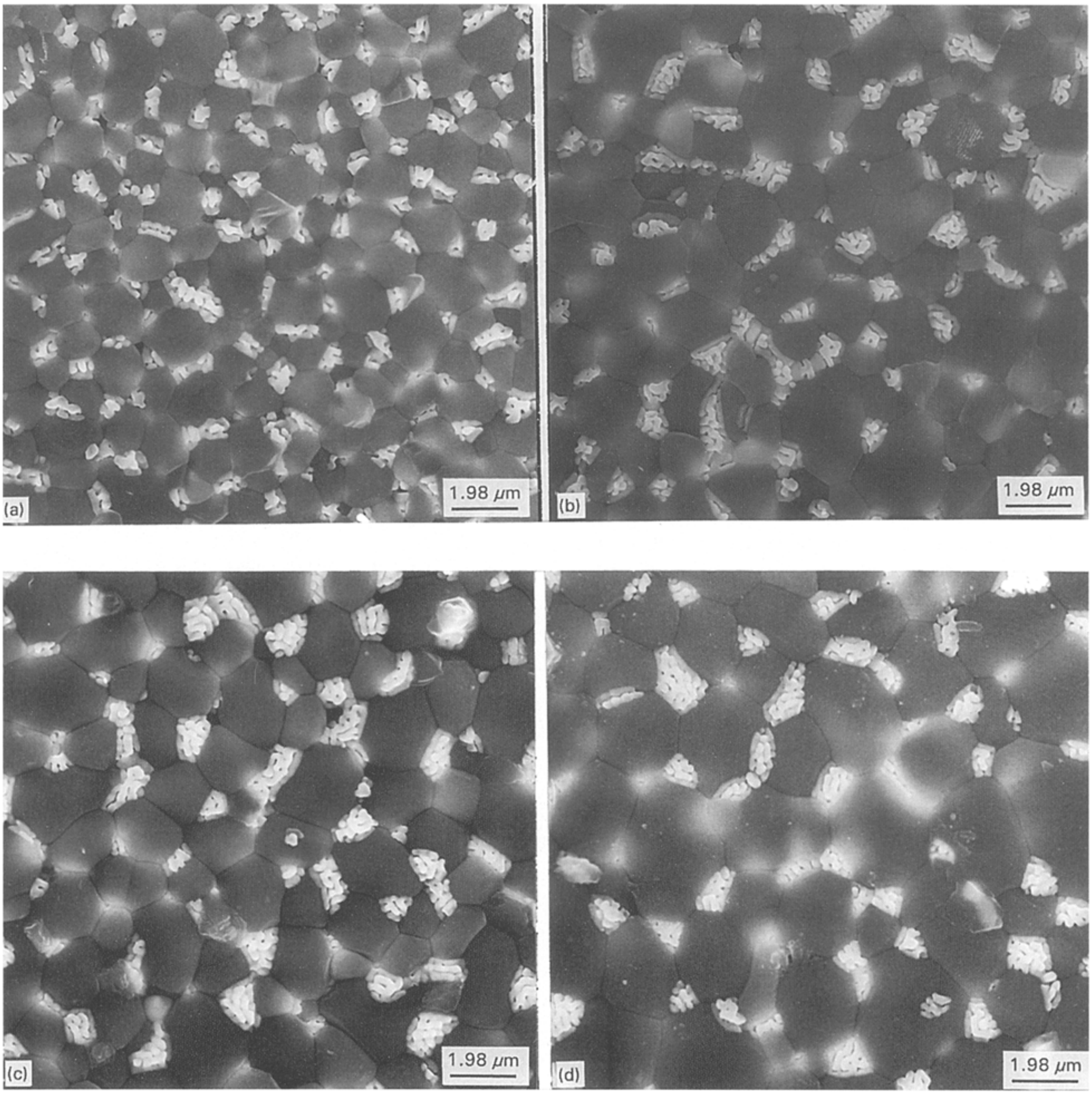

Figure 5 SEM photographs of spinel–ZrO$_2$ composites (55 wt % Al$_2$O$_3$–20 wt % ZrO$_2$–25 wt % MgO) sintered at various temperatures: (a) 1600 °C for 2 h, (b) 1650 °C for 2 h, (c) 1650 °C for 4 h, and (d) 1650 °C for 8 h.

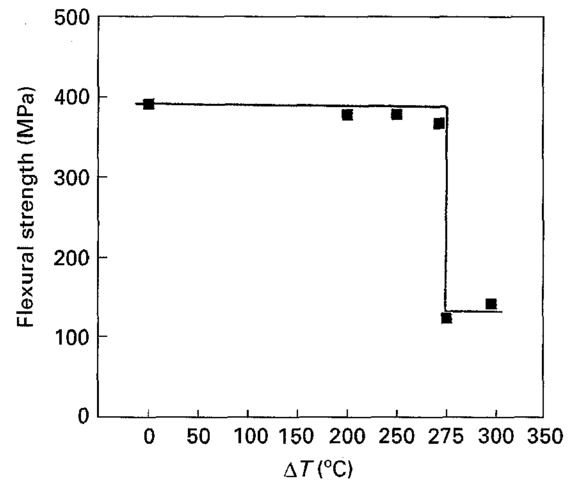

Figure 6 Variation of flexural strength of spinel–ZrO_2 composites as a function of thermal shock temperature difference (ΔT).

sintering temperature and time. In the SEM photographs of spinel–ZrO_2 composites, ZrO_2 agglomerates and spinel matrix grains grew larger as sintering temperature and time were increased and the coalescence process of the ZrO_2 particles could be clearly observed. As the uniformly distributed ZrO_2 agglomerates were formed during the sintering process, there was a difference to that observed with the previous reported structure (group III) in that the ZrO_2 agglomerates used the agglomerated ZrO_2 powders as the starting material.

We investigated the composition range in which ZrO_2 agglomerates were built up. It was found that the duplex spinel–ZrO_2 structure was formed with the weight ratio of Al_2O_3/MgO being within 1.67 to 2.20 and the amount of ZrO_2 addition being within 5 to 25 wt%. Though the values of relative density and flexural strength of the duplex ceramics were higher than those of spinel produced by the same process, the fracture toughness of the duplex spinel–ZrO_2 ceramics was the same as that for spinel because the ZrO_2 form existing in the ZrO_2 agglomerate was cubic. The relative density, fracture toughness, flexural strength, and critical temperature difference of the spinel–ZrO_2 composite (Fig. 6) were 97.8%, 1.98 $\text{MPam}^{0.5}$, 390 MPa, and 275 °C, respectively. If we could transform cubic ZrO_2 agglomerates into the tetragonal form, this would be effective in increasing toughness, and a considerable increase in the mechanical properties of duplex spinel–ZrO_2 composite would be expected.

4. Conclusions

The results indicated that the droplet size of the emulsion was between 1 and 2 μm and that the synthesized spinel–ZrO_2 powders calcined at 1100 °C had the average particle size of 0.2 μm and a narrow size distribution. The sintered duplex spinel–ZrO_2 ceramics which had the composition 55 wt% Al_2O_3–20 wt% ZrO_2–25 wt% MgO consisted of a spinel matrix, whose grain size was in the range of 1.5 to 2.0 μm, and uniformly dispersed zirconia agglomerates having grain sizes ranging from 1.0 to 2.0 μm. The ZrO_2 grains grew by a coalescence process during the later stages of sintering in the duplex spinel–ZrO_2 ceramics. It was also found that the spinel–ZrO_2 duplex structure was formed with the weight ratio of Al_2O_3/MgO being within 1.67 to 2.20 and the amount of ZrO_2 addition being within 5 to 25 wt%. The values of relative density and flexural strength of the duplex ceramics were higher than those for spinel produced by the same emulsion–hot kerosene method. The fracture toughness of the duplex spinel–ZrO_2 ceramic could be increased if it were possible to make the cubic ZrO_2 agglomerate transform into the tetragonal form.

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