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Conductivity and strength behaviour of alumina$_{\text{whisker}}$–zirconia composites

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Yttria stabilized zirconia (8 mol%) composites were fabricated by tape casting with either alumina powder or alumina whiskers, and pressureless sintered. Sintering behaviour, ionic conductivity and mechanical strength were analysed. For all compositions analysed, increasing alumina content reduced the sintered density. For whisker-reinforced zirconia, the rigid whiskers prevented matrix densification along their axis. The ionic conductivity was measured by the complex impedance method from 500–1000 °C and the activation energy for ionic conduction calculated over that range. The ionic conductivity of the alumina–zirconia composites decreased with increasing alumina content as expected by the rule of mixtures. However, the ionic conductivity of the whisker–zirconia composites decreased more than expected possibly due to contamination from the whiskers. The strength of the whisker–zirconia composites was also found to be affected by the porosity. At 5 vol%, the average strength was measured at 39.9 kgf mm^{-2}, which decreased to 24 kgf mm^{-2} at 20 vol%.

1. Introduction

In solid oxide fuel cells (SOFC), yttria-stabilized zirconia (8 mol% yttria, 8YSZ) is the material of choice for use as the oxygen ion conducting electrolyte. 8YSZ has a high oxygen ionic conductivity, ≈ 0.18 S cm^{-1} at 1000 °C, and is very stable chemically and structurally. However, 8YSZ is not a strong ceramic. The complex thermal and mechanical stresses during processing, assembly, and operation at 1000 °C currently limit the possible uses of 8YSZ to simple applications. Strong 8YSZ is required to allow fabrication and development of the highly efficient large planar fuel cell systems.

Several types of reinforcements are possible for use in ceramics, such as particulate, platelet, whisker, and continuous fibre. Understanding the roll of particulate reinforcements has led to the development of stronger ceramics [1–3] which has been applied to the zirconia alumina system. Alumina was reported to be a suitable reinforcing agent because it improves the microstructure and grain boundaries of zirconia [4] and to be also non-reactive in 8YSZ [5]. Research then expanded to include investigations of alumina in partially stabilized zirconia [6–8] and fully stabilized zirconia [9, 10]. Alumina was found to improve the mechanical properties from room temperature to over 1000 °C. The improvement in mechanical properties was investigated for possible use in fuel cell applications. Ishizaki *et al.* [11] analysed the properties of alumina 8YSZ composites from 0–30 wt% alumina powder. The biaxial flexure strength increased by 50% with the addition of 30 wt% alumina. However, the resistivity at 1000 °C also increased by 150% for 30 wt% alumina. Hernandez *et al.* [12] investigated the effect of alumina powder on the electrical properties of a series of zirconia alloys ranging from tetragonal zirconia polycrystals (TZP), yttria partially stabilized zirconia (Y-PSZ), and fully stabilized 8YSZ. Hernandez *et al.* found an increase in ionic conductivity in Y-PSZ with a 10 wt% addition of alumina. The other alloys decreased in conductivity with the addition of alumina. Yamamoto *et al.* [13] examined the strength and electrical behaviour in more detail, as a function of temperature and alumina content (0, 10, 20, 30 wt%) in 8YSZ. The strength, measured by three-point bending, was found to be mildly affected by temperature with a maximum room-temperature strength of 33 kgf mm^{-2} with 20 wt% (27 vol%) alumina, as seen in Fig. 1. The problem is a concurrent 50% decrease in ionic conductivity from 0.18 S cm^{-1} (0 vol%) to 9.4×10^{-2} S cm^{-1} (27 vol%).

The limitations of particulate-reinforced zirconia for high-temperature use were noted early by Claussen [14]. He recommended, besides the addition of hard, high-modulus particles, the use of whisker or fibre reinforcement. Tamari *et al.* [15] produced alumina whisker-reinforced 3 mol% yttria TZP. They found an improvement of all mechanical properties from

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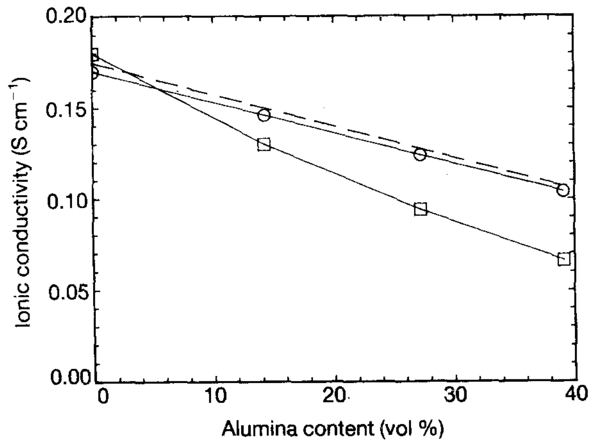

Figure 1 Published values of ionic conductivity at 1000 °C versus volume per cent alumina powder: (○) [11], (□) [13].

room to high temperatures. However, the composites required hot pressing at 1500 °C to achieve greater than 99% density.

The purpose of this research was to conduct a preliminary investigation of alumina whisker-reinforced 8YSZ made by pressureless sintering of tape-cast material. This will be compared with alumina powder-reinforced 8YSZ, made by the same method. Pressureless sintering and tape casting are the main methods of fabrication of planar SOFC materials because hot isostatic pressing is impractical for such large, flat components. It was hypothesized that there would be a suitable improvement of mechanical properties at low volume fractions of alumina whiskers before significant degradation in other properties occurs. The sintering behaviour, ionic conductivity, activation energy, and ageing behaviour of powder- and whisker-reinforced zirconia are measured and compared. The mechanical strength of whisker-reinforced zirconia was measured and compared with values reported in the literature.

2. Experimental procedure

Samples were prepared by standard tape-casting methods using organic solvents (isopropanol and toluene), dispersant (fish oil), and polymers (polyvinylbutyral, di-*n*-butyl phthalate (plasticizer), and polyethylene glycol mono-*p*-iso-octylphenyl (defoamer, Triton X)). The ceramic materials used were 8 mol% yttria-stabilized zirconia (Tosoh 8YS), alumina powder (Marumoto Molar 0.3 μm 99% Al_2O_3), and alumina whiskers (Denka ≈5 μm diameter 98% Al_2O_3 2% SiO_2 fibre). Powdered alumina and 8YS zirconia were milled together for 24 h prior to tape casting. The whiskers were prepared by chopping the alumina fibre blanket for 1 min in a blender then drying. The whiskers were added to the 8YS zirconia slurry 45 min prior to the end of milling to prevent excessive reduction in size to the whiskers. The resulting slurry was then tape cast. The compositions prepared were 2, 3, 5, 10, 20 vol% alumina powder in zirconia; and 3, 5, 10, 20 vol% alumina whiskers in zirconia, and one sample with no alumina prepared by dry pressing techniques. The whisker length and aspect ratio were not measured owing to the difficulty of the measurement. The milling itself would also change the whisker lengths, requiring a remeasurement of the aspect ratio after separation of the whiskers from the powder slurry. Preliminary investigations identified that a minimum of 1 min blender time and 45 min ball-mill time gave a suitable slurry for tape casting. Shorter times (and longer whisker lengths) resulted in an unmanageable slurry for tape casting.

Plates were fabricated by laminating the tape-cast sheets. Lamination was done by placing sheets moistened with solvent on top of each other, removal of bubbles and voids, and drying under a weight. Samples for conductivity analysis were cut both parallel and perpendicular to the tape-casting direction from the green laminated plates. All samples were sintered to 1500 °C for 4 h then furnace cooled. Density was measured by Archimedes' method. The per cent linear fired shrinkage (%LFS) was calculated from the change in green and as-fired dimensions.

Ionic conductivity was measured using the complex impedance method with two porous platinum electrodes from 500–1000 °C with the activation energy calculated over that range. The effect of whisker orientation and tape-casting direction with respect to conductivity was investigated. The effect of the alumina reinforcement on the ageing behaviour of the 8YSZ matrix was also investigated. Ionic conductivity at 1000 °C and activation energy were measured both before and after ageing for 500 h at 1000 °C. The samples tested were 0%, 5 vol% powder (both perpendicular and parallel to the tape-cast direction), and 5 vol% whisker (both perpendicular and parallel to the tape-cast direction).

The strength of the whisker-reinforced 8YSZ was measured for the 5, 10, and 20 vol% samples for comparison with literature values. The samples were fabricated by cutting the fired composite plates into bars, nominally 2 mm × 3 mm × 40 mm in size. The tensile and compressive faces were polished with 1000 grit SiC paper to remove machining damage, and the corners chamfered. Strength was then measured by the four-point bending technique with an outer span of 30 mm and an inner span of 10 mm, and with a cross-head speed of 0.2 mm min^{-1}.

3. Results and discussion

The sintering behaviour of the tape-cast pressureless sintered alumina composites was analysed. In Fig. 2, the relative densities of the powder and whisker composites are plotted versus volume per cent alumina. The powder composites decreased in density with increasing content, achieving only ≈ 83% of theoretical density with 20 vol% alumina. The whisker composites decreased in density with increasing content similar to the powder composites. However, for the 20 vol% whisker composite, the density decreased sharply, achieving only 64% theoretical density.

The per cent linear fired shrinkage (%LFS) is shown in Fig. 3 for the powder and whisker composites. The powder composites show only a moderate decline in

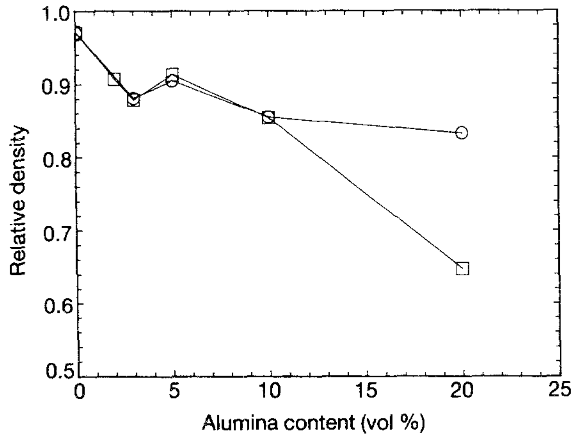

Figure 2 Relative sintered densities versus volume per cent for alumina (○) powder- and (□) whisker-yttria-stabilized zirconia matrix composites.

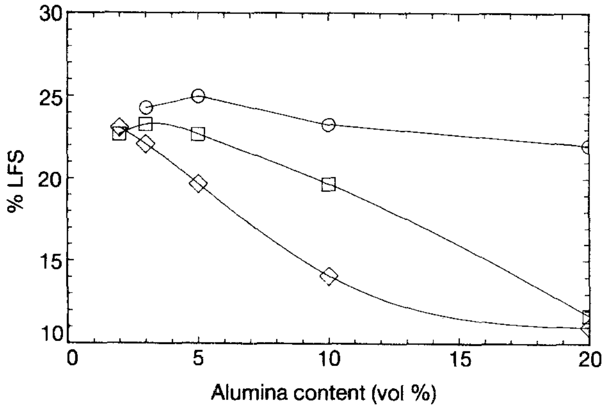

Figure 3 Per cent linear fired shrinkage (%LFS) versus volume per cent for alumina (○) powder and (□, ◇) whisker–yttria-stabilized zirconia matrix composites. The effect of whisker orientation with respect to shrinkage is presented: (□) perpendicular, (◇) parallel.

the average sintering shrinkage with increasing alumina content. There was no difference in shrinkage with respect to tape-casting direction. For the whisker composites there is a clear effect of tape-casting and whisker orientation. With tape casting, the whiskers are generally oriented in the direction of the flow of the tape-casting. The sintering shrinkage parallel to the whisker orientation and tape-casting direction is adversely affected by the whiskers. The sintering shrinkage perpendicular to the whiskers is also affected, decreasing with increasing whisker content. The cause is that these whiskers are already 100% dense and therefore will not shrink during firing. The zirconia powder matrix is constrained from shrinking during sintering by the dense whiskers. This results in the poor densification of the composites with increasing whisker content.

The ionic conductivity at 1000 °C was measured for both the whisker and powder composites as a function of orientation with respect to tape casting. No effect of orientation of sample fabrication on conductivity was found. The average ionic conductivities of the whisker and powder composites are plotted in Fig. 4 and compared with data from Yamamoto *et al.* [13]. There is a decrease in ionic conductivity greater than the Rule of Mixtures (ROM) theoretical prediction for all composites presented.

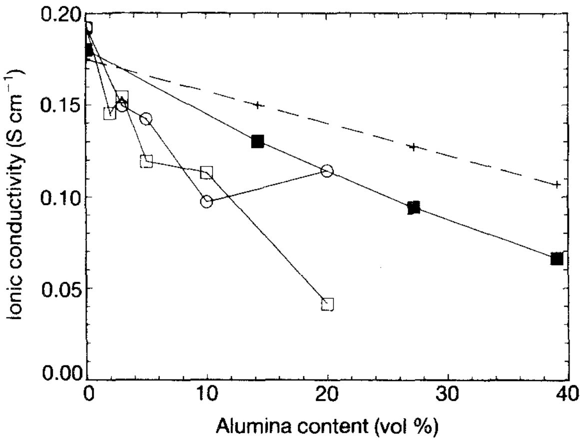

Figure 4 Ionic conductivity at 1000 °C versus volume per cent alumina (○) powder and (□) whiskers, compared with published data. (+) ROM, (■) [13].

The Rule of Mixtures is a theoretical calculation where the ionic conductivity is decreased in proportion to the volume fraction of a non-conducting phase. In this calculation, it is assumed that the samples are 100% dense and the non-conducting phase is only alumina. A possible cause for the decrease in conductivity beyond the Rule of Mixtures is porosity and in the case of the whiskers, silica contamination. For both types of composites, calculations were made to include the porosity as the non-conducting phase with alumina to allow comparison between measured and theoretical conductivities. For the powder-reinforced composite, the corrected values more closely approach the Rule of Mixtures prediction than the whisker composites. However, both were less than the predicted values. The possible causes are unknown at this time.

The ionic conductivity was measured by the complex impedance method with a two-point probe of porous platinum electrodes. For all temperatures, an excitation voltage of 75 mV for the frequency range of 5 Hz to approximately 2 MHz was found to give the best results with a minimum of noise. Shown in Fig. 5 is a typical complex impedance plot measured at 500 °C for the 5 vol% whisker sample (aged for 500 h at 1000 °C). The large arc, going from a resistance of 70 kΩ to the origin, is due to the combination of the bulk resistance arc and the grain-boundary resistance arc.

The ionic conductivity for the powder and whisker composites at 800 and 500 °C are plotted in Figs 6 and 7, respectively. The ionic conductivity is similar for both powder and whisker composites up to 10 vol% alumina for both temperatures. For composites with more than 10 vol% alumina, the whisker sample is noticeably lower in conductivity.

The activation energy, calculated over the range 500–1000 °C, is plotted for all samples in Fig. 8. The activation energy is approximately the same for all samples, except for the 20 vol% whisker sample; the activation energy significantly increased for that sample. It is hypothesized that 2 wt% SiO_2 in the Denka alumina whiskers affected the conductivity

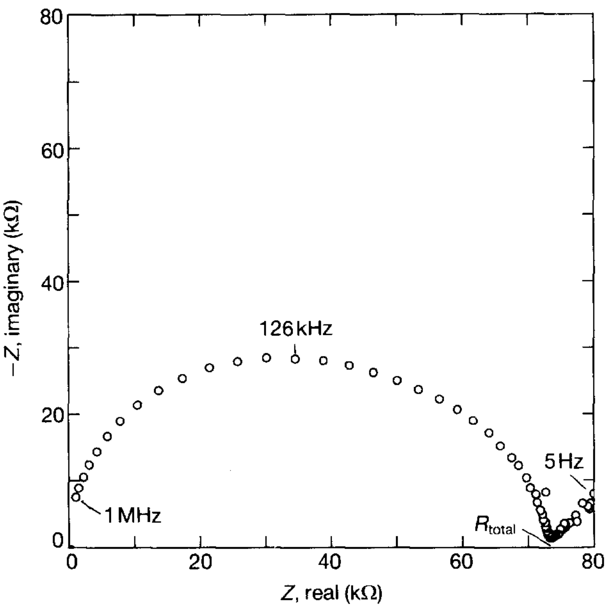

Figure 5 Typical complex impedance plot for the 5 vol% whisker 8YSZ sample measured at 500 °C, aged 500 h at 1000 °C.

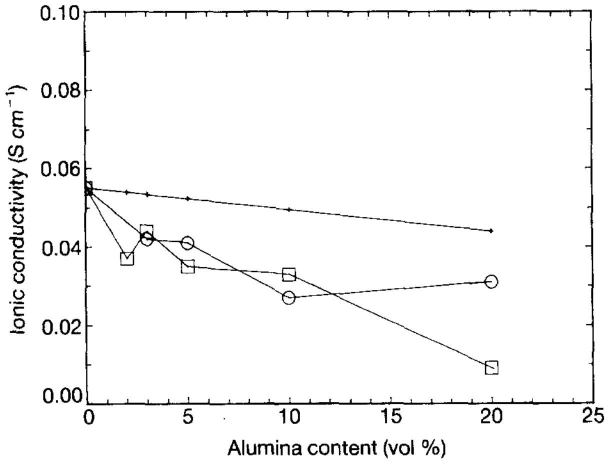

Figure 6 Ionic conductivity at 800 °C versus volume per cent alumina (○) powder and (☐) whiskers. (+) ROM.

when significant amounts of SiO_2 from the whiskers became available.

Several samples were selected to evaluate the effect of the reinforcement on the ageing behaviour of the 8YSZ composite matrix. In Table I, the as-processed ionic conductivity at 1000 °C and activation energy for the 0 and 5 vol% powder samples (both perpendicular and parallel to the tape-cast direction) and 5 vol% whisker samples (both perpendicular and parallel to the tape-cast direction) is shown. After ageing for 500 h at 1000 °C, the activation energy does not significantly change. The ionic conductivity decreased by approximately 25% except for the 5 vol% powder (parallel) and 5 vol% whiskers (perpendicular), which decreased only 6.3% and 14%, respectively. This difference is hypothesized to be due to changes and/or differences in the platinum electrodes and interface during the ageing intervals. The electrodes had to be repainted on a couple of samples owing to degradation during handling and measurement.

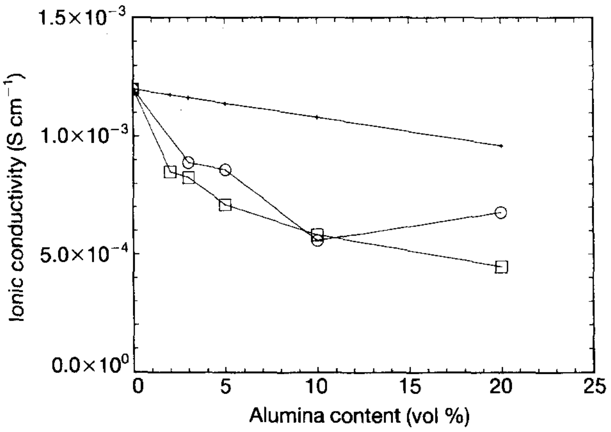

Figure 7 Ionic conductivity at 500 °C versus volume per cent alumina (○) powder and (☐) whiskers. (+) ROM.

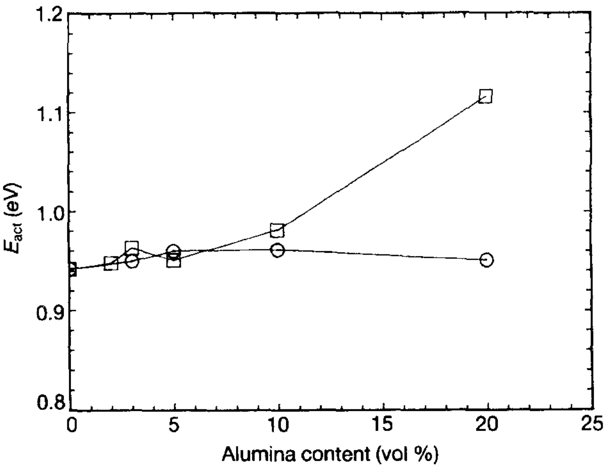

Figure 8 Activation energy for ionic conduction (eV), versus volume per cent alumina (○) powder and (☐) whiskers.

Badwal [16] measured the ionic conductivity at 1000 °C versus time (5000 min) for 8 mol% YSZ and found a 16% decrease in conductivity. The cause of the ageing was postulated by Badwal [16] to be due to either the ordering of the cation/anion sublattices or the decomposition of the metastable phases. Badwal also showed that the composition with the highest conductivity occurs at 8 mol% yttria. According to the zirconia–yttria phase diagrams summarized by Yoshimura [17], the 8 mol% composition occurs either at or inside the cubic_{ss} and cubic_{ss} + tetragonal_{ss} phase boundary at 1000 °C. It was further found by Ciacchi and Badwal [18] that in the ternary system ZrO_2–Y_2O_3–Sc_2O_3, all compositions with less than 8 mol% (Y_2O_3 + Sc_2O_3) showed ageing behaviour. For Y_2O_3-rich compositions, a redistribution of Y_2O_3 and precipitation of the tetragonal phase was found to occur during ageing.

In Fig. 9, the strength of three whisker composites, as measured by four-point bending is plotted versus volume per cent alumina. Also plotted are strength data values for powder composites as measured by Yamamoto *et al.* [13] using three-point bending. As noted by Yamamoto *et al.* [13], there is an increase in strength with increasing powder alumina content up to a maximum of 33 kgf mm^{-2} at 27 vol% (20 wt%) alumina. For the whisker composites, the maximum in

TABLE I Conductivity before and after ageing at 1000 °C for 500 h

	0 vol%	5 vol% powder		5 vol% whisker	
		Perpendicular	Parallel	Perpendicular	Parallel
σ_{1000}					
As-processed	0.192	0.153	0.143	0.114	0.125
Aged	0.144	0.109	0.134	0.098	0.091
Change (%)	– 25.0%	– 28.7%	– 6.29%	– 14.0%	– 27.2%
E_a					
As processed	0.942	0.944	0.951	0.966	0.954
Aged	0.926	0.958	0.953	0.991	0.993
Change (%)	– 1.7%	+ 1.5%	+ 0.2%	+ 2.6%	+ 4.1%

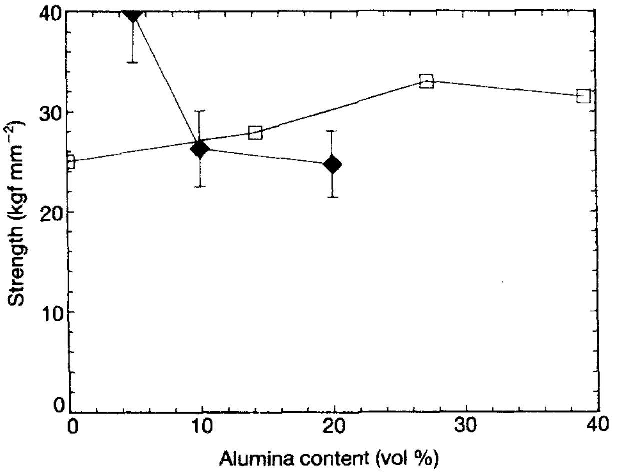

Figure 9 Strength of (◆) alumina whisker-reinforced yttria-stabilized zirconia versus volume per cent alumina, compared with (□) published data [16] for alumina powder-reinforced yttria-stabilized zirconia.

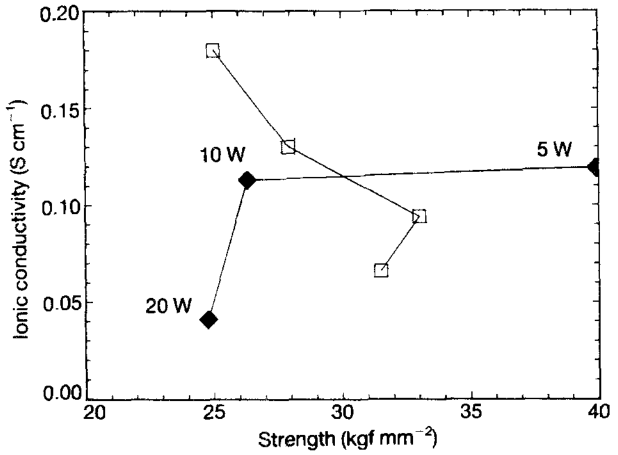

Figure 10 Ionic conductivity at 1000 °C plotted versus strength for (◆) alumina whisker-reinforced yttria-stabilized zirconia. Compared with (□) published data [16] for alumina powder-reinforced yttria-stabilized zirconia.

strength, of 39.9 kgf mm^{-2} occurs at 5 vol% and then decreases with increasing whisker content. This decrease in strength is due to the increasing porosity of the composite with increasing whisker content. What is notable is that with only 64% theoretical density, the 20 vol% whisker composite has approximately the same strength as the 0 vol% material.

To help identify the optimum composition that yields maximum strength with a minimum decrease in conductivities, data from the composites is plotted as ionic conductivity (at 1000 °C) versus strength as shown in Fig. 10. Yamamoto *et al.*'s [13] data show that with increasing alumina content, there is an increase in strength up to the maximum noted at 27 vol% (20 wt%), followed by a decrease. For the whisker composite, the maximum in strength was achieved with 5 vol% whisker followed by a decrease in both strength and conductivity with increasing whisker content. Also notable in Fig. 10 is that with only 5 vol% whiskers, the strength and conductivity is greater than the 27 vol% (20 wt%) powder composite.

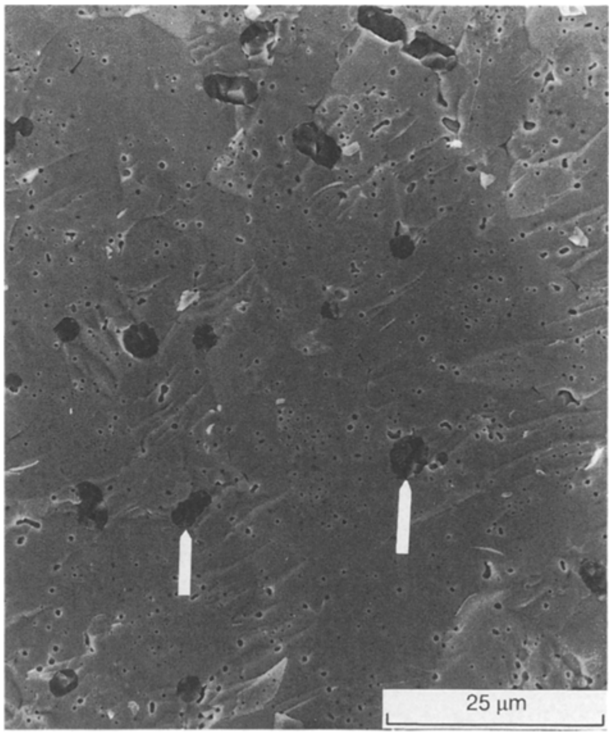

Figure 11 Scanning electron micrograph of a fracture surface of the 5 vol% whisker-reinforced 8YSZ composite. The white arrows indicate typical whiskers in the fracture surface.

A preliminary investigation was conducted by scanning electron microscopy of the fracture surface to ascertain the toughening mechanisms, if any. In Fig. 11, a scanning electron micrograph of a fracture surface of the 5 vol% whisker 8YSZ composite is shown. The fracture surface is perpendicular to the tape-casting direction. It can be noted that the

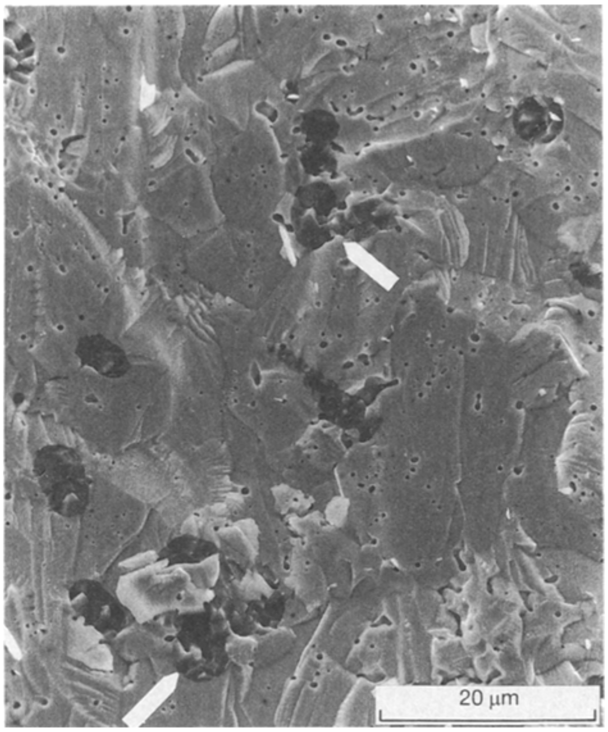

Figure 12 Scanning electron micrograph showing detail of the interaction of whiskers with crack front. Note there is no pull-out of whiskers. The white arrows indicate typical whiskers in the fracture surface.

whiskers (highlighted by an arrow) were well dispersed and oriented by the tape-casting procedure. Also noted is the dispersed porosity in the sample. The fracture-toughening mechanism that was expected and desired is whisker pull-out, because it will provide maximum toughening. As seen in Fig. 11, there is no pull-out. Upon closer examination of the surface, shown in Fig. 12, some interaction is seen to have occurred. The crack-front stress fields interacted with the whiskers as shown by the surface ripples around the fibres (arrow). Further investigations are required.

4. Conclusions

The addition of alumina whiskers to 8YSZ adversely affected the densification where only 64% theoretical density was achieved when 20 vol% whiskers were added. However, an increase in strength occurs with the addition of whiskers. Despite the decrease in density and strength, the 20 vol% whisker composite had a strength equal to that of unreinforced 8YSZ. Evaluation of the fracture surface indicated that there was no pull-out of the whiskers during fracture. Therefore, little toughening can be expected by whisker pull-out. An optimum composition was identified containing 5 vol% whiskers with a maximum in strength and minimum in degradation of properties. The plotting of conductivity versus strength is a good method to help identify optimum compositions. SiO_2 from the whisker reinforcement is hypothesized to cause the increase in activation energy in the whisker composites.

Future work will focus on the improvement of the processing to achieve higher densities which will result in the improvement of the mechanical and electrical properties. Once the processing is improved, an optimum composition needs to be identified which has a strength greater than 400 MPa while retaining a conductivity at 1000 °C greater than $0.15\ S\,cm^{-1}$. There is also a need to reduce the expected problems of SiO_2 from the whiskers used.

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