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SiC and Y_2O_3 co-coated zirconia composites prepared by Y_2O_3 coated ZrO_2 powder

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5 wt% submicron SiC particle reinforced 3 mol% yttria co-coated zirconia composites were prepared using hot pressing. The microstructure and properties of these composites have been investigated. The hot pressing temperature is a major factor that affects their mechanical properties. This can be ascribed to the monoclinic phase content in the composites. The monoclinic phase content increases with a decrease in the sintering temperature due to low yttrium diffusion. This increases the amount of transformation toughening produced by the residual tensile stress in the tetragonal phase. However, this residual tensile stress deteriorates the strength. The fracture is originated by the large cubic grain aggregates. The fine grained microstructure of the composite contributes to the high grain boundary electrical resistance.

1. Introduction

The zirconia–yttria alloy system has excellent mechanical properties, with a strength of up to 2000 MPa and a toughness of up to 20 MPa $m^{1/2}$ [1], however these properties are highly dependent on the yttria content. The best combination of the mechanical properties is obtained for the alloy containing 2–3 mol% yttria, in which a small tetragonal grain structure produces the high strength value whilst the low yttria content results in transformation toughening. However, the tetragonal zirconia polycrystals (TZP) suffer from serious low temperature degradation due to a tetragonal–monoclinic transformation on their surface during ageing. Increasing the yttria content and decreasing the grain size decreases the probability of the tetragonal–monoclinic transformation and thus increases the resistance to ageing. Therefore, 3 mol% yttria ZrO_2 (3Y–TZP) is the most intensively studied Y–TZP ceramic. However, transformation toughening is small for systems with a small grain structure [2].

Second phases such as Al_2O_3 and SiC have been added in order to improve the properties of the materials. The addition of SiC particles increased the room temperature and high temperature mechanical properties [3] due to a microcrack toughening mechanism [4]. The toughness of 3Y–TZP has also been improved with the addition of SiC whiskers due to a crack bridging mechanism [5] and the addition of SiC platelets due to load transfer and crack deflection mechanisms [6]. However, both the toughness and strength values have been reported to decrease with an increasing platelet content in pressureless sintered SiC platelet reinforced 3Y–TZP due to porosity [7]. The addition of Al_2O_3 has increased the toughness [8] and also the ageing resistance [9] of 3Y–TZP. The toughness increment has been observed to be insignificant in the 3Y–TZP matrix composites, and transformation toughening has been reported not to be the major toughening mechanism in the composites.

However, the above phenomena are only observed in TZP prepared from co-precipitated yttria–zirconia powder, in which, the yttria is expected to be uniformly distributed in the zirconia particles. In 3Y–TZP samples prepared from co-coated yttria–zirconia powder, in which the yttria is coated on to nano-sized zirconia particles [10], optimized strength and toughness values can be obtained by controlling the sintering conditions resulting in significant transformation toughening [11]. In addition, the ageing resistance of the material has been reported to be improved by using co-coated powder [12]. Transformation toughening in Al_2O_3 particle reinforced coated Y–TZP has been reported to be significant [13]. In the present study, submicron SiC particles are added to co-coated yttria–zirconia powder in order to prepare 3Y–TZP/5 wt% SiC composites using hot pressing. The microstructures and mechanical properties are examined and then related to the hot pressing conditions. Finally, the impedance characteristics of the composites are examined.

2. Experimental procedure

3 mol% Y_2O_3 co-coated ZrO_2 powder (with an average powder size of 70 nm) was obtained from

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Tioxide Specialities Ltd., UK and as-received α-SiC particles, (A10) from H. C. Stark, Germany and β-SiC particles (less than 1 μm) from Superior Graphite, Chicago IL USA, were used as the starting materials. 5 wt % of SiC particles were mixed with the 3Y–TZP powder matrices by wet-milling and then dried. The composites were fabricated using hot pressing with an induction furnace, in the temperature range of 1300–1550 °C and an applied pressure of 20 MPa.

The densities of the hot pressed discs were measured using the water immersion method. X-ray diffraction was used to examine the crystal phases of the zirconia in the composites, the measurement being performed on polished surfaces. The monoclinic phase content was evaluated from the intensity of the (111) reflection, using the equations given by Toraya *et al.* [14, 15]. The Vickers indentation test was performed using a load of 49N on polished surfaces in order to measure the hardness and indentation toughness. The equation used to calculate the toughness is [16]:

$$K_{IC} = 0.016(E/H_V)^{1/2}P/C^{1.5} \qquad (1)$$

where K_{IC} is the indentation toughness, E the Young's modulus, H_V the Vickers hardness, P the indentation load and C the radius of the indentation radial crack.

The strength of the composites was tested on a Mayes testing machine by three-point bending, the sample size being 1.5 × 2 × 24 mm. The microstructure of the composites was examined by JSM-6310 scanning electron microscopy (SEM) and JEM-2000FX transmission electron microscopy (TEM). The electrical conductivity of the composites in the temperature range of 250–450 °C was measured by a.c. impedance spectroscopy in the frequency range of 0.1 Hz to 1 MHz using a Solatron 1260 frequency response analyser.

3. Results

3.1. Densification and microstructure

Fig. 1 shows the densification as a function of the hot pressing temperature. The solid square is for the β-SiC reinforced composites whilst the solid diamond is for the α-SiC reinforced composites. The composites can be densified at temperatures as low as 1400 °C with no obvious difference in densification behaviour between the α-SiC and β-SiC composites being observed. A reason for the observed low densities in samples sintered at 1300 and 1350 °C is the high monoclinic phase content in these composites. The theoretical density of the composites can be obtained from the expression; $5.83 - 0.23F_m$ (F_m is the monoclinic ZrO_2) content which produces a value of 5.76 g/cm^3 for a sample containing 30 vol % monoclinic phase. Fig. 2 shows the monoclinic phase content on the polished surface in the composites. The monoclinic content decreases with an increase in the sintering temperature with up to 30% of the monoclinic phase being observed in the composites prepared at 1300 and 1350 °C. No cubic phase was detected. The polytype of the second phase (α or β Si) does not have any effect on the monoclinic content. The α-SiC particle reinforced composite, hot pressed at a temperature of 1300 °C, was observed to be spontaneously cracked, from which it can be inferred that the composites has a high monoclinic content. Only small monoclinic phase contents were detected in the co-precipitated 3 mol % Y_2O_3–ZrO_2 matrix composites [3].

The relationship between the monoclinic phase content and hot pressing temperature is attributed to the diffusion of the yttria coated onto the ZrO_2 powder grains. It is expected that little yttrium is diffused into the ZrO_2 at low sintering temperatures and short times (less than 30 min). The grains with a small yttria content are transformed into the monoclinic phase during the cool down from the fabrication temperature, whilst those with a high yttria content stay in the tetragonal phase. As the sintering temperature increases, the diffusion of yttrium into the ZrO_2 particles increases and the monoclinic phase content decreases, since the diffusion rate increases exponentially with temperature. By controlling the hot pressing temperature and time, the monoclinic level in the tetragonal phase can be controlled.

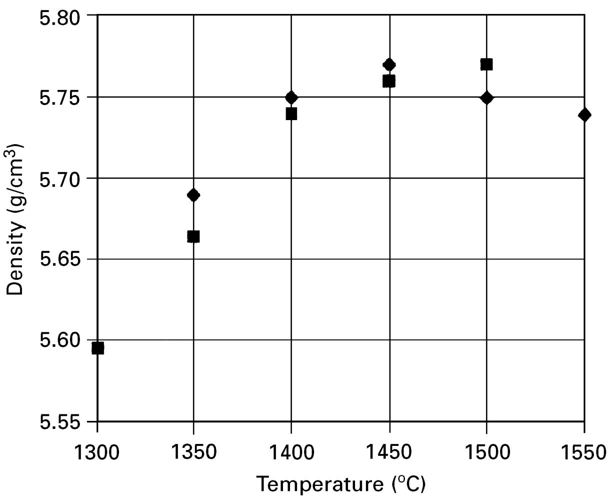

Figure 1 The effect of hot pressing temperature on the densification of the 3Y–TZP/5 wt % SiC composites. Key: (■) β SiC and (◆) α SiC.

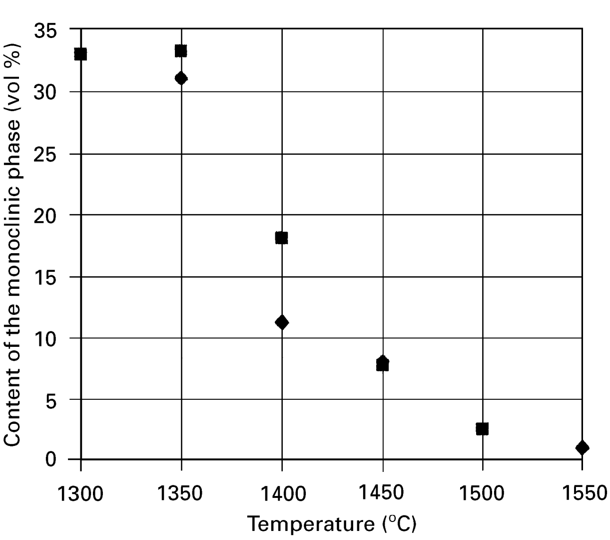

Figure 2 The monoclinic contents of the two 3Y–TZP/5 wt % SiC composites, as a function of hot pressing temperature. Key: (■) β SiC and (◆) α SiC.

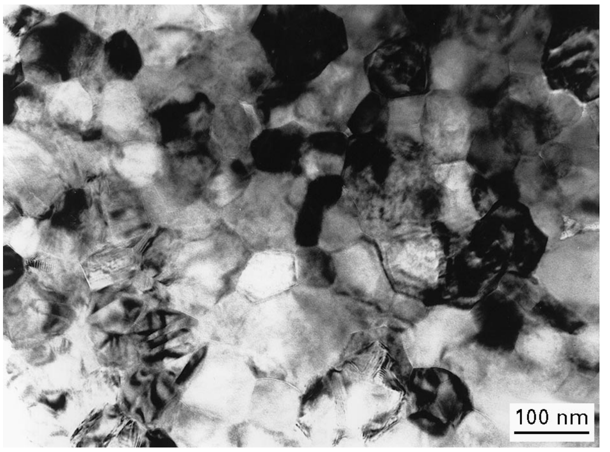

Figure 3 A typical microstructure of the 3Y–TZP/SiC particulate composites.

Fig. 3 shows a typical micrograph of the microstructure of the composites. The ZrO_2 grain size is about 100 nm. Increasing the hot pressing temperature increases the ZrO_2 grain size, from less than 100 nm at a temperature of 1350 °C to 300 nm at a temperature of 1500 °C. Some monoclinic grains are distributed in the tetragonal continuous phase, in the form of a typical twin structure. Some of the monoclinic phase is in the form of a core–shell grain structure, (the outside layer, the shell, of the grains is tetragonal, whilst the core of the grains is monoclinic), which has been previously observed in the 3Y–TZP prepared from the yttria-coated zirconia powder [11, 17]. However, since the zirconia grains hardly grow during the hot-pressing, the corel–shell grain structure in the composites was suppressed.

3.2. Mechanical properties

Fig. 4 shows the Vickers hardness of the composites as a function of the hot pressing temperature. Similarly to the trend of the density and tetragonal content, the hardness increased with increasing the hot pressing temperature. The indentation toughness is shown in Fig. 5. High toughness for the composites were obtained by hot pressing in the temperature range of 1350–1450 °C, the toughness value being similar to that observed in Y–TZP ceramics with a high degree of transformation toughening. As the hot pressing temperature increased to values greater than 1500 °C, the toughness decreased to about 4–5 $\mathrm{MPa\,m^{1/2}}$, a value similar to that observed in TZP materials that do not undergo transformation toughening. These results indicate that high levels of transformation toughening occurred in the composites prepared at temperatures less than 1500 °C, and as the temperature increased to 1500 °C or higher, the transformation toughening dramatically decreased. Fig. 6 shows the strength of the composites which increased with the sintering temperature. The strength of the matrix prepared by pressureless sintering was measured using a bi-axial bending test (ball-on-ring). The measured strength value is 933 MPa for a sintering temperature of 1400 °C and 1008 MPa for 1450 °C. At these sintering conditions, the matrix predominantly consists of

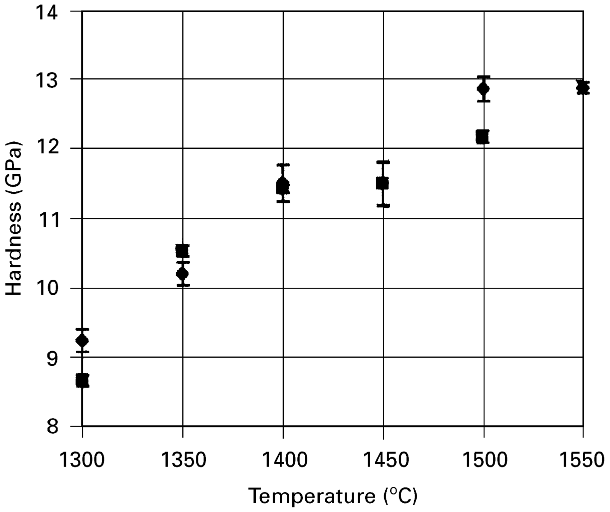

Figure 4 Vickers hardness of the two 3Y–TZP/5 wt % SiC composites, as a function of the hot pressing temperature. Key: (■) β SiC and (◆) α SiC.

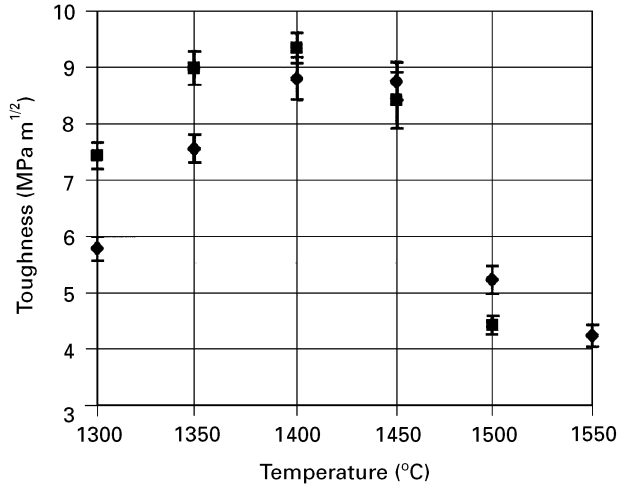

Figure 5 Effect of hot pressing temperature on the fracture toughness of the 3Y–TZP/5 wt % SiC composites. Key: (■) β SiC and (◆) α SiC.

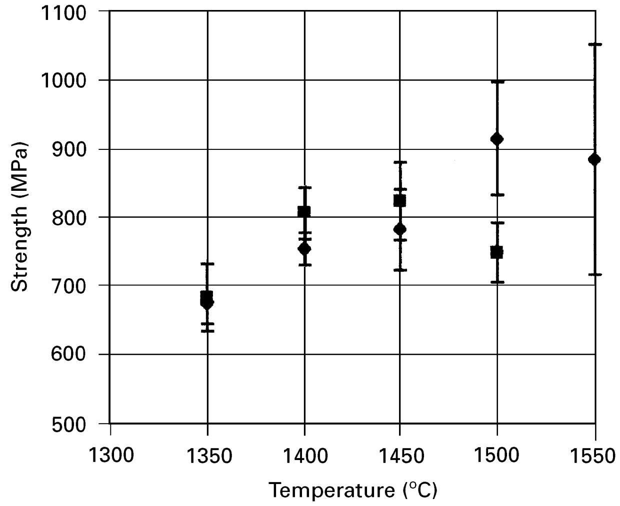

Figure 6 The strength of the two 3Y–TZP/5 wt % SiC composites as a function of the hot pressing temperature. Key: (■) β SiC and (◆) α SiC.

the tetragonal phase. Some differences in strength were observed between the matrix and composites which can be attributed to the following factors: (i) the testing technique, (ii) the residual stress generated by the monoclinic phase and secondary phases and (iii) grain size and cubic phase aggregates which were observed in the materials.

The wear behaviour of the composites has been examined [18]. The experimental results showed that the composites have a very high wear resistance, which can attribute to the very fine and uniform zirconia grains and the homogeneously distributed SiC particles.

The experimental results show that there is no significant difference in the microstructure and mechanical properties of the α-SiC and β-SiC composites.

3.3. Fracture surface observation

The fracture surfaces of the bending-test specimens were examined by SEM, and Fig. 7(a–d) shows some of these observations. The fracture origin can be readily observed on or just beneath the tensile surface. A hemi-spherical zone occurs around the origin, which is about 25–50 μm in depth. The large grain aggregates acting as fracture origins are readily observed in the zones, the grain size being larger than 2–3 μm. The high Si and Ca concentrations that were detected in most of the large grains by energy dispersive X-ray (EDX) spectroscopy, could have come from impurities as well the oxidation of SiC. In the samples prepared at the low hot pressing temperature of 1350 °C, the large grains do not show any obvious differences in their Si and Ca content from that of the normal grains. No large grain aggregates were observed in the fracture zone that forms the origin in the samples hot pressed at 1300 °C.

The fracture origins formed by large grain aggregates have been previously observed in 3Y–TZP samples [19], the large grains probably being the cubic phase. The high Si and/or Ca contents detected on the large grains could be due to an amorphous phase in the grain boundaries of the cubic grains. The large cubic grain aggregates are the weak links that form the fracture origins, due to the elastic and thermal mismatch as with the surrounding tetragonal phase.

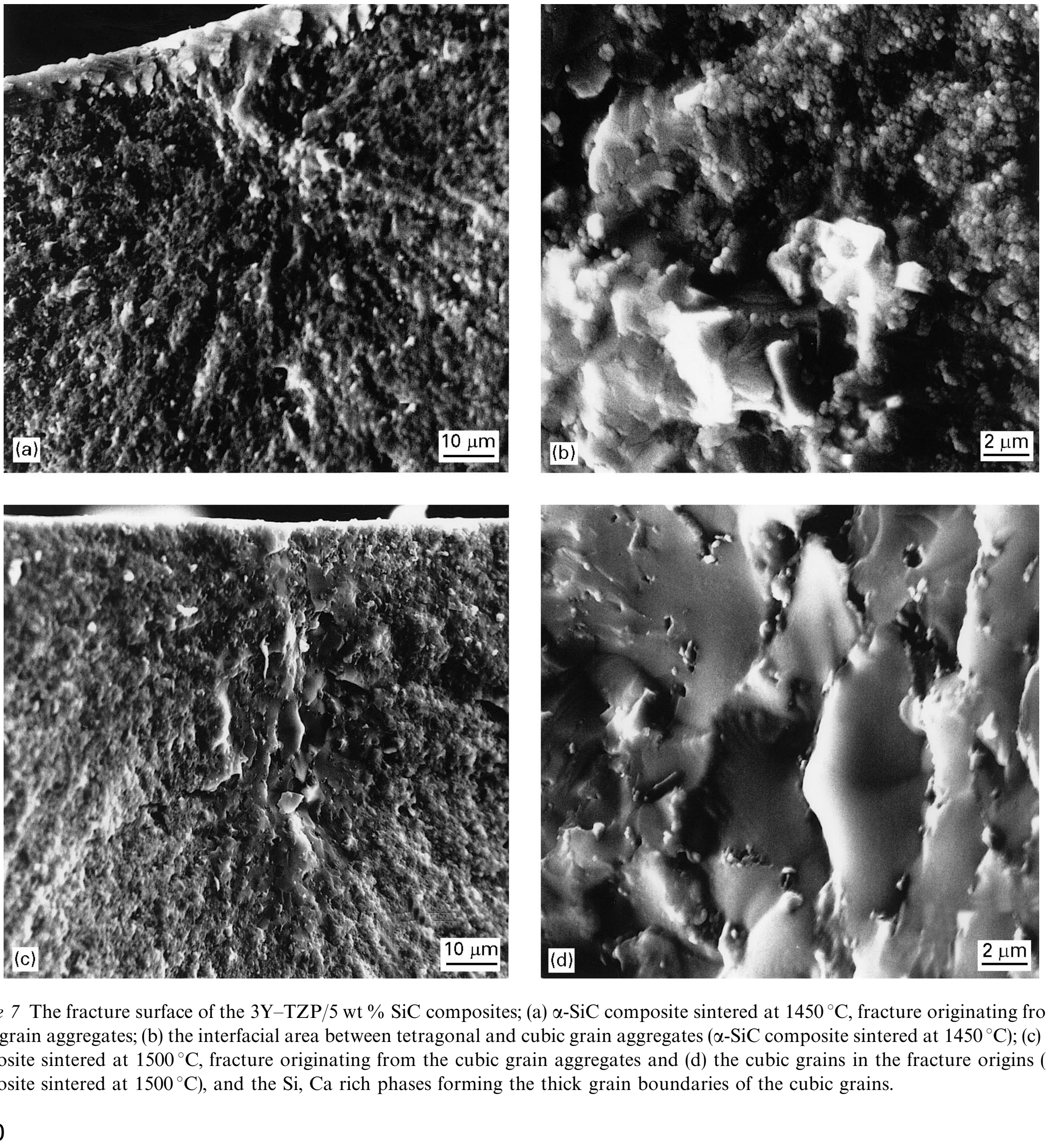

Figure 7 The fracture surface of the 3Y–TZP/5 wt % SiC composites; (a) α-SiC composite sintered at 1450 °C, fracture originating from the cubic grain aggregates; (b) the interfacial area between tetragonal and cubic grain aggregates (α-SiC composite sintered at 1450 °C); (c) β-SiC composite sintered at 1500 °C, fracture originating from the cubic grain aggregates and (d) the cubic grains in the fracture origins (β-SiC composite sintered at 1500 °C), and the Si, Ca rich phases forming the thick grain boundaries of the cubic grains.

3.4. Electrical measurements

Fig. 8(a and b) show the bulk and grain boundary conductivity of the composites as a function of temperature, for comparison purposes the conductivity of the matrix shown in Fig. 8 is also included. The activation energies for the composites are 89.7–92.6 kJ/mol for the grain interior and 110.9–115.7 kJ/mol for the grain boundary which are in an agreement with the activation energies of the matrix materials: grain interior, 92.6 kJ/mol, and grain boundary, 107.1–109.9 kJ/mol, similar to those reported in 3Y–TZP [20, 21]. There is no significant difference in the grain interior conductivity values between the composites and the matrix, but the grain boundary resistance of the composites is more than one order of magnitude higher than that of the matrix. The grain boundary amorphous phase has a high blocking effect on the oxygen diffusion through the grain boundaries [20, 22, 23]. SiO_2, which is the major phase that forms amorphous phases with ZrO_2 and Y_2O_3, was detected on the large grain boundary that forms the fracture origin. The SiO_2 was probably formed by SiC oxidation. However, the grain boundary amorphous phase was not readily observed in the TEM studies. Another contribution to the high grain boundary resistance is the grain size of the ZrO_2, or surface area [20]. The ZrO_2 grain size in the composites is 100 nm, which is much smaller than that in the matrix or other ZrO_2 materials reported in the literature. This can also be confirmed by the decrease in the grain boundary resistance with sintering temperature, that occurred in both the composite and the matrix.

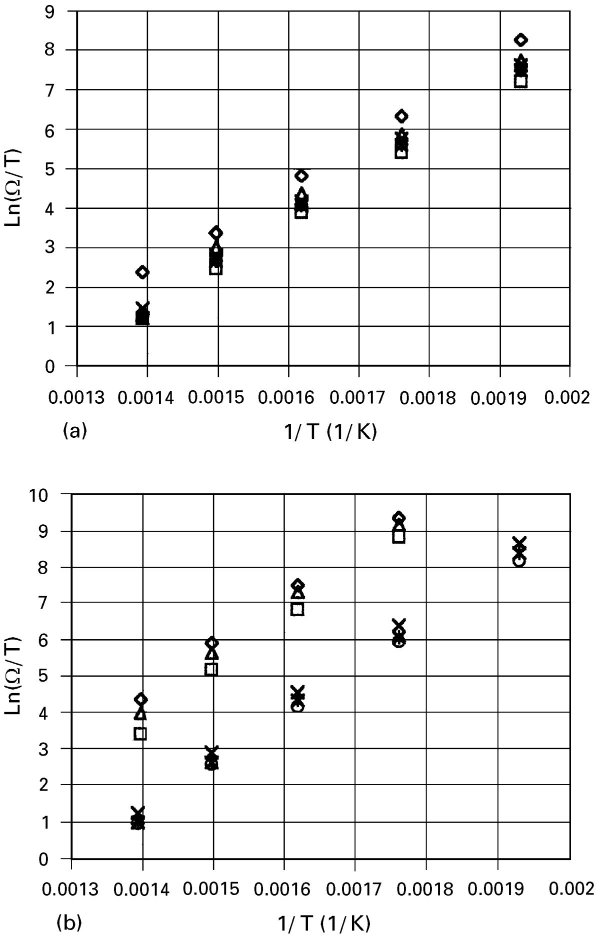

Figure 8 The Arrhenius plots for the (a) grain interior and (b) grain boundary. Key: α-SiC composites hot-pressed at (◇) 1450 °C and (□) 1500 °C, (△) β-SiC composites hot-pressed at 1450 °C. The matrix sintered at (×) 1400 °C, (∗) 1450 °C and (○) 1500 °C.

4. Discussion

In ZrO_2 matrix composites, the toughening mechanisms observed in other particulate composites such as microcracking [4] and crack deflection [6, 8] are also expected to occur in addition to transformation toughening. Previous investigations on the co-precipitated 3Y–TZP powder composites have indicated that the dominant toughening mechanisms are the conventional mechanisms (microcracking, crack deflection). The toughness increment generated, therefore, depends on the grain size and reinforcement contents [24–28]. In the ZrO_2 composites studied in the present work, the SiC particle size is small and the content is low, 5 wt % (8.9 vol %). It is expected that the toughness increment generated by the toughening mechanisms, such as crack deflection and microcracking, is small. In ZrO_2 ceramics, however, the dominant toughening mechanism is transformation toughening which is caused by the stress-induced tetragonal–monoclinic transformation. The transformation toughening is given by [27–29]:

$$\Delta K_{IC} = \alpha E V e^{T} h^{1/2}/(1 - \nu) \quad (2)$$

where E is the Young's modulus, ν is Poisson's ratio e^T is a constrained strain generated due to the structural transformation, with a value of 0.04–0.06. V is the volume fraction of the particles that transform in the zone near the crack tip and α is a constant determined by the nature of the transformation. The transformation zone height h, is given by [30]

$$h = [3^{1/2}(1 + \nu)^2/(12\pi)](K_I/\sigma_m^C)^2 \quad (3)$$

where K_I is the stress intensity factor, and σ_m^C is the critical stress for transformation. The transformation toughening increases with increasing transformation zone height. In other words, the transformation toughening increases with decreasing the critical stress for transformation, σ_m^C. The tensile residual stress is expected to decrease σ_m^C and increase the transformation toughening. Both the SiC particles and the initial monoclinic phases create the residual tensile stress in the tetragonal grains. The residual stress can be evaluated using the Eshelby model [31], as is shown in Fig. 9. The effect of the monoclinic phase on increasing the tensile stress in the tetragonal grains is significant. Hence, a higher monoclinic content results in a low critical stress for transformation and a higher transformation toughening. In addition, the presence of the monoclinic phase will induce the tetragonal–monoclinic transformation due to the residual stress and strain accommodation in the grains in the TZP ceramics. On the other hand, a higher level of the monoclinic phase means a lower tetragonal content, and thus fewer transformable tetragonal grains. Therefore, the fracture toughness of the composites can be explained by the presence of the monoclinic phase and yttria distribution. The high toughness of

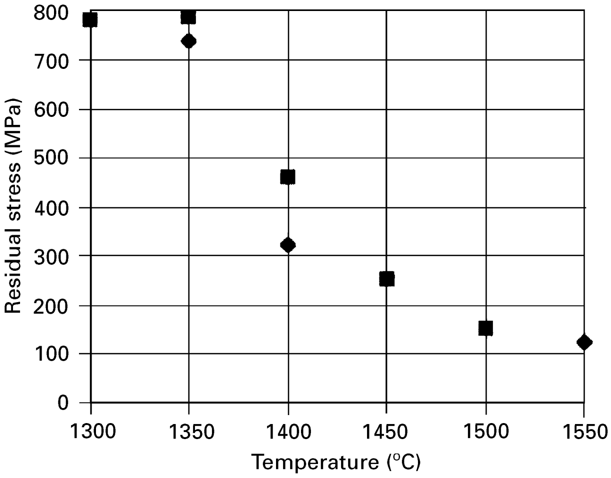

Figure 9 The effect of both the SiC particle and monoclinic contents on the residual stress in the tetragonal grains in 3Y–TZP/SiC composites. (■) β-SiC composite, (◆) α-SiC composite.

the composites sintered at temperatures less than 1450 °C, is a consequence of transformation toughening, due to the high residual stress in the tetragonal phase generated by high monoclinic levels. In addition, the yttria distribution in the zirconia within the composites, sintered at low temperature, is less uniform. Tetragonal grains with a lower yttria content are ready to transform under an applied load. As the hot pressing temperature is increased up to 1500 °C, the yttria distribution in the ZrO_2 grains is more uniform, and the monoclinic content significantly decreased along with the low tensile residual stress in the tetragonal grains. As expected, the degree of transformation toughening was significantly lower. In a discussion of the transformation behaviour using the arguments of yttria distribution and monoclinic content, one would expect that the composites prepared from co-precipitate powder would develop a lower degree of transformation toughening [4–7] than those prepared by coated powder as observed in the present study.

The strength increase in the composites with increasing hot pressing temperature can thus be attributed to a decrease in the monoclinic content, since the residual tensile stress in the dominant tetragonal phase decreases, and the size of microcracks is consequently also decreased.

5. Conclusions

The monoclinic phase is present in the SiC particle reinforced co-coated yttria–zirconia composites. The monoclinic content increases with decreasing the sintering temperature due to the low yttrium diffusion rate. The strength increased with decreasing the monoclinic content.

The toughening mechanisms in the composites are dominated by transformation toughening, but the contribution to the toughness increment decreases significantly for the composites prepared at high temperatures, such as 1500 and 1550 °C.

Fracture of the composites mainly originates from the large cubic zirconia grain aggregates.

The grain interior impedance of the composites is similar to that of the matrix, but the grain boundary impedance of the composites is much higher than that of the matrix.

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