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Ni_3Al intermetallic compound as second phase in Al_2O_3 ceramic composites

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Abstract

Several metals have been proposed as second phases in ceramic matrix composites in order to improve their fracture toughness. Unfortunately, the use of metals is limited by low melting temperature, as for Al and Ag, poor oxidation resistance, as for Ni, Mo and W, and decrease of mechanical strength as temperature increases. In these respects, high temperature structural intermetallics show better properties. This work presents the preparation and the characterization of a Ni_3Al reinforced-alumina. A ceramic composite containing 10 vol% Ni_3Al powder was prepared by hot-pressing at 1350°C for 1.5 h green compacts of the mixture of ceramic and intermetallic powder. Microstuctural features were investigated by scanning electron microscopy (SEM). Elastic modulus, flexural strength and fracture toughness were measured at room and high temperatures and correlated to the microstructural characteristics of the material. A toughening mechanism due to plastic deformation of the intermetallic particles during crack propagation was seen to operate both at room and at high temperature. © 1997 Elsevier Science S.A.

Keywords: Composite; Ni_3Al; Alumina; Strength; Fracture toughness; High-temperature

1. Introduction

One of the most promising approaches for improving the toughness of brittle ceramics involves the incorporation of a ductile phase. The toughening mechanisms actually operating will depend upon the ductile phase morphology. In the case of fibres, foils, etc., crack bridging will most likely occur and the fracture energy is dissipated by the plastic deformation of the ductile phase. Such mechanisms are particularly effective when limited debonding between the brittle matrix and the ductile second phase occurs [1].

For particulate systems the situation is more complex owing to the larger influence of microstructural aspects. Crack bridging can still be an important toughening mechanism. However, partial debonding can be difficult to control and, in general, a strong particle-matrix adhesion is recommended in order to achieve a sufficiently high level of plastic deformation of the ductile dispersion.

Several metallic phases have been considered so far in the attempt of improving toughness of alumina, one of the most popular ceramic material whose widespread use as structural material is limited by unreliable values of fracture toughness and strength. Nickel [2–4], a Ni–Ti alloy [4], iron [5], silver [6], etc., have been used as second phases and have usually provided interesting results in improving room temperature fracture toughness. On the other hand the selection of a metal may present some drawbacks related to a comparatively lower melting temperature, as compared to the ceramic component, poor mechanical properties at intermediate and high temperatures and limited oxidation resistance.

Therefore it is interesting to explore the capabilities offered in this field by suitable intermetallic phases, with better mechanical and surface stability properties. A NiAl powder was incorporated inside an alumina matrix to produce composite compacts having excellent mechanical properties [7]. Another nickel aluminide, i.e. Ni_3Al, is currently under investigation (unpublished). In the present study some microstructural and mechanical aspects of alumina composites with a Ni_3Al dispersion are discussed.

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2. Experimental

2.1. Sample preparation

The starting powders were a commercial alumina powder and an intermetallic atomised powder, kindly made available by Wright and Knibloe (Idaho Nat. Eng. Lab., USA), based on the Ni_3Al phase, having a composition (at%) 73.12Ni–18.82Al–8.06Cr–0.019Mo–0.1B plus traces of S, N and O as impurities. The presence of chromium is mainly meant to improve the mechanical strength, via solid solution strengthening [8], but certainly has also a beneficial effect on the oxidation resistance of the alloy. Boron is a ductilizer, as it segregates along grain boundaries, improves their cohesion and reduces the intergranular fracture propagation mode.

Powder mixtures containing 10 vol% Ni_3Al-base particles were prepared. These were introduced after a preliminary ball-milling process, which deformed the initially spherical grains in order to improve the sintering behaviour of the mixture. Near full density samples were consolidated by hot pressing the powder mixtures for 90 min at 1350°C under a reducing hydrogen atmosphere and with a pressure of 25 MPa.

2.2. Microstructural and mechanical techniques

Specimen bars were obtained from the original hot-pressed disk for the mechanical characterization. Both elastic modulus, E, and strength, σ_f, were measured on a universal mechanical testing machine equipped with a high temperature furnace. Tests were performed in air at temperature up to 1000°C using silicon carbide fixtures. The heating rate was controlled at $\approx 160°C\ min^{-1}$ and sample was tested ≈ 10 min after the selected temperature was reached.

The elastic modulus was measured by four-point bending tests with inner and outer span equal to 20 and 40 mm, respectively. Bars with sizes equal to 45 mm $\times$ 4 mm $\times$ 3 mm were used in these tests. The elastic modulus was evaluated from the deflection of the bar measured by an extensometer. At least four measurements were perfomed at each temperature.

The bending strength was evaluated from three-point bending tests. A span equal to 20 mm was used. Specimen sizes were around 25 mm $\times$ 3 mm $\times$ 2 mm. The prospective tensile face was previously polished and the edges were chamfered using diamond paste up to 3 μm. Four measurements were performed at each temperature.

Fracture toughness, K_c, was measured at room temperature by an indentation technique. Vickers indentations were produced on polished surfaces of the composite using loads of 98 and 294 N. The length of the radial cracks developed from the corner of the indentation site were measured and was calculated on the basis of the formula proposed by Anstis et al. [9]:

$$K_C = 0.016\left(\frac{E}{H}\right)^{0.5}\frac{P}{c^{1.5}} \quad (1)$$

where P is the indentation load, c, the radial crack length and H, the Vickers hardness.

Fracture toughness was also measured at higher temperatures by flexure of notched beams. Through-thickness sharp cracks were introduced in 25 mm $\times$ 3 mm $\times$ 2 mm bars by using the technique presented by Pancheri et al. (unpublished). Crack lengths in the range 1 mm–2 mm were obtained. Notched spacimens were then subjected to three-point bending tests and K_c was evaluated from the maximum load and the crack length by the arguments proposed by Nose and Fujii [10]. At least two measurements were performed at each temperatures.

3. Results and discussion

The elastic modulus as a function of testing temperature is shown in Fig. 1. The elastic modulus is constant for temperatures up to 800°C. It abruptly decreases at higher temperatures. This decrease can be related to the stiffness variation of the intermetallic dispersion with temperature [8]. The experimental value measured at room temperature can be compared with the value which can be calculated on the basis of the elastic moduli of pure polycrystalline Al_2O_3 and Ni_3Al. Values equal to 397 and 179 GPa can be taken for the ceramic and the intermetallic compound, respectively. The calculation can be accomplished by using Voigt and Reuss models which correspond to the upper and lower limit for elastic modulus [11]. The Voigt model (rule of mixtures) furnishes a value of equal to 375 GPa while by the Reuss model a value of 354 GPa can be calculated. The experimental value (337 ± 3 GPa) is slightly lower than the theoretical values. This disagreement can be related to the residual porosity ($\approx 2\%$) present in the hot pressed material. Such porosity results from a minor mismatch in the thermal expansion coefficients (TEC) of the intermetallic and ceramic phases. As a matter of fact, the intermetallic compound has a TEC slightly larger than alumina ($\approx 10.10^{-6}$°C^{-1} for Ni_3Al as compared to $\approx 8.10^{-6}$°C^{-1} for Al_2O_3 [12]). Therefore, tensile stresses are created upon cooling after the hot pressing process. These stresses can promote the formation of microcracks, as shown in the SEM micrograph reported in Fig. 2, and decrease the strength of the interface.

The evolution of the bending strength, σ_f, with temperature is shown in Fig. 3. A different behaviour, as compared to the elastic modulus, is shown by σ_f, which in fact continuously decreases as the testing temperature increases.

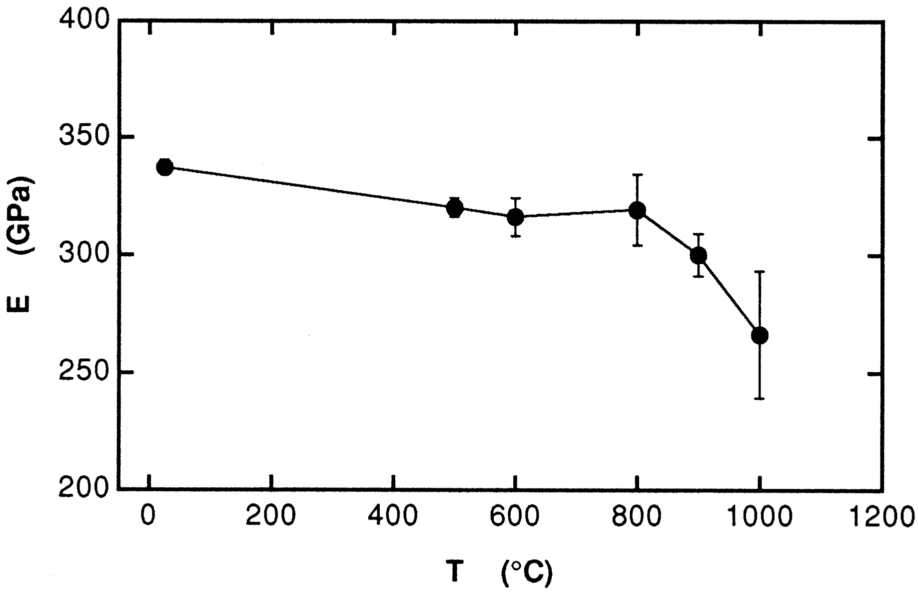

Fig. 1. Evolution of the elastic modulus, E, as a function of the testing temperature.

Eq. (1) was used for the determination of fracture toughness at room temperature by indentation. Vickers hardness was measured to be equal to 15.0 ± 1.2 GPa. This value is lower than the hardness of pure polycrystalline alumina ($\approx 16-18$ GPa) and can be related to the presence of 10 vol% of Ni_3Al whose hardness can be estimated to be equal to 1.8–2.0 GPa as the yield stress of Ni_3Al at room temperature is around 600 MPa [8]. Values of fracture toughness equal to 2.8 ± 0.4 MPa$\sqrt{m}$ and 3.2 ± 0.3 MPa$\sqrt{m}$ were measured at 98 and 294 N, respectively. It must be reminded that fracture toughness measured by indentation is usually considered as the fracture toughness associated to small defects. The artificially high crack opening displacement (COD) values as found in Vickers indentation cracks sometimes prevent the development of the toughening mechanisms [13,14] related to bridging effects between crack faces [15]. In this respect K_c measured by indentation should not be greatly affected by any toughening mechanism [13]. In fact, fracture toughness for pure alumina is around 3 MPa$\sqrt{m}$ [17]. Conversely, K_c values measured by flexure of precracked beams allow to point out the presence of toughening effects. The fracture toughness measured on precracked specimens at various temperatures is shown in Fig. 4. Similar trend is shown by σ_f and K_c as function of testing temperature at least up to 800°C (Figs. 3 and 4).

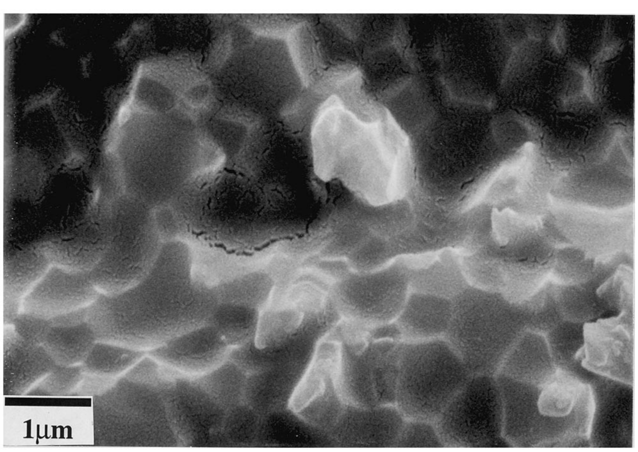

Fig. 2. Secondary electron SEM micrograph showing microcracks at the Al_2O_3 matrix (darker)–Ni_3Al particle (brighter) interface.

At room temperature a fracture toughness value of ≈ 7 MPa$\sqrt{m}$ are obtained. This value is sensibly larger than the results obtained by indentation and more than double with respect to typical K_c values for pure alumina [16,17]. These results reveal the presence of an R-curve effect, i.e. of a strong toughening mechanism which can be associated to the plastic deformation of the intermetallic particles.

The fracture surfaces obtained at room temperature, 600 and 1000°C from the specimens used for K_c and σ_f measurement are shown in Fig. 5. Ni_3Al particles are aligned along a prefential direction, perpendicular to the symmetry axis of the original disk obtained from the hot pressing procedure. Different features are observed at various temperatures. First of all, at increasing testing temperatures a larger number of Ni_3Al particles are pulled-out resulting in a larger number of cavities.

A closer look at the intermetallic second phase shows severe plastic deformation at room temperature (Fig. 6(a)). Ni_3Al particles are stretched to failure by necking to a line. These particles act as plastic bridges [15] during crack propagation and account for the measured relatively high fracture toughness of the composite. The

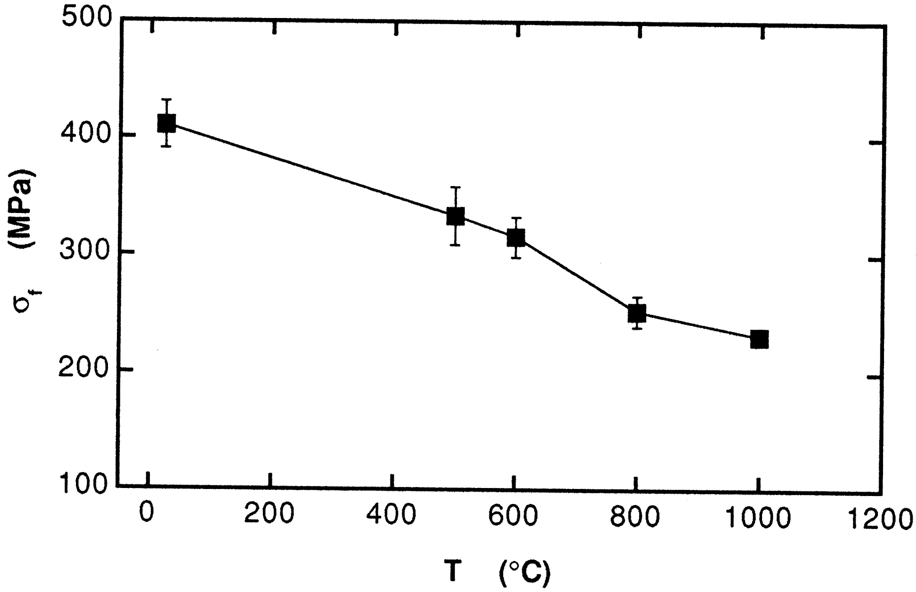

Fig. 3. Evolution of the bending strength, σ_f, as a function of the testing temperature.

observation of fracture surfaces allows point out that this plastic deformation is always accompanied by a clear debonding from the alumina matrix. Plastic deformation is more evident for irregularly shaped particles. When the shape of the intermetallic particles is smooth, fracture becomes brittle and no debonding is observed (Fig. 6(b)). These observations reveal that the mechanical interlocking of the Ni_3Al particles within the alumina matrix represents a stronger effect than the chemical bond between the two phases. Owing to the highly reducing hot-pressing atmosphere, no significant reactions are expected to occur at the metal-ceramic interface, as observed for similar systems, e.g. Al_2O_3-Ni [18], when treated in oxidizing atmospheres. The strength of the interface is also decreased by thermal stresses and microcracks previously discussed (Fig. 2) caused by the difference in the thermal expansion coefficients of the two phases.

At intermediate temperatures, e.g. 500–600°C, the fractured intermetallic particles are considerably deformed. Moreover debonding, determined by the weakening of the mechanical interlocking between particles and ceramic matrix, is present (Fig. 7).

At higher temperature a lower amount of plastic deformation is observed in Ni_3Al particles. Moreover, debonding at the interface can be observed on simply pulled-out particles. Fig. 8 shows detail of the fracture surface of a sample tested at 1000°C. The Ni_3Al particle has kept its original shape and does not appear significantly deformed. This is apparently in contrast with the typical behaviour of Ni_3Al compound at high temperature. This intermetallic compound has a yield strength which is constant up to 700°C and then decreases for higher temperatures. Conversely, the total tensile elongation initially decreases up to 800°C and then increases sensibly for higher temperatures [8]. The results of this work may suggest that the load transfer at the metal-oxide interface decreases as the temperature is increased. Therefore, the toughening effect which is active at room temperature is partially lost at high temperature and this is reflected by the decrease of K_c and the failure stress.

The effect of testing temperature is also important on the fracture morphology of the alumina matrix. At room temperature fracture is mainly transgranular while, at higher temperatures, larger amount of intergranular failure can be detected. Apparently, the addition of Ni_3Al has a significant effect on the alumina grain boundary strength at various temperatures. The strength and fracture toughness of pure polycrystalline alumina is substantially constant for temperatures up to 1000°C and no transition fromtransgranular to intergranular fracture is observed [16]. Conversely, the occurrence of intergranular fracture at high temperature in the composite used in this work is an indication of the reduction of alumina grain boundary strength and fracture energy. This effect contributes to the decreasing of strength shown in Fig. 3.

The toughening effect of the intermetallic phase can be quantified on the basis of the results of previous theoretical analysis [15,17]. When a ductile phase is dispersed within a brittle matrix the toughening increment is proportional to the yield stress σ_y^p, the rupture strain, ε^p, the volume fraction, V^p and the radius, r^p, of the dispersed particles through the relation [17]:

$$\Delta K_c = \sqrt{\alpha E \sigma_y^p \varepsilon^p V^p r^p} \quad (2)$$

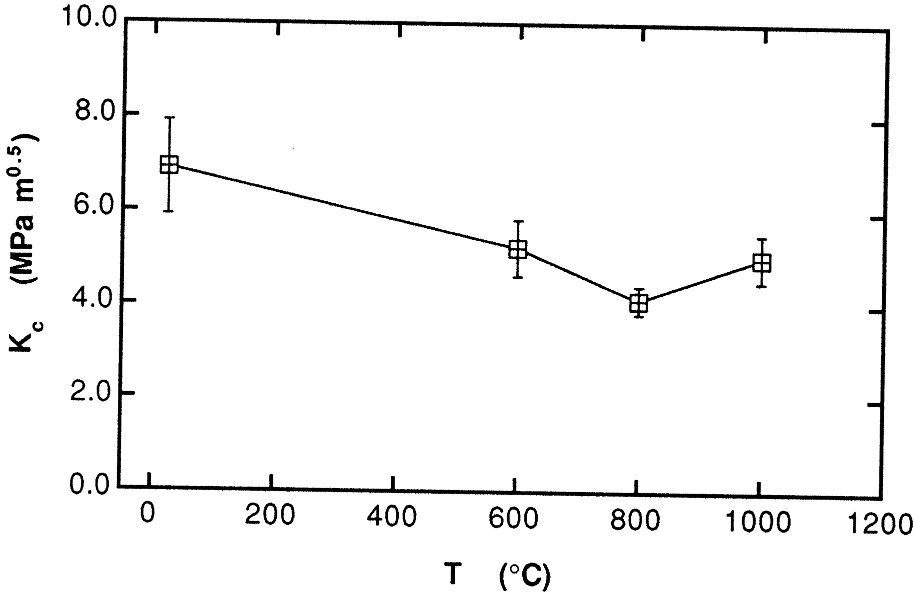

Fig. 4. Fracture toughness, K_c, as a function of the testing temperature.

where E is the elastic modulus of the composite and α is a numerical coefficient (≈ 1) depending on the mode of particle detachment from the matrix, the work hardening rate, etc. [15,17]. Substituting the values corresponding to the composite considered in this work in Eq. (2) ($\sigma_y^p \approx 600$ MPa [8], $\varepsilon^p \approx 0.4$ [8], $V^p \approx 0.1$, $r^p \approx 20$ μm, $E \approx 340$ GPa) the toughening increment at room temperature is equal to ≈ 13 MPa$\sqrt{\text{m}}$. This value is larger than the measured fracture toughness. Nevertheless, from SEM observation it can be estimated that about one third only of the intermetallic particles undergo plastic deformation and, therefore, participate to the toughening process (Fig. 5(a)). Therefore, the value for V^p should be corrected accordingly. The toughening increment, ΔK_c, becomes ≈ 6 MPa$\sqrt{\text{m}}$ and the total fracture toughness is ≈ 9 MPa$\sqrt{\text{m}}$ which is in good agreement with measured K_c values. The presence of residual stresses, the irregular shape of the Ni_3Al particles and the imperfect load transfer between the particles and the matrix can account for the discrepancy between calculated and measured fracture toughness values.

At higher temperatures the toughening effect depends strongly on the yielding and rupture behaviour of the Ni_3Al particles. The decrease of the fracture toughness, as well as that of failure stress, is smooth up to 600°C. Then, both K_c and σ_f show a marked drop between 600 and 800°C. This behaviour can be correlated to the marked decrease of yield stress shown by Ni_3Al in this temperature range [8]. σ_y^p is equal to ≈ 600 MPa and ≈ 400 MPa at 600 and 800°C, respectively, while no evident variations are detected for ε^p. In addition, the decrease of K_c can be also influenced by the fracture behaviour of the alumina matrix as already pointed out. At 1000°C the rupture strain of the intermetallic phase sensibly increases (≈ 1) [8] and this can account for the slight increase of K_c between 800 and 1000°C. Correspondingly, the bending strength remains almost constant in this temperature range (Fig. 3).

These observation allow to point out that a strong toughening effect has been achieved by adding the Ni_3Al particles to the alumina matrix. Though a chemical bond has not been fully developed between the two phases, the interlocking effect of the intermetallic particles correlated to their irregular shape is sufficient for the development of toughening mechanisms by plastic deformation of the second phase. Due to the pure mechanical nature of the interaction between Ni_3Al particles and alumina, the toughening effect decreases at 800°C, even though the experimental K_c value still remains larger than typical values for fine grained-alumina. The possibility of introducing an intermediate connecting phase between the matrix and the particles certainly would allow to obtain larger K_c values both at room and at high temperature.

4. Conclusions

An alumina matrix composite containing 10 vol% Ni_3Al base alloy powder was prepared by hot-pressing. Elastic modulus, flexural strength and fracture toughness were measured over a temperature interval ranging from 25 to 1000°C. Flexural strength is only slightly affected by the temperature up to 600°C as a consequence of the toughening effect of the metallic particulate. A good mechanical interlocking between the matrix and the intermetallic phase, which allows load transfer and plastic deformation of the metal, is the dominant mechanism at this stage. At higher temperatures a softening of the metallic component occurs and

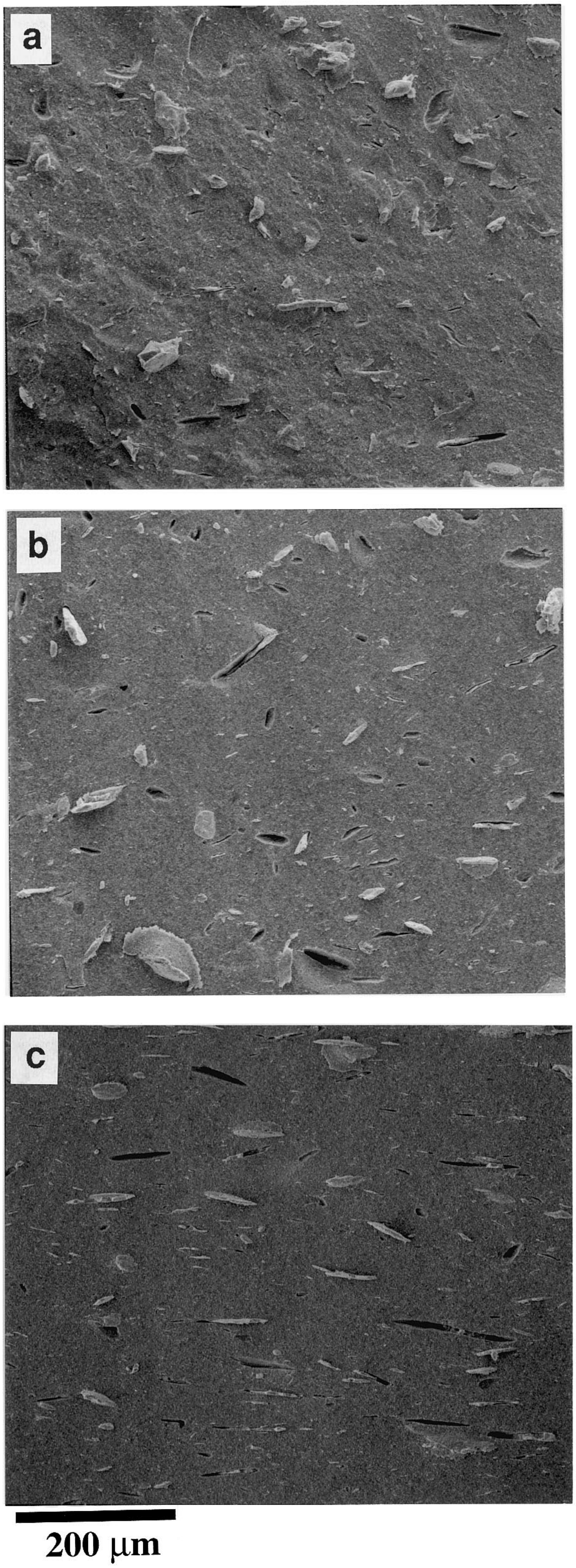

Fig. 5. Secondary electron SEM micrographs showing fracture surfaces of the samples tested at: (a) room temperature; (b) 600°C; and (c) 1000°C.

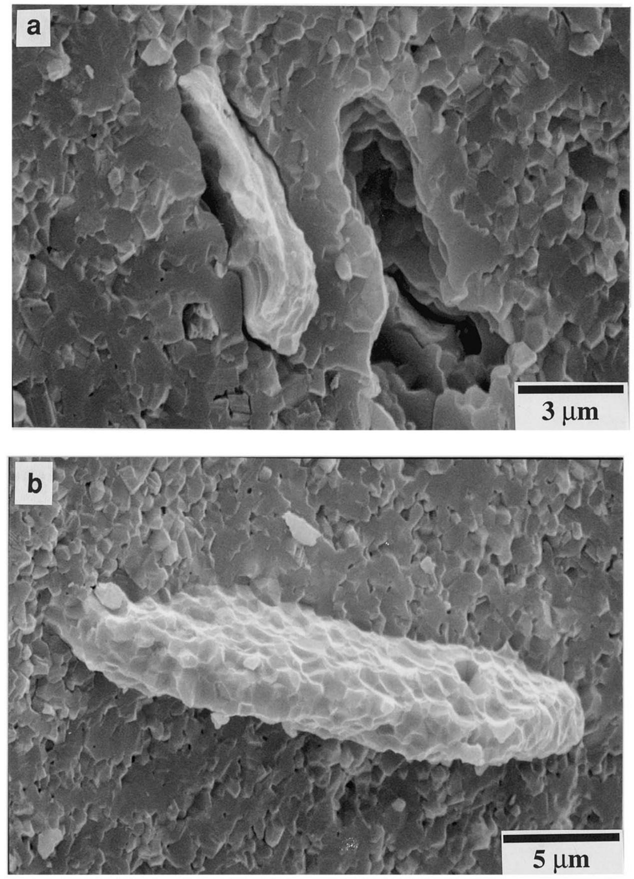

Fig. 6. Secondary electron SEM micrographs showing details of the fracture surface of the specimen tested at room temperature. (a) Irregurarly shaped particle which undergoes heavy plastic deformation. An empty site is also visible. (b) Debonded particle featuring a smooth surface on which the traces of the matrix grains are visible.

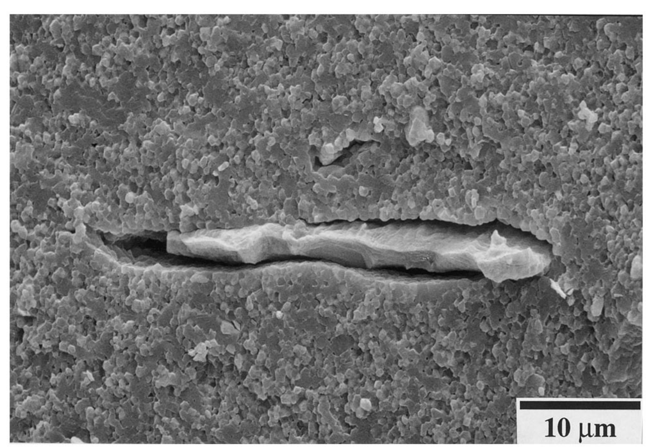

Fig. 7. Secondary electron SEM micrograph showing the fracture surface of the sample tested at 500°C. The intermetallic particle is consistently plastically deformed to fracture.

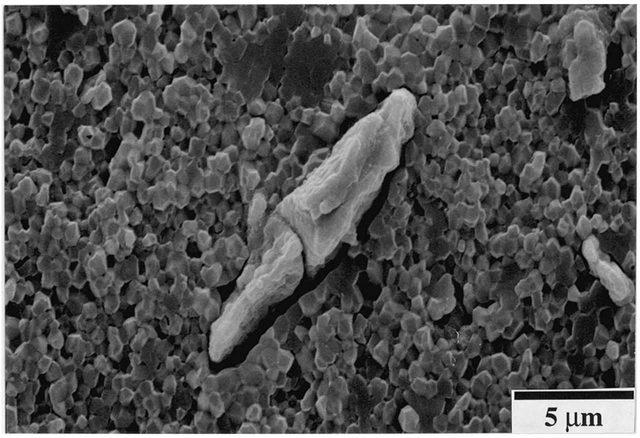

Fig. 8. Secondary electron SEM micrograph showing the fracture surface of the sample tested at 1000°C.

this reduces the adhesion strength between matrix and particles. Correspondingly a reduction in the fracture toughness is also observed. However K_c still remains at higher values than those typically measured for pure alumina.

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