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The Toughening of Alumina with Nickel Inclusions

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Abstract

Brittle solids can be toughened by the introduction of ductile metallic inclusions. In the present study, the mechanical properties and oxidation resistance of Al_2O_3/Ni composites are investigated. The oxidation resistance of the ceramic/metal composite ($8 \times 10^{-11}\ g^2\ cm^{-4}\ s^{-1}$ at 1300°C) is comparable to that of many silicon nitrides. The fracture toughness of the composite containing 13 vol.% nickel is twice that of alumina alone. The square of the toughness enhancement for composites containing various amounts of nickel exhibits a linear relationship with the product of volume fraction and inclusion size, as predicted in theoretical models. For the alumina/nickel composite system, it is demonstrated that dissolved oxygen in the nickel increases the yield strength of nickel and enhances the toughness of the composite.

Die Zähigkeit spröder Materialien kann durch den Zusatz einer duktilen metallischen Phase gesteigert werden. In dieser Arbeit wurden die mechanischen Eigenschaften und die Oxidationsbeständigkeit von Al_2O_3/Ni Verbundwerkstoffen untersucht. Die Oxidationsbeständigkeit des Keramik/Metall Verbundwerkstoffs ($8 \times 10^{-11}\ g^2\ cm^{-4}\ s^{-1}$ bei 1300°C) ist mit der vieler Siliziumnitride vergleichbar. Die Bruchzähigkeit des Verbundwerkstoffs mit 13 vol.% Nickel ist doppelt so hoch wie die des reinen Aluminiumoxids. Das Quadrat der Zähigkeitssteigerung für Zusammensetzungen mit verschiedenen Nickelgehalten hängt, wie es von theoretischen Modellen vorhergesagt wird, von dem Produkt aus Volumenanteil und Partikelgröße linear ab. Am System der Al_2O_3/Ni Verbundwerkstoffe wird gezeigt, daß im Nickel gelöster Sauerstoff die Streckgrenze von Nickel und die Zähigkeit des Verbundwerkstoffs erhöht.

On peut augmenter la ténacité des solides fragiles par l'ajout d'inclusions métalliques ductiles. On a étudié ici les propriétés mécaniques et la résistance à l'oxydation de composites Al_2O_3/Ni. La résistance à l'oxydation de ce composite céramique/métal ($8 \times 10^{-11}\ g^2\ cm^{-4}\ s^{-1}$ à 1300°C) est comparable à celle de nombreux nitrures de silicium. La ténacité du composite contenant 13% en volume de nickel est le double de celle de l'alumine seule. Le carré de l'accroissement de ténacité pour les composites de teneurs diverses en nickel est une fonction linéaire du produit de la fraction volumique par la taille des inclusions, comme l'annoncent les modèles théoriques. On démontre que, pour le système composite alumine/nickel, l'oxygène dissous dans le nickel augmente la limite apparente d'élasticité de celui-ci et améliore la ténacité du composite.

1 Introduction

Ceramics are superior in their hardness, their chemical stability, and their refractory character. However, the application of ceramics as engineering parts is handicapped by their brittleness. A major research objective has therefore been to improve their toughness. The addition of second phase inclusions which influence the propagation of cracks has been one much-studied approach. Inclusions which produce transformation toughening or toughening by microcracking have brought dramatic benefits.[1] Ceramic inclusions whose strength is higher than that of the ceramic matrix have been

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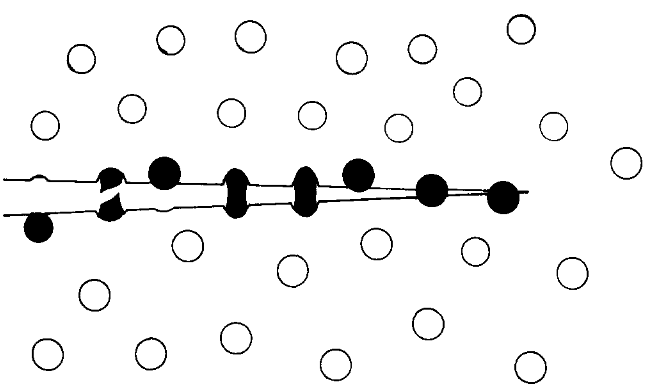
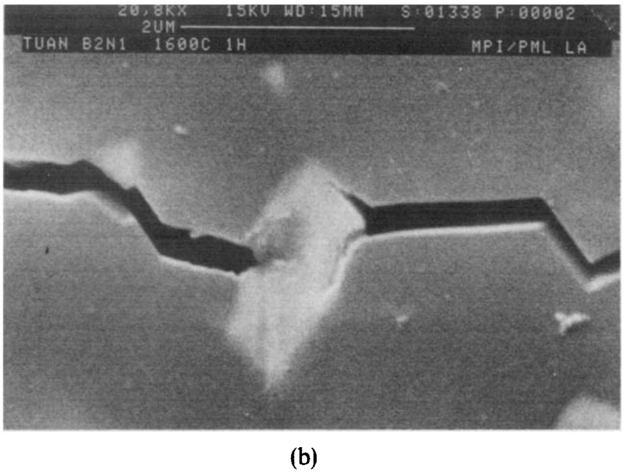
used as reinforcements; for example, SiC whiskers in an alumina matrix,[2] or SiC whiskers in a Si_3N_4 matrix,[3] have been found to bring benefits, although considerable difficultires can be imposed by the processing of such whisker composites.

Al_2O_3/Al composites have been developed using directed oxidation of aluminium alloy in air;[4] during the process, the aluminium alloy is not fully oxidized and residual aluminium inclusions are present. The toughness of the composites is 2·8 times that of alumina alone.[5] The toughening of ceramics with metallic inclusions thus provides a clear direction for research activity.

The toughening mechanism believed to be effective in ceramic/metal composites is the plastic stretching of metallic inclusions bridging the growing crack;[6,7] as the crack reaches the ceramic/metal interface, the difference in the deformation ability between the ductile particle and the brittle matrix causes the crack to be blunted locally; the crack segments are forced to circumvent the particle and the crack is thus bridged by the stretched particles (Fig. 1). The plastic deformation of the ductile particles contributes to the toughness enhancement of the composite. Two conditions have to be fulfilled in order for the plastic deformation to be fully exploited: firstly, to ensure that the crack is attracted by the metallic particle, the elastic modulus of the metal should be lower than that of the ceramic matrix; secondly, the metallic particles need to be firmly bonded to the brittle matrix which means that they should be kept below the critical size at which thermal mismatch stresses become sufficient to induce cracks.[8]



(a)



(b)

Fig. 1. (a) For particles, as opposed to fibres, the possibility exists for the crack to run around the inclusion. A certain fraction of the particles is therefore relatively undisturbed by the fracture process. (b) Bridging nickel particles observed in the Al_2O_3/Ni composites. Note the debonding at the interface.

The metallic inclusion is constrained by the brittle and rigid matrix and it has been found that the deformation behaviour of constrained particles is quite different from that of unconstrained ones.[6] As far as the bonding between the ceramic and metal is concerned, if the particle is weakly bonded to the matrix, the crack will propagate along the interface and the contribution from the ductility to the toughness will be negligible. If the bonding between the ceramic and metal is very strong, the deformation will be confined to the ligament between the crack surfaces, i.e. the effective 'gauge length' (the part which can be deformed freely) is not the whole particle but that part lying between the crack surfaces. Short gauge lengths result in limited toughness increase. For bonding with intermediate bonding strength, a fraction of the interface is debonded as the crack reaches the interface and the effective gauge length is thereby increased with improvement in the toughness.

The toughness increase of the composite results from the work of fracture of the metallic inclusions. This work of fracture is the product of the flow stress, σ, and flow strain, u, of the constrained particles, namely[6]

$$\Delta G = F\int_0^{u^*} \sigma(u)\,\mathrm{d}u \tag{1}$$

where F is the volume fraction of the metallic particles (equivalent to the area fraction on the crack plane) and u^* is the effective gauge length.

Scaling the flow stress with the yield stress, σ_Y, of the inclusion and scaling the effective gauge length with the size of the metal particle, d, (particle extension is related to size if all particles show identical fracture strain)

$$\Delta G = CF\sigma_Y d \tag{2}$$

where C is a constant which depends on the interfacial strength. As discussed, intermediate interfacial strength is to be preferred.[6] For glass/lead-filament composites, the values of C have been found to vary from 1 to 6. For particulate composites, the toughness increase, ΔK_{IC}, is then related to the volume fraction, elastic modulus (E), yield strength, and size of the metallic particles as

$$\Delta K_{IC} = (SCFE\sigma_Y d)^{1/2} \quad (3)$$

where S is the fraction of the particles lying adjacent to the crack which are active in the toughening mechanism (Fig. 1).

The interfacial strength depends strongly on the processing conditions.[9] In the present study, particulate composites consisting of an alumina matrix and nickel inclusions have been investigated. The composites are prepared by a selective reduction process. The mechanical properties and oxidation resistance of the composites are reported.

2 Experimental

Alumina (AKP-30, mean size 0·45 μm, Sumitomo Chem Co. Ltd, Tokyo, Japan) and 0–50 wt% nickel oxide (Alfa product, 16·5 μm, Johnson Matthey Co., Danvers, USA) were attrition-milled together for 4 h in isopropanol with alumina balls as grinding media. The slurry of the powder mixtures was dried in an oven at 70°C for three days. The dried lumps were crushed and passed through a plastic sieve (0·112 mm aperture size). The particle size distribution of the powders was measured before and after milling (Granulometer HR 850, Cila-Alcatel Co., France). Powder pellets, 2 cm in diameter and 0·4–0·5 cm in height, were formed by cold isostatic pressing at 200 MPa. The green compacts had 55% relative density as prepared using a theoretical density for alumina of 3980 kg m^{-3}, for nickel oxide of 6800 kg m^{-3}, and for nickel of 8880 kg m^{-3}. The sintering was performed in a box furnace at temperatures between 1400°C and 1700°C for 1 h. The heating and cooling rates were 5°C min^{-1}. A graphite powder bed surrounded the powder compacts; this generated a reducing atmosphere ($P_{O_2} = 10^{-16}$ atm at 1400°C, $P_{O_2} = 10^{-15}$ atm at 1700°C)[10] at the sintering temperatures used. Alumina was stable in this atmosphere; nickel oxide was reduced to nickel.

Several nickel oxide pellets, about 0·4 cm in diameter and 0·2 cm in height, were also prepared. Nickel spheres were obtained after reduction at 1500–1700°C for 1 h. The oxygen content of these nickel spheres was determined by IR spectrometry (TC-436, LECO Co., Michigan, USA).

The final density was determined by Archimedes' principle. Before submerging the specimen in water, a wax was applied to the surface to prevent water penetration. Phase identification was performed by X-ray powder diffractometry with CuKα radiation. The powder was obtained by crushing the fired specimens with a tungsten carbide lined shatter-box. Mechanical failure characteristics in the composites were investigated by examining indentation induced cracks by scanning electron microscopy (SEM). The polished surfaces were prepared by cutting the samples along the axial direction of the discs and polishing with diamond paste to 1 μm. The size of the nickel inclusions was determined using the linear intercept technique on micrographs taken from the polished sections. Indentation was performed on a Zwick microhardness tester with a Vickers diamond indenter and a 50N load, the relationship proposed by Lawn *et al.*[11] being used to calculate values of K_{IC}. The measurement of hardness and fracture toughness was only performed on specimens with relative density above 94%. Oxidation testing of the composites was conducted in a tube furnace in air; the composites used contained 15 and 30 wt% nickel oxide originally, and had been subsequently sintered at 1700°C for 1 h. No special treatment was given to the surface of the specimens prior to the oxidation test.

3 Results

The mean particle size of the powder mixtures of alumina and nickel oxide after attrition milling is below 0·5 μm. The X-ray results show that trace amounts of nickel oxide can still be detected in composites sintered at 1400°C. For the specimens sintered at 1500–1700°C, only alumina and nickel are detected. The oxygen content and hardness of the nickel spheres obtained by reducing NiO pellets at 1600 and 1700°C for 1 h are shown in Table 1. The values reported in Table 1 are the average values for three measurements.

The relative density of the composites sintered at 1600°C and 1700°C is shown as a function of nickel content in Fig. 2, and the inclusion size of nickel in the composites as a function of the amount of nickel in Fig. 3. Typical microstructures obtained by the

Table 1. The oxygen content and the hardness of nickel spheres obtained by reducing nickel oxide powder compacts in carbon monoxide

Reducing conditions	*Oxygen content (ppm)*	*Hardness (MPa)*
1600°C/1 h	185	770
1700°C/1 h	232	960

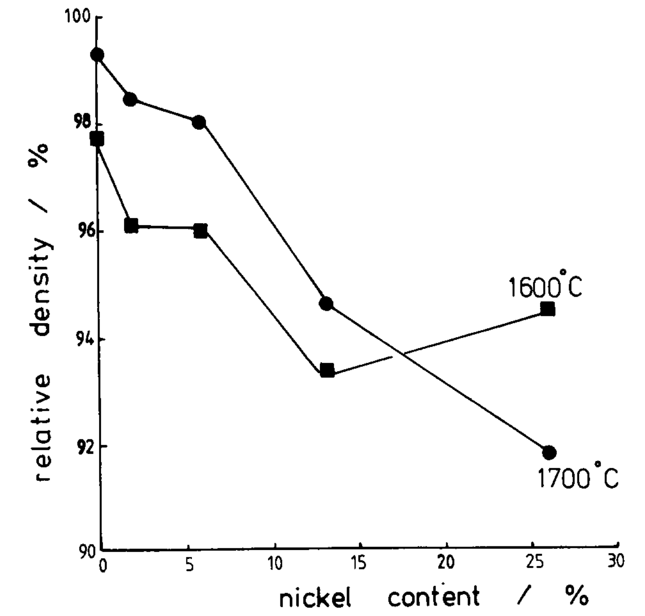


Fig. 2. The density of the composites as a function of nickel content with the samples sintered at the indicated temperatures for 1 h.

process are shown in Fig. 4(a)–(c). The composites contain 2, 6 and 13 vol.% nickel, respectively. All composites in the figure were sintered at 1700°C for 1 h. The nickel particles are well distributed within the alumina matrix. The hardness and the fracture toughness of the composites are shown as a function of nickel content in Figs 5 and 6, respectively. The hardness is decreased by an increase in the nickel content, but the fracture toughness is seen to increase. Cracks induced by indentation are also shown in the microstructures in Fig. 4.

The square of the weight gain per unit area of exposed surface in composites containing 6 and 13 vol.% nickel is shown as a function of the

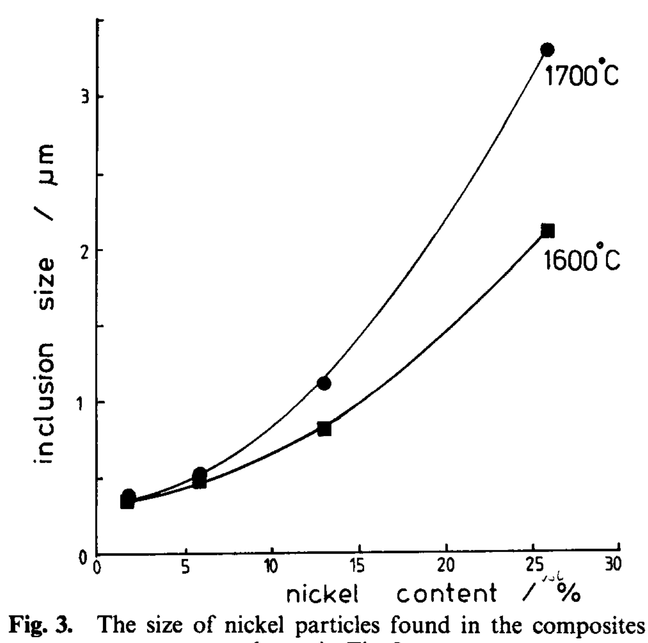


Fig. 3. The size of nickel particles found in the composites shown in Fig. 2.

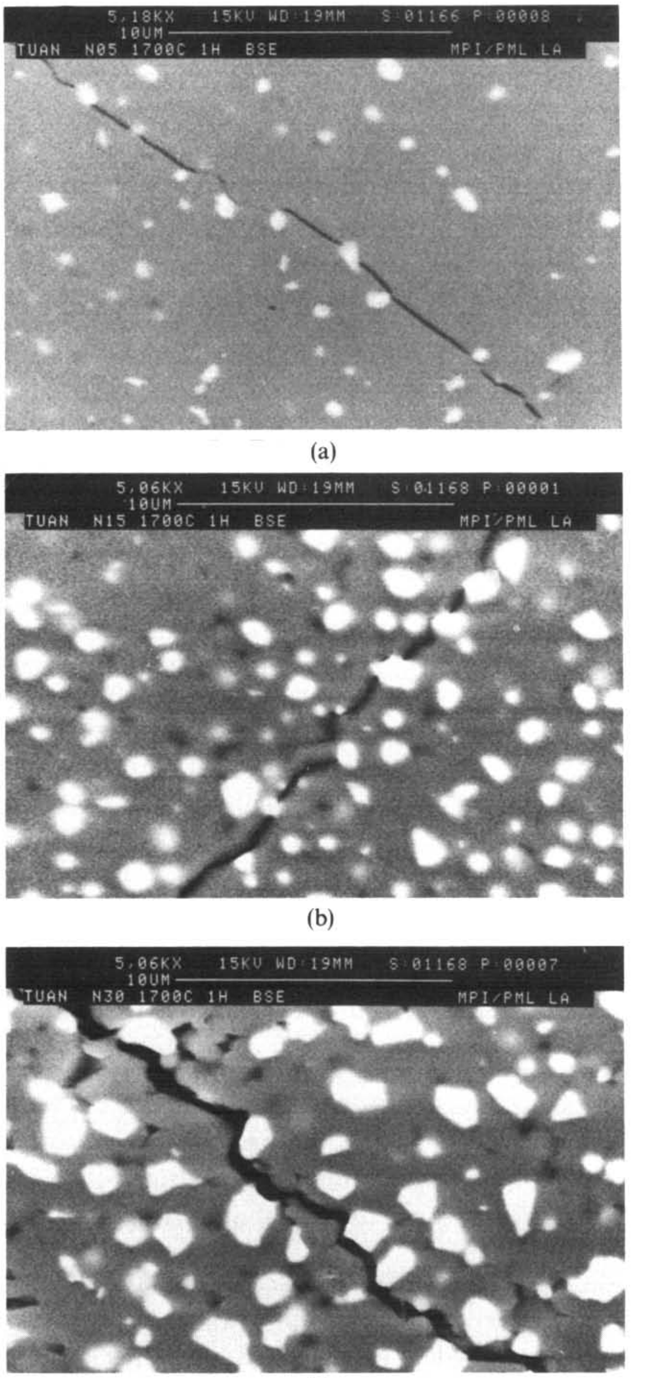


Fig. 4. Typical microstructures of Al_2O_3/Ni composites. The vol% of nickel in the composites shown is (a) 2, (b) 6, (c) 13. The composites are sintered at 1700°C for 1 h and the cracks introduced by indentation.

oxidation temperature in Fig. 7. The composites were heated in air at the indicated temperatures for 72 h. The square of the weight gain per unit area of the composites is shown as a function of time at 1200°C in Fig. 8. A fracture surface of the specimen oxidized at 1300°C for 72 h is shown in Fig. 9. The X-ray results show that the dense layer formed on the surface of the oxidized specimen is composed of nickel aluminate spinel.

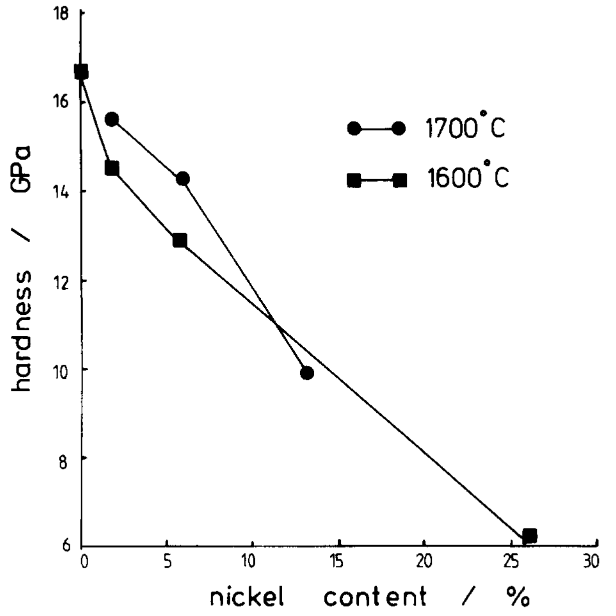


Fig. 5. The hardness of the composites in Fig. 2 as a function of nickel content.

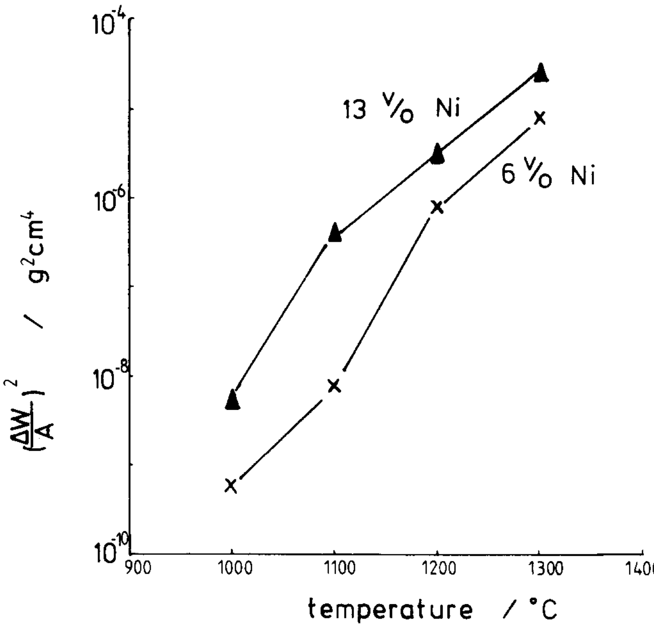


Fig. 7. The square of the weight gain per unit area of the composites containing 6 and 13 vol% nickel as a function of oxidation temperature. The samples were oxidized at the indicated temperatures for 72 h. W is the weight of the sample with exposed area A.

4 Discussion

The melting point of nickel is 1453°C. Reduction of nickel oxide to nickel is accelerated above this temperature. With the sintering atmosphere used, nickel oxide can be fully reduced to nickel above 1500°C in a 1-h heat treatment with samples of the size used in this work.

Attrition milling is a powerful method to comminute ceramic particles. The nickel oxide is milled from 16·5 μm to below 0·5 μm. Composites initially containing such fine nickel oxide inclusions can be sintered pressurelessly to above 90% of the theoretical density.

The thermal expansion coefficient of nickel (15 MK^{-1}) is higher than that of alumina (9 MK^{-1}). A radial tensile stress is therefore induced due to the thermal expansion mismatch at the interface during the cooling process. This tensile stress may generate circumferential cracks when the nickel particle size exceeds a critical value.[8] However, for the composites prepared by the selective reduction process,

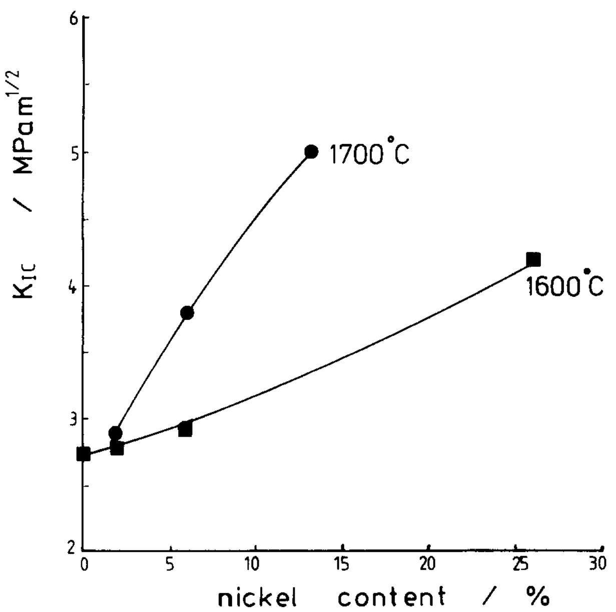


Fig. 6. The fracture toughness determined by the indentation technique for the composites shown in Fig. 2 as a function of nickel content.

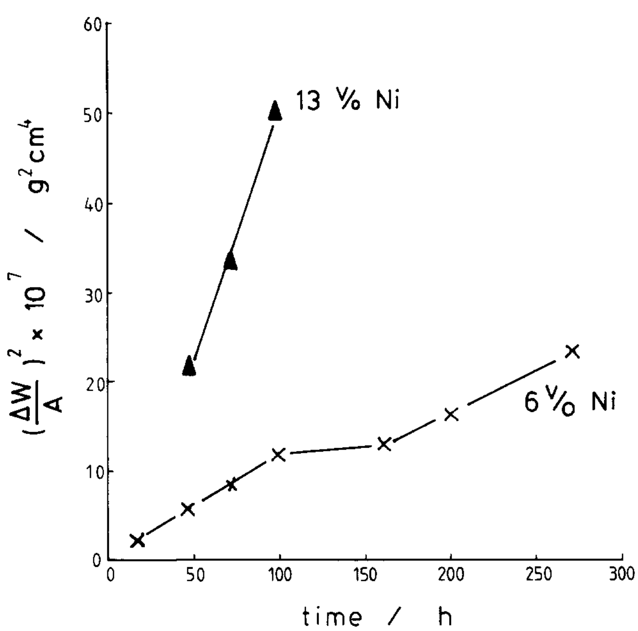


Fig. 8. The square of the weight gain per unit area for composites containing 6 and 13 vol% nickel as a function of oxidation time at 1200°C.

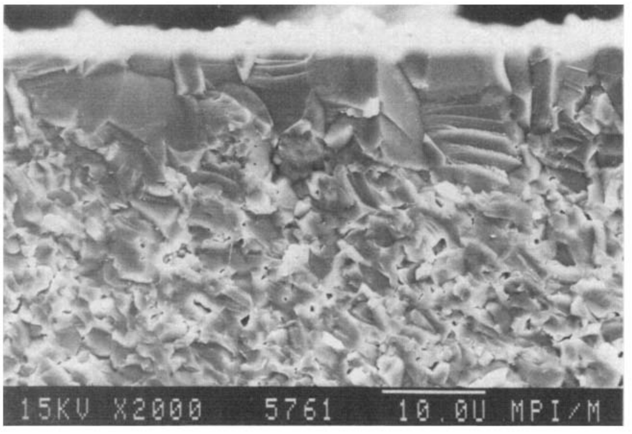


Fig. 9. The fracture surface of an oxidized composite containing 13 vol% nickel. The sample was oxidized at 1300°C for 72 h.

no circumferential cracks around inclusions could be observed. The nickel particles were seen to be firmly bonded to the matrix.

In is interesting to assess the oxidation resistance of the composites by making a comparison with the behaviour of typical silicon nitride materials prepared by hot-pressing; depending on additives, values for the oxidation rate constant lie between 10^{-10} and $10^{-12}\,g^2\,cm^{-4}\,s^{-1}$ for 1320–1400°C.[12] For the present composites containing 13 vol% nickel, the value at 1300°C is $8 \times 10^{-11}\,g^2\,cm^{-4}\,s^{-1}$. Some silicon nitrides show much higher values. The weight gain of the composites is in the same order as that of a high-purity reaction sintered silicon nitride.[13] There is a reduced rate of weight gain for the composite exposed in air at 1200°C which occurs at about 100 h (Fig. 8); this coincides with the formation of the dense layer of nickel aluminate spinel.

The hardness of the composites decreases with increasing nickel content, in part due to the softer character of the nickel particles and in part due to the lower density of samples with higher nickel content (Fig. 10).

From microstructural observation of the interactions between the crack and the nickel particles,

Table 2. The frequency of the active particles (those stretched or divided by the crack) found along the length of cracks induced by indentation in the Al_2O_3/Ni composites

Composition (vol. % Ni)	*Frequency (%)*	*Number of particles counted*
2^a	31	137
6^a	31	218
2^b	27	88
6^b	33	151
13^b	37	190

^{a} 1600°C/1 h.
^{b} 1700°C/1 h.

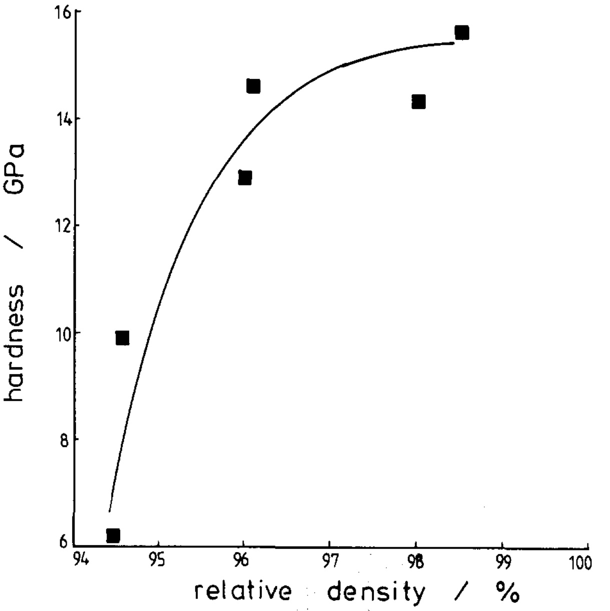


Fig. 10. The hardness as a function of relative density.

the crack may either propagate along the interface, or bypass the bridging particle (Fig. 4). It is found (Table 2) that the fraction of plastically deformed particles remains constant for all processing conditions, allowing the experimental results to be compared with the theoretical predictions. According to eqn (3), the toughness increase is porportional to the square root of the product of volume fraction and inclusion size.[6] The experimental results for Al_2O_3/Ni composites are compiled in Fig. 11. When the composites are sintered at the same temperature, the expected linear relationship is indeed found.

Figure 11 shows that the slope for the composites sintered at 1700°C is three times that of the

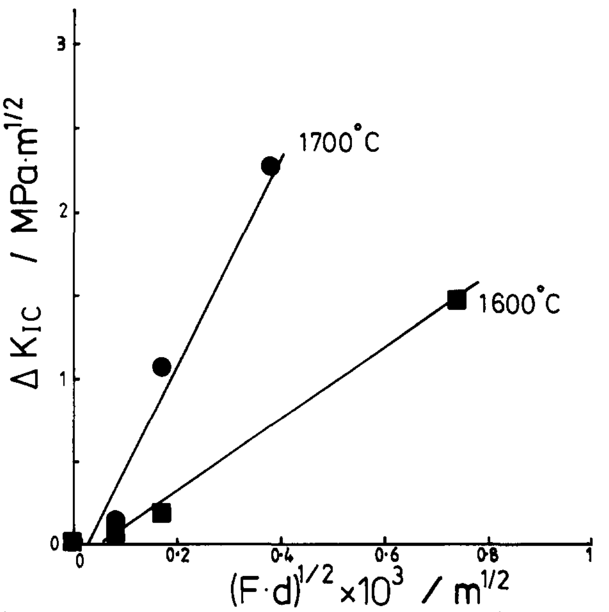


Fig. 11. The fracture toughness increase as a function the square root of the product of volume fraction and inclusion size. The sintering temperatures are indicated.

composites sintered at 1600°C, indicating that the value of ($SCE\sigma_Y$) is increased nine times. From Table 2, S is found to be relatively constant with a value of 1/3. The higher processing temperature results in higher oxygen solubility in the nickel, which in turn increases the hardness (Table 1). By estimating that the yield strength of the nickel is one-third of the hardness,[14] and that the elastic modulus is relatively unaffected by the dissolved oxygen (E = 200 GPa),[15] the value of C for the composites sintered at 1600°C is found to be 0·24 and that for the composites sintered at 1700°C 1·8. This reflects an apparent influence of dissolved oxygen on the bonding strength between the particles and the matrix.

The formation of an interfacial phase between alumina and nickel depends on the oxygen content of the nickel.[16] When the oxygen content of nickel is higher than some 200 ppm, nickel aluminate spinel is formed between nickel and alumina. At lower oxygen contents, no interfacial phase is formed. The interfacial strength is expected to depend on the phase formed at the interface. For the sintering and reduction conditions used in the present study, higher processing temperature results in a higher oxygen content in the nickel; a beneficial interface is found to result. For the glass/lead composite,[6] no interfacial phase is formed for the preparation conditions used.

5 Conclusions

Alumina/nickel composites are prepared by a selective reduction process in which powder mixtures of alumina and nickel oxide are reduced selectively to alumina and nickel. The nickel oxide particles are below 0·5 μm in size, and the resulting nickel inclusions in the alumina matrix do not induce circumferential cracks. The composites can be sintered to above 90% without external pressure. The oxidation resistance of the Al_2O_3/Ni composites is comparable to that of typical hot-pressed silicon nitrides.

The toughness of composites containing 13 vol.% nickel and sintered at 1700°C for 1 h is twice that of alumina alone. Strained nickel particles are observed in the polished section, suggesting a toughening mechanism involving plastic deformation of the metal particles. The experimental results for the toughness increase are consistent with the theoretical predictions of Ashby *et al.*[6] Guidelines for manufacturing ceramic/metal composites suggested by the present study include:

(1) The benefit, as in the model, of large volume fraction and large particle size (but small enough to retain coherence with the matrix);
(2) the benefit of solutes in the metal capable of raising the yield strength;
(3) the benefit of solutes in the metal capable of influencing the bonding with the matrix.

For alumina/nickel composites, improved interface strength is found at higher oxygen content in the nickel inclusions; this can be achieved by processing based on the sintering and reduction of composite nickel oxide–alumina powders.

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