Journal of the European Ceramic Society **11** (1993) 487–496

Alumina Ceramics with Particle Inclusions

Thommy Ekström

Department of Inorganic Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden

(Received 20 May 1992; revised version received 23 September 1992; accepted 20 November 1992)

Abstract

Alumina composites have been prepared with particle inclusions of 0–30 wt% titanium carbonitride and/or 0–5 wt% nickel, or nickel plus molybdenum metal. The metal was added in three different ways; as metal powder, as metal oxide, or as the intermetallic compound Ti_2Ni. Pressureless sintering at 1750°C gave densities varying from 90% of theoretical density to full density. All materials were post-HIPed to full density at 1600°C before measurement of mechanical properties. Addition of metal alone increased the fracture toughness from 3·0 to 3·7 MPa m$^{1/2}$, but decreased the Vickers hardness, HV 10, from 1650 to 1500. The simultaneous addition of hard titanium carbonitride inclusions compensated for the decrease in hardness and gave a further increase in fracture toughness. The alumina composites with 5 wt% metal and 30 wt% Ti(C,N) inclusions had a hardness of 1800 and a fracture toughness of about 5 MPa m$^{1/2}$.

Aluminiumoxid-Verbunde mit einem Anteil teilchenförmiger Einschlüsse von 0–30 Gew.% Titankarbonitrid und/oder 0–5 Gew.% Nickel oder einer Mischung von Nickel und Molybdän wurden hergestellt. Das Metall wurde in drei verschiedenen Formen zugegeben: als Metallpulver, als Metalloxid oder vorlegiert, als intermetallische Verbindung Ti_2Ni. Druckloses Sintern bei 1750°C führte zu Dichten oberhalb 90% der theoretischen Dichte. Alle Materialien wurden anschließend durch HIP'en bei 1600°C vollständig verdichtet, bevor ihre mechanischen Eigenschaften bestimmt wurden. Der Zusatz von Metall bewirkt eine Zunahme der Bruchzähigkeit von 3·0 auf 3·7 MPa m$^{1/2}$, senkt allerdings die Vickershärte (HV 10) des Materials von 1650 auf 1500 herab. Die gleichzeitige Zugabe von harten Titankarbonitrid Einschlüssen kompensiert die Abnahme der Härte und führt zu einer weiteren Erhöhung der Bruchzähigkeit. Aluminiumoxid-Verbunde mit 5 Gew.% Metall-Zusatz und 30 Gew.% Ti(C,N) Einschlüssen zeigen eine Härte von 1800 und eine Bruchzähigkeit von etwa 5 MPa m$^{1/2}$.

Des composites alumineux ont été préparés par dispersion de 0 à 30% en poids de carbonitrure de titane et/ou 0 à 5% de nickel, ou de nickel avec du molybdène. Ce métal a été additionné de 3 façons différentes, sous forme de poudre métallique, d'oxyde ou de composé intermétallique Ti_2Ni. Le frittage naturel à 1750°C permet d'obtenir des densités variant de 90 à 100% de la densité théorique. Tous les matériaux ont été postfrittés sous pression isostatique (HIP) à 1600°C, avant d'être testés mécaniquement. L'addition de métal seul permet d'accroître le facteur critique d'intensité de contrainte de 3·0 à 3·7 MPa m$^{1/2}$, mais conduit à une diminution de la dureté Vickers (HV 10), de 1650 à 1500. L'addition simultanée de carbonitrure de titane compense la diminution de dureté et conduit à une augmentation de la ténacité. Les composites contenant 5% en poids de métal et 30% de Ti(C,N) présentent une dureté de 1800 et une ténacité d'environ 5 MPa m$^{1/2}$.

1 Introduction

The field of ceramics is vast and varied, but alumina can be considered a typical representative of the engineering ceramics group. This class of materials is intended to serve as structural parts subjected to mechanical stress and in most cases also high temperatures. The commercial use of alumina ceramics goes back to the beginning of this century, but it is mainly during the last twenty years that the technical and economic importance of high performance alumina has grown. The utility of a ceramic material in an engineering application is, however, critically determined by its mechanical behaviour, and alumina ceramics are probably among the most

Journal of the European Ceramic Society 0955-2219/93/$6.00

extensively studied engineering ceramics. Both its favourable and unfavourable properties are well known, and the most important of the latter is its brittle fracture behaviour, depending on the absence of plastic deformation at low or medium temperatures.

Many efforts have been made to increase the reliability of alumina ceramics by increasing the strength, increasing the fracture toughness or decreasing the flaw size; these parameters being related to each other by the well-known Griffith equation. A number of methods are in use, but this paper will concentrate on the toughening of alumina by secondary phases, both metallic and ceramic, which essentially serve to impede the propagation of crack fronts. Early experiments and models related the increase in fracture toughness to size, shape and concentration of secondary phase particles.[1-4] Plastic stretching of metal inclusions that bridge the growing crack is also an effective toughening mechanism.[5,6] Among the first metallic dispersions used in alumina were molybdenum particles[1,2] and molybdenum wires,[7,8] and especially in the latter case a strong positive effect was noted. Other popular metallic dispersions have been nickel,[9-12] nickel–zirconium alloys,[13] chromium,[14] and Al_2O_3–Al composites prepared by oxidation of aluminium alloys.[15] Ceramic dispersions in alumina have also been studied, and one composite that has gained commercial use as a metal-cutting tool material is Al_2O_3–TiC, where the effect on the fracture toughness has been reported to be positive, but fairly small.[16-18]

Alumina ceramics are normally manufactured from oxide powder mixtures that can in most cases be sintered in air. In alumina composites, where metal and/or metal carbide/nitride dispersions are wanted, the sintering atmosphere has to be controlled. Metals can be added directly to alumina and sintered in an inert atmosphere or added as metal oxides and subsequently reduced during the sintering process. Similarly, metal carbides/nitrides can be directly mixed with alumina or formed by 'reaction sintering'. The latter technique can be exemplified by (TiO_2 + AlN) mixtures forming (Al_2O_3 + TiN) during sintering or an intermetallic compound like $NiAl_3$ intermixed with alumina, which selectively oxidizes to (Al_2O_3 + Ni).[9]

In a recent study of alumina with nickel inclusions, it was shown that the fracture toughness is twice of that alumina alone for a composite with 13 vol.% Ni.[11,12] The hardness, however, was found to decrease fairly drastically from about 16 to 10 GPa with increasing nickel content. This decrease was attributed in part to the softer character of the nickel particles and in part to the low density of the Ni-containing material (about 95% of theoretical density). The study by Tuan & Brook,[11] however, clearly demonstrated the toughness enhancement obtainable in carefully prepared alumina composites with metal inclusions.

In the present study, alumina ceramics with particle inclusions comprising both metals and hard titanium carbonitrides have been investigated. The purpose of using a hard particulate phase is both to improve the toughness somewhat and, especially in combination with the metal inclusions, to compensate for otherwise occurring drop in hardness. The alumina composites were prepared by the well-known technique of adding metal or metal oxide powders, or with the new concept of 'reaction sintering' from Ti_2Ni. The densification, microstructure and mechanical properties results will now be reported.

2 Experimental

The selected compositions for this study have Al_2O_3 as the parent, with additions of 0, 2·5 and 5 wt% of a metal inclusion and additional amounts of 0, 15 and 30 wt% of titanium carbonitride. The metal was pure nickel or a '70/30 nickel–molybdenum alloy' made from Ni + Mo metal added in the ratio 70/30. The metal was added in three different ways to the alumina ceramics. In one series the metal was added as a fine-grained metal powder and milled with the other powder components before sintering. The second series contained metal added as nickel oxide (NiO) or molybdenum oxide (MoO_3), which was reduced with hydrogen gas in the initial stage of the sintering. Finally, the nickel was added in the form of the intermetallic compound Ti_2Ni which was 'reaction sintered' in nitrogen gas to form nickel metal and titanium nitride. When appropriate, molybdenum metal was added simultaneously with Ti_2Ni. The titanium carbonitride was formed from TiN and TiC powders added in the ratio 70/30. All additives used were of analytical purity and were mixed with aluminium oxide (Alcoa, grade A16SG). The alumina starting material used was found by sediograph measurements to be mainly submicron-sized, with $d_{50} = 0{\cdot}8\ \mu m$. The oxide additives MoO_3 and NiO, the metal additives Mo and Ni and TiC and TiN have d_{50} values 10, 8, 9, 14, 15 and 13 μm, respectively.

The starting powders were carefully weighed in a total batch size of 500 g for each composition, mixed in water-free propanol and milled for 48 h with a cemented carbide milling medium. The milling of the mixed powder compositions was, in general, effective and gave d_{50} values for all mixtures well below 1·5 μm. However, the compositions with metal added as Ni or Mo metal were found to have an

'abnormal' particle size distribution with a tail of about 5–10% of the particles being above 5 μm. Optical microscopy showed the larger particles in these latter milled powders to be mainly flake-like metal grains; the metal was too plastic to be effectively milled to smaller grains. After drying in a protective atmosphere of nitrogen gas, the powder mixes were dry-pressed (75 MPa) into compacts of size 25 × 8 × 8 mm. The green bodies had a density about 55% of theoretical.

Investigation by thermal analysis had shown that NiO reduces to Ni metal at 315°C in hydrogen gas and that MoO_3 reduces to MoO_2 at 508°C and finally to Mo metal at 710°C. The selected sintering cycle, when the metal was added as pure metal or as metal oxides, was an initial heating in hydrogen gas up to 750°C followed by heating in 'vacuum' (about 0·1 torr) to 1750°C, with a hold time of 2 h at this temperature. When Ti_2Ni was added, the powder compacts were heated in hydrogen gas to 750°C, the hydrogen gas atmosphere was then replaced by nitrogen gas and the samples were heated to 1200°C and held for a period of 2 h. Finally, the samples were heated to 1750°C and the furnace was evacuated (to less than 0·1 torr) before the final holding time of 2 h at this temperature. All materials were also hot isostatically pressed (HIP) at 1600°C for 1 h in a 200 MPa argon atmosphere, to allow measurements of mechanical properties on fully dense materials. The materials with open porosity were encapsulated before the HIP.

Density measurements using Archimedes' principle were made on the as-sintered samples, and the sintered materials were prepared for physical characterization using standard techniques. Hardness (HV 10) and indentation fracture toughness (K_{IC}) at room temperature were obtained with a Vickers diamond indenter using 98 N (10 kg) load. The indentation fracture toughness was evaluated according to the method of Anstis *et al.*[19] Values for Young's modulus (E) were calculated with the rule of mixtures, $E = E_1 \times V_1 + E_2 \times V_2$, etc., where the two major constituents Al_2O_3 and Ti(C, N) have $E_1 = 380$ and $E_2 = 305$, respectively, and V_1 and V_2 are corresponding volume fractions. The accuracy of the indentation fracture toughness with this method by repeated measurements on the same sample was $\pm 0{\cdot}2$ MPa $m^{1/2}$ and the accuracy of the Vickers hardness was ± 30.

The phase analysis was based on X-ray powder patterns recorded by a Rigaku diffractometer with a rotation Cu anode working at 10 000 W. Scanning electron microscopy was performed on carbon-coated materials, using a Jeol JSM 820 instrument equipped with a Link AN 10 000 EDS analyser. The electron microprobe analysis was made with a Cameca Camebax instrument, equipped with a number of different spectrometer crystals.

3 Results

3.1 Starting materials and densification

By pressureless sintering for 2 h at 1750°C, alumina alone or alumina with only 2·5 wt% metal addition gave densities above 99% of theoretical density (TD), see Table 1. With a metal content of 5 wt% and, especially, when increasing amounts of Ti(C, N) were added simultaneously, the materials became porous, the level of porosity depending on the amount of Ti(C, N). As an example, alumina–Ti(C, N) composites achieved 99% TD at 15 wt% Ti(C, N) additions, whereas the material with a 30 wt% Ti(C, N) addition achieved around 97% TD.

The way the metal was added had a great influence on the porosity of the sintered metal-containing materials. The addition of metal as oxide or as Ti_2Ni gave materials with a closed porosity (above around 95% TD), even at the highest additions of metal (5 wt%) and Ti(C, N) (30 wt%). The porosity in these cases, as seen by optical or scanning electron microscopy (SEM), was present as a uniformly distributed microporosity. However, when the metal was initially added as pure metal, the bonding of the coarse metal inclusions to the matrix was observed to be poor. In this case some of the porosity was found in the contact zone between metal grains and the matrix. These latter materials had an open porosity and reached only 90–92% TD for an addition of 5 wt% metal plus 30 wt% Ti(C, N).

After hot isostatic pressing at 1600°C in argon, most samples achieved a density of around 99% TD, with the exception of the few specimens already mentioned, with open porosity; these had to be

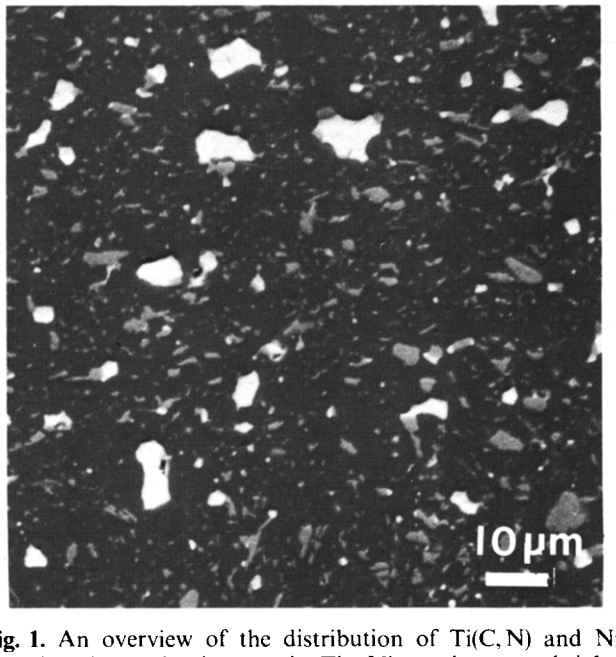

Fig. 1. An overview of the distribution of Ti(C, N) and Ni inclusions in an alumina matrix. The Ni metal appears bright, the titanium carbonitride grey, and the alumina matrix is dark in the SEM micrograph. The overall composition of the ceramic composite material is 5 wt% Ni and 15 wt% Ti(C, N) in alumina, and the Ni was added in metallic form.

Table 1. The investigated alumina composites and the starting material for the metallic addition

Overall composition	*Metal additive*	*Observed density (%TD)*	
		PS 1750°C	*HIP 1600°C*
—	—	99·7	99·7
15Ti(C, N)	—	99·0	99·7
30Ti(C, N)	—	97·3	99·8
2·5Ni	As metal	99·1	99·3
2·5Ni + 15Ti(C, N)	As metal	95·6	99·4
2·5Ni + 30Ti(C, N)	As metal	92·1	99·2[a]
5Ni	As metal	96·0	99·5
5Ni + 15Ti(C, N)	As metal	93·6	99·2[a]
5Ni + 30Ti(C, N)	As metal	90·3	99·0[a]
2·5Ni(Mo)	As metal	99·1	99·0
2·5Ni(Mo) + 15Ti(C, N)	As metal	96·0	99·3
2·5Ni(Mo) + 30Ti(C, N)	As metal	93·7	98·4[a]
5Ni(Mo)	As metal	95·4	98·7
5Ni(Mo) + 15Ti(C, N)	As metal	93·4	99·0[a]
5Ni(Mo) + 30Ti(C, N)	As metal	92·8	98·7[a]
2·5Ni	As oxide	99·5	99·3
2·5Ni + 15Ti(C, N)	As oxide	97·1	99·7
2·5Ni + 30Ti(C, N)	As oxide	96·6	98·6
5Ni	As oxide	98·0	98·8
5Ni + 15Ti(C, N)	As oxide	95·8	99·5
5Ni + 30Ti(C, N)	As oxide	95·4	99·5
2·5Ni(Mo)	As oxide	99·3	99·1
2·5Ni(Mo) + 15Ti(C, N)	As oxide	98·0	99·0
2·5Ni(Mo) + 30Ti(C, N)	As oxide	96·2	99·3
5Ni(Mo)	As oxide	97·9	99·3
5Ni(Mo) + 15Ti(C, N)	As oxide	96·6	99·5
5Ni(Mo) + 30Ti(C, N)	As oxide	95·8	99·3
2·5Ni + 5·3TiN	As Ti_2Ni	99·3	99·7
2·5Ni + 15Ti(C, N)	As Ti_2Ni	98·8	100
2·5Ni + 30Ti(C, N)	As Ti_2Ni	97·8	98·8
5Ni + 10·5TiN	As Ti_2Ni	98·2	100
5Ni + 15Ti(C, N)	As Ti_2Ni	97·7	99·8
5Ni + 30Ti(C, N)	As Ti_2Ni	96·4	99·8
2·5Ni(Mo) + 3·7TiN	As Ti_2Ni + Mo	98·2	99·8
2·5Ni(Mo) + 15Ti(C, N)	As Ti_2Ni + Mo	97·2	100
2·5Ni(Mo) + 30Ti(C, N)	As Ti_2Ni + Mo	95·2	99·0[a]
5Ni(Mo) + 7·3TiN	As Ti_2Ni + Mo	96·3	98·5
5Ni(Mo) + 15Ti(C, N)	As Ti_2Ni + Mo	96·0	99·9
5Ni(Mo) + 30Ti(C, N)	As Ti_2Ni + Mo	94·6	98·9[a]

The overall compositions are given as wt% of added metallic and ceramic particle inclusions. The observed densities are given as % of theoretical density (%TD) and TD is calculated with the rule of mixtures. Densities are measured on as-sintered specimens after pressureless sintering (PS) for 2 h at 1750°C and after subsequent post-HIP at 1600°C for 1 h and 200 MPa pressure.
[a] Encapsulated before post-HIPing.

encapsulated before the hot isostatic pressing to high density.

3.2 X-Ray diffraction phase analysis

Analysis by X-ray diffraction verified the presence of α-Al_2O_3 (corundum) as the major phase in all the sintered preparations. No trace of Ti_2Ni, NiO, MoO_3, TiC or TiN was found in the sintered materials when these phases had been added in the powder compacts prior to sintering, showing that a complete reaction occurred during sintering. In these cases single-phase titanium carbonitride and/or minor amounts of metal phase were found.

The cubic unit cell dimension of the observed titanium carbonitride was 0·4268 nm, i.e. between the parameter of TiN, $a = 0{\cdot}4240$ nm (JCPDS Card No. 6-642) and TiC $a = 0{\cdot}4328$ nm (No. 32-1383).[20] Assuming linear expansion of the lattice with increasing carbon content (Vegard's law), the formula $Ti(C_{0{\cdot}32}N_{0{\cdot}68})$ was derived, which is in fair agreement with the added TiC/TiN = 30/70.

3.3 Microstructure analysis

The microstructures were carefully examined by SEM and electron microprobe analysis to observe the bonding between the particulate inclusions and

the matrix and also the distribution of the added secondary phases. The Ti(C, N) grains were always found to be fairly uniformly distributed in the alumina matrix. When the metal was added as metal powder it was observed to be rather unevenly distributed in the sintered microstructure. Many of the metal inclusions are found as large particles, typically around 6 μm, see Fig. 1. The Ni grains have a bright contrast, the Ti(C, N) grains are grey and the alumina matrix appears dark in the micrograph. The bonding of the metal to the alumina matrix seems to be poor, as some microporosity or cracking occasionally occurs at the interfaces between the larger metal grains and the alumina.

Analysis by electron microprobe showed that when only Ni metal was added, this phase also contained some small amounts of Al. When Ni metal was added together with Ti(C, N), some Ti was also found dissolved in the Ni grains. This was best verified by point analysis, and the Al and Ti content could reach up to 5wt%. The presence of Al and Ti in the Ni grains could also be illustrated by the element mapping shown in Fig. 2(a)–(d). The material contains 15 wt% Ti(C, N) and 5 wt% Ni in the form of metal additive. The coarse Ni metal grains in the sintered structure are seen to contain Ti and Al.

Very little microporosity or cracking was noted in the metal–alumina interface when the metal was added as oxide. In this case the metal inclusions were uniformly distributed in the material, and the metal grain size was significantly smaller, typically 1–3 μm.

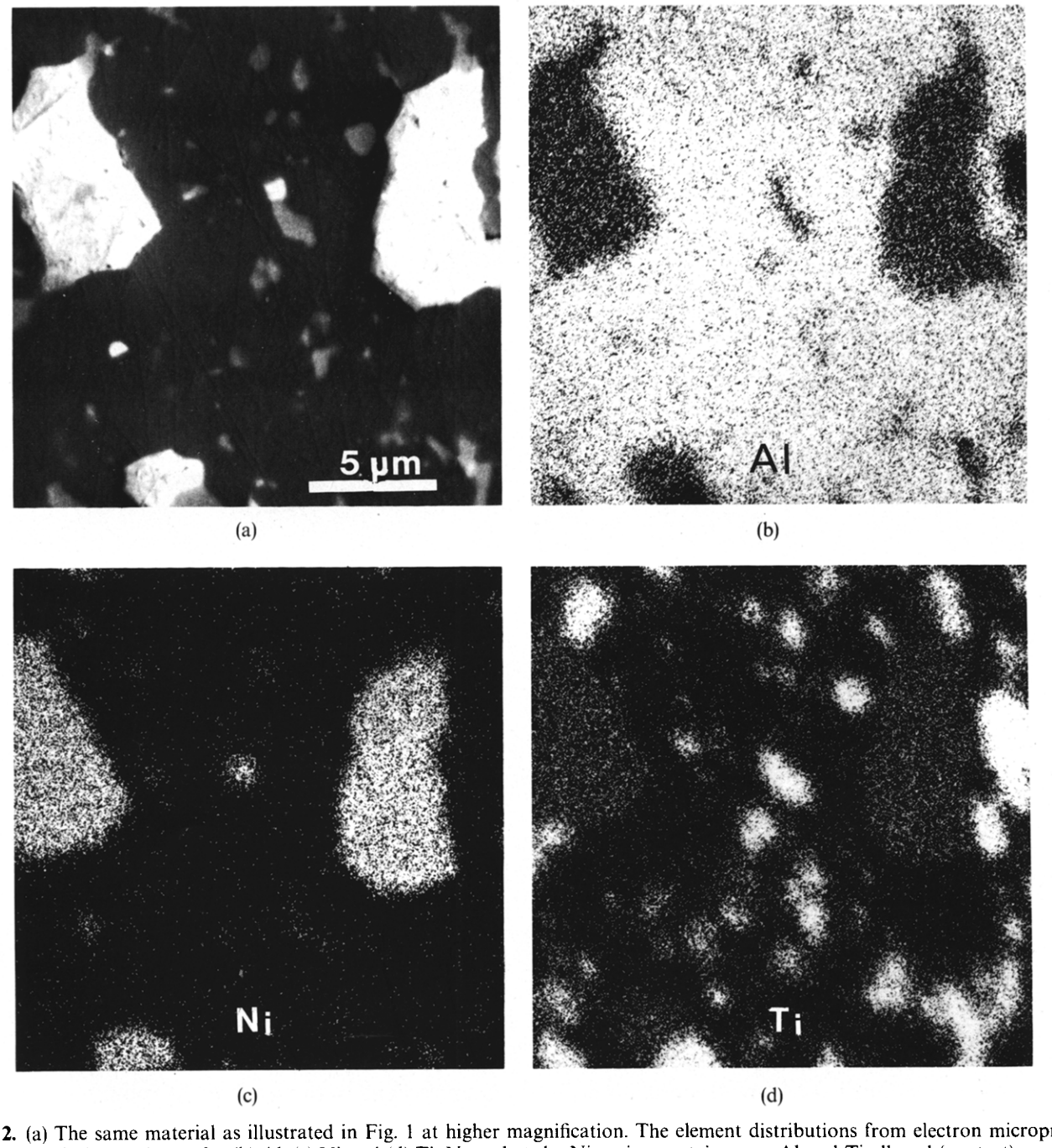

Fig. 2. (a) The same material as illustrated in Fig. 1 at higher magnification. The element distributions from electron microprobe analysis are shown for (b) Al, (c) Ni and (d) Ti. Note that the Ni grains contain some Al and Ti alloyed (see text).

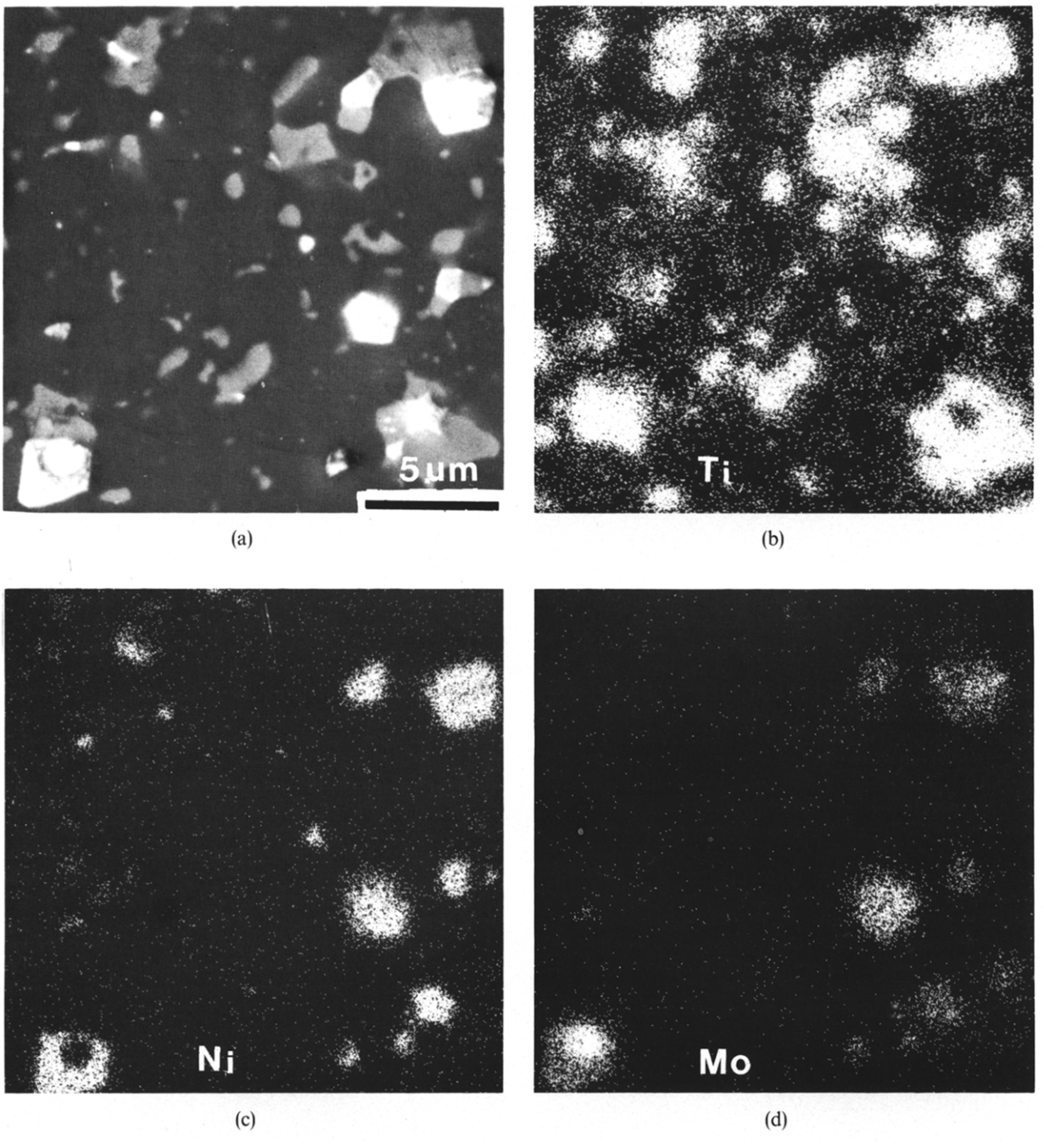

Fig. 3. (a) The microstructure and the distribution of the elements, (b) Ti, (c) Ni and (d) Mo in a material of overall composition 5 wt% Ni–Mo and 15 wt% Ti(C, N). Ni was added as Ti_2Ni and the Ni to Mo ratio was adjusted to 70/30 by separately added Mo metal.

Many of the metal inclusions were found in contact with the titanium carbonitride phase, and the interface contained no microporosity. Electron microprobe analysis revealed that the Ni grains dissolved some Al and Ti also in this case.

When the Ni metal was added in the form of Ti_2Ni, the bonding between the metal and the alumina matrix was very good, and no microporosity was observed at the interface. As a consequence of the 'in-situ' formation of Ni and TiN, the metal inclusions are always found in close contact with the titanium carbonitride particles. The formed Ni metal grains contained some small amounts of Ti and Al.

In the samples with both Ni and Mo added, it was found that the two metals alloyed to some extent, but a wide variation of composition was found, from almost pure Ni to pure Mo, see Fig. 3(a)–(c). Note especially the Mo particle embedded in a larger Ni grain, situated in the lower left corner of each micrograph. Mo has dissolved in the Ni metal, whereas very little, if any, Ni has entered the Mo metal in this particular case.

3.4 Mechanical properties

The hardness and indentation fracture toughness of all the dense materials from the post-HIPing preparations were measured at room temperature, and the hot hardness up to 1100°C was investigated for a number of selected composites.

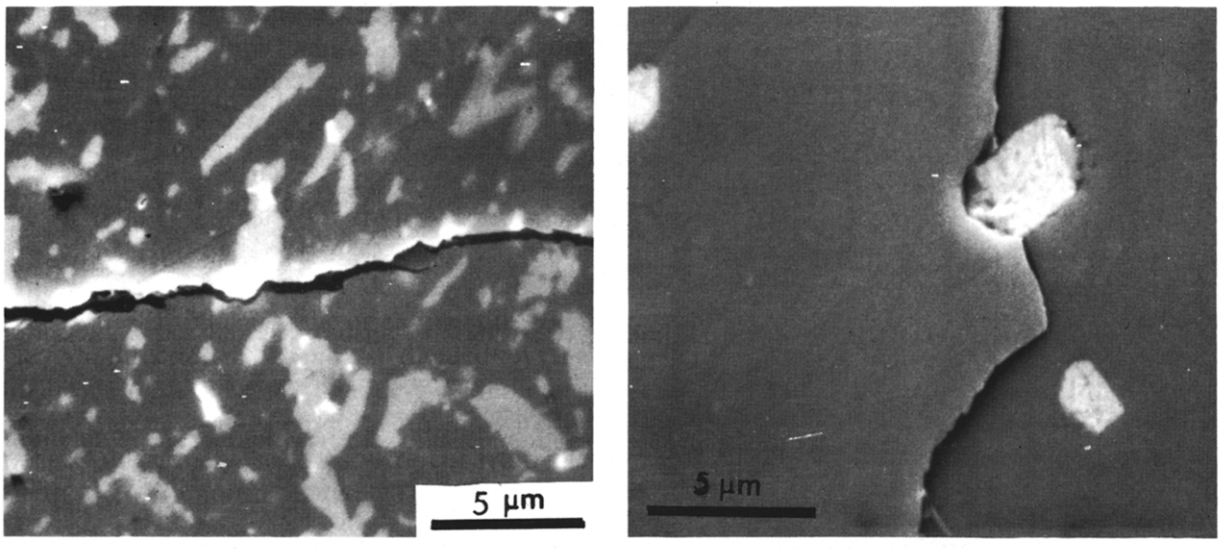

Fig. 4. The indentation crack path in an alumina material containing (a) 30 wt% Ti(C, N) inclusions or (b) 5 wt% Ni inclusions.

The crack path in the microstructure is illustrated for an alumina–Ti(C, N) composite and an alumina–Ni composite in Fig. 4(a) and (b), respectively. It is seen that the crack proceeds both around and through the Ti(C, N) grains. In the case of the coarse Ni grain, the crack runs around the inclusion. Note the poor bonding of this Ni grain to the alumina matrix; this will be discussed further.

Pure alumina ceramics had a hardness, HV 10, of 1650 and a fracture toughness of 3·0 MPa $m^{1/2}$. The hardness generally decreased and the fracture toughness slightly increased with addition of metal inclusions. Thus by 5 wt% metal addition, the mechanical properties typically were 1500 and 3·7 MPa $m^{1/2}$.

Adding titanium carbonitride alone to alumina increased the hardness as well as the fracture toughness. For a level of 30 wt% Ti(C, N), the hardness was 1800 and the fracture toughness 3·8 MPa $m^{1/2}$. With addition of further metal inclusions, the fracture toughness increased still somewhat while the hardness decreased, see Fig. 5(a) and (b).

At a constant amount of added metal (5 wt%), both the hardness and fracture toughness increased with addition of Ti(C, N), see Fig. 6(a) and (b). In both Figs 5 and 6 it can be seen that the addition of metal in the form of metal oxide gave a somewhat better combination of properties than in the materials where the addition was metal.

Finally, the effects of adding Ti_2Ni to alumina and the combination with hard particle inclusions are demonstrated in Fig. 7(a) and (b). It is not possible to prepare a material where only Ni metal is added, as some TiN (5–10%) always will be inherently present depending on the amount of Ti_2Ni added prior to sintering. However, the general trends already seen were also found here, i.e. the hardness decreased with metal content and increased with content of titanium carbonitride. The fracture toughness increased with both metal and carbonitride addition. It is notable that the alumina composite with 5 wt% metal and 30 wt% Ti(C, N) has a hardness of about 1800 and a fracture toughness of about 5 MPa $m^{1/2}$. The hot hardness, HV 1, was measured

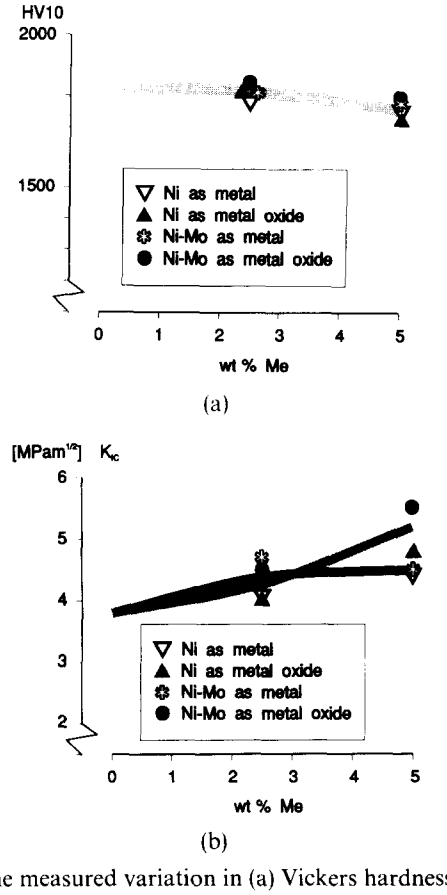

Fig. 5. The measured variation in (a) Vickers hardness, HV 10, and (b) indentation fracture toughness, K_{IC}, at room temperature with varying amount of added metal. The alumina matrix in all preparations was a composite with 30 wt% Ti(C, N).

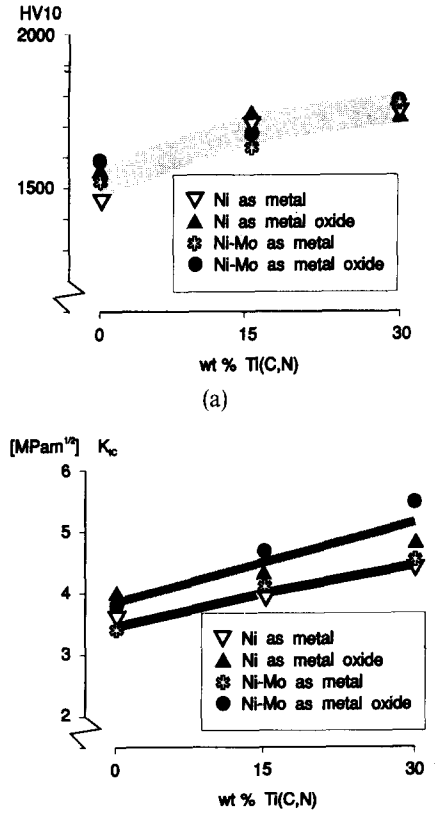

Fig. 6. The measured variation in (a) Vickers hardness, HV 10, and (b) indentation fracture toughness, K_{IC}, at room temperature with varying amount of added Ti(C, N). The alumina matrix in all preparations was a composite with 5 wt% metal added.

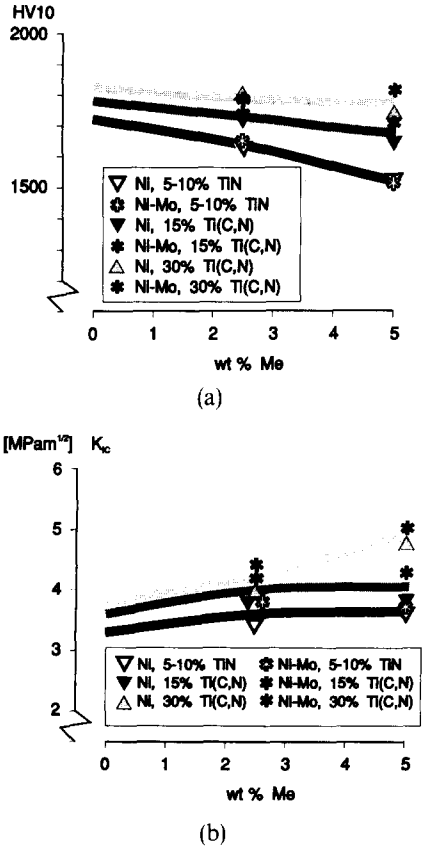

Fig. 7. The measured variation in (a) Vickers hardness, HV 10, and (b) indentation fracture toughness, K_{IC}, at room temperature with varying amount of added metal and Ti(C, N). In all preparations Ti_2Ni has been added, and the materials are 'reaction sintered' (see text).

Table 2. Examples of hot hardness, HV 1, measured from room temperature up to 1100°C with a Vickers diamond indenter on alumina composites

Temperature (°C)	*Hot hardness HV 1*				
	A	*B*	*C*	*D*	*E*
25	2110	2150	1955	1980	2040
200	1605	1630	1450	1455	1475
400	1300	1360	1120	1170	1210
600	1090	1120	970	985	1010
800	900	960	770	780	830
1000	695	730	540	560	625
1100	655	675	515	520	570

The following materials were selected: A denotes pure Al_2O_3, B is Al_2O_3 + 30 wt% Ti(C, N), C is Al_2O_3 + 5 wt% Ni (as metal), D is Al_2O_3 + 5 wt% Ni (as oxide), and E is Al_2O_3 + 5 wt% Ni (as Ti_2Ni) + 10·5 wt% TiN.

with a 9·8 N load (1 kg) from room temperature up to 1100°C. All the composite materials showed a similar smooth decrease in hardness with raised temperature, as found for pure alumina over this temperature range, see Table 2. Thus, the hardness, HV 1, diminished from about 2000–2100 at room temperature to about 500–700 at 1100°C.

4 Discussion

The densification and the sintered microstructure of the materials were affected by the starting materials and their particle size distribution. The latter parameter was investigated by sediograph measurements for the purpose of explaining some of the observed effects. It was found that the milling of metal grains was poor when Ni or Mo metal was added. Consequently, the corresponding sintered materials were found to be porous, the metal inclusions in the microstructure were coarse and the bonding to the alumina matrix was poor, with microcracking at the interface. These microcracks at the interface might be caused by a combination of a poor bond and the fact that the metal shrinks faster than the matrix. The thermal expansion mismatch is almost a factor of 2, and considerable radial tensile stresses will occur and contribute to circumferential cracks.[21] When the metal was added as metal oxide or Ti_2Ni and subsequently reduced and nitrided, respectively, the resulting metal grain sizes in the microstructure were much smaller. This gives less tensile stress, and no formation of microcracks was seen at the interface.

The materials were sintered at 1750°C, which should be compared with the melting points of Ni (1450°C) and Mo (2620°C). The Ni metal will thus melt, whereas the Mo metal will be present as solid particles and this will affect the affinity or possibility of the two metals to be alloyed with other elements

present. The electron microprobe analysis showed that some amounts of Ti, Al or Mo would alloy with Ni. Very small amounts of Ni could also dissolve in Mo grains, but pure Mo grains were often found in the microstructure. As demonstrated in Fig. 3, an almost intact Mo metal grain was found in direct contact with a Ni metal grain, the latter being melted during sintering. The trend of the observed metal solubilities is in fair agreement with reported possible solid solution extensions in the binary alloy systems Ti–Ni, Al–Ni and Mo–Ni. Thus, a Ni-rich melt cooled from high temperatures might dissolve up to 12 at.%, 20 at.% and 30 at.% Ti, Al or Mo in a solid solution of the Ni phase, respectively. On the other hand, even if a reaction takes place between melted Ni and solid Mo grains, the formed Mo(Ni) phase will contain at most 2 at.% Ni. It should be stressed, however, that in the case of the refractory compounds Ti(C, N) and Al_2O_3 in contact with melted nickel metal, the binary metal alloy systems already mentioned only indicate possible solubility trends.

The hardness of the alumina composites with metal inclusions only was found to be decreased, as expected from the presence of 'soft' metal particles and this behaviour was also seen and discussed by Tuan & Brook.[11,12] In the present study it has been demonstrated, however, that simultaneous addition of hard Ti(C, N) particles could compensate for the loss in hardness caused by the metal inclusions.

The measured hardness of pure alumina and the alumina composites decreased by increasing temperature in a typical manner noted earlier for ceramic materials and by plotting the logarithm of the hot hardness against temperature the curves will achieve fairly straight lines. The hot hardness of Al_2O_3 is in good agreement with the earlier reported values,[22–24] considering the different loads used. The hardness decrease in ceramics has been attributed to a combined effect of microplasticity and tensile microfracture (by subsurface indentation deformation).[24]

In the present study the indentation fracture toughness of alumina was observed to increase from around 3·0 to 3·8 MPa $m^{1/2}$ by the addition of 30 wt% Ti (C, N) only. This is in fair agreement with careful investigations of Al_2O_3–TiC composites, where the increase in toughness was from around 3·7 to 4·8 MPa $m^{1/2}$ when 40 wt% TiC was added to alumina.[25] The mechanism for the increase in toughness was discussed in detail in Ref. 25 and it was suggested to be a result of increased grain boundary strength or 'grain boundary toughness'. Thus the interface between grains was found to be of great importance.

Tuan & Brook have shown that the fracture toughness of alumina with nickel inclusions only was raised considerably, with the toughness of the composite containing 13 vol.% Ni being twice that of alumina alone.[11] The interaction between the propagating crack and the nickel particles was discussed in detail by these authors. A toughening mechanism involving plastic deformation of the metal particles was suggested and it was shown that the bond between the metallic particles and the brittle matrix was of great importance. The interfacial strength found in a composite sintered at a higher temperature was shown to be stronger compared to a lower sintering temperature, due to higher oxygen solubility in the metallic phase. This resulted in a higher fracture toughness of the former composite material.[11] The increase in fracture toughness found in the presently prepared Ni–Al_2O_3 materials varied somewhat depending upon the way the metal was added (and sintered) and one reason might be differences in the nickel metal to alumina matrix bond. Thus, when nickel was added as oxide or Ti_2Ni, the increase in toughness was generally found to be higher than when pure metal was added.

The interfacial strength of a metal–ceramic bond might depend on factors like the wetting, as sintering takes place well above the melting point of nickel. It is known that the wetting between metals and alumina is generally poor, but the wetting of nickel metal in composite materials with other refractory ceramic constituents like TiN, TiC, etc. (so called 'cermets'), is improved by addition of metals like Mo and W. This was one of the reasons for adding Mo to some of the preparations in this study. No significant differences were observed, however, between materials with pure Ni or Ni–Mo (70/30) added.

In addition, the bond between the metallic particles and the surrounding ceramic matrix is highly influenced by the degree of interfacial reaction. For example, an intermediate phase was used to obtain a strong bond between metal and alumina by Suh & Fillion.[13] The use of an interfacial reaction in a slightly oxidizing atmosphere has been described earlier by Cho *et al.* in a composite between alumina and Cr metal[14] and it has been shown that dissolved oxygen in the nickel phase of Ni–Al_2O_3 composites improved the bonding.[11] In the latter case interfacial reactions to form a spinel phase, $NiAl_2O_4$, might take place when the oxygen content is exceeding 200 ppm.[26] Similarly, in the present preparations high oxygen contents in the Ni metal or the presence of 'NiO' on the metal grain surface will, at the sintering temperatures, react to form a very thin layer of the spinel phase. Point analysis by electron microprobe did not reveal any significant levels of oxygen in the metal phase of the prepared composites and the presence of a very thin reaction zone corresponding to a spinel phase was

not resolved by the electron microprobe. The occurrence of any interfacial reactions in these materials needs further studies by high-resolution analytical transmission electron microscopy to be clarified.

When both metal and ceramic inclusions were added to alumina, the fracture toughness was observed to be higher than for either alumina with only metal added or for alumina with only Ti(C, N) added. This indicates a combined effect of the different toughening mechanisms already mentioned briefly and discussed in detail in Refs 11 and 25.

Finally, it can be said that using intermetallic compounds like Ti_2Ni, and nitriding or carburizing these during sintering seems to be an attractive process opening many possibilities to produce new composite materials. By using 'reaction sintering', the constituent phases will be very closely mixed with good bonding between the present phases.

5 Conclusions

When metal powder was added, the sintered materials were porous and the coarse-grained metal inclusions had a poor bond to the matrix. The use of metal oxide gave a uniform microstructure with fine-grained metal inclusions, but the composites were still somewhat porous. The addition of the intermetallic compound Ti_2Ni resulted in uniform microstructures with less pores, and the bond to the matrix was very good.

Addition of the metal as oxide, with a subsequent reduction step during sintering, or as an intermetallic compound, with 'reaction sintering', gave fine-grained materials with good mechanical properties. Composites of alumina, reinforced with particle inclusions, can reach toughness levels almost twice that of alumina alone with a maintained hardness, by appropriate admixtures of metal and titanium carbonitride inclusions. The material with 5 wt% Ni and 30 wt% Ti(C, N) made from Ti_2Ni had room temperature properties corresponding to a Vickers hardness HV 10 = 1800 and an indentation fracture toughness of about 5 MPa $m^{1/2}$. The measured hot hardness up to 1100°C showed no abnormal softening of the alumina composites containing metal inclusions compared with alumina alone.

Acknowledgement

The author is indebted to Marian Mikus and Erik Antemar, without whose help this study would not have been possible. AB Sandvik Hard Materials is thanked for permission to publish these results.

References

1. McHugh, C. O., Whalen, T. J. & Humenik Jr, M., Dispersion-strengthened aluminum oxide. *J. Am. Ceram. Soc.*, **49** (1966) 486.
2. Rankin, D. T., Stiglich, J. J., Petrak, D. R. & Ruh, R., Hot-pressing and mechanical properties of Al_2O_3 with a Mo-dispersed phase. *J. Am. Ceram. Soc.*, **54** (1971) 277.
3. Lange, F. F., The interaction of a crack front with a second-phase dispersion. *Phil. Mag.*, **22** (1970) 983.
4. Evans, A. G., The strength of brittle materials containing second phase dispersions. *Phil. Mag.*, **26** (1972) 1327.
5. Flinn., B., Ruehle, M. & Evans, A. G., Toughening in composites of Al_2O_3 reinforced with Al. *Acta Metall.*, **37** (1989) 3001.
6. Budiansky, B., Amaziga, J. C. & Evans, A. G., Small-scale crack bridging and the fraction toughness of particulate-reinforced ceramics. *J. Mech. Phys. Solids*, **36** (1988) 167.
7. Simpson, L. A. & Wasylyshin, A., Fracture energy of Al_2O_3 containing Mo fibres. *J. Am. Ceram. Soc.*, **54** (1971) 56.
8. Lloyd, D. J. & Tangri, K., Acoustic emission from Al_2O_3–Mo fibre composites. *J. Mater. Sci.*, **9** (1974) 482.
9. Jellinghaus, W., Sinterwerkstoffe aus Nickel oder Nickel-aluminid mit Aluminiumoxyd. *Archiv Eisenhuttenwesen*, **32** (1961) 187.
10. Djali, P. D. & Linger, K. R., The fabrication of nickel–alumina cermets. *Brit. Ceram. Soc. Proc.*, **26** (1976) 113.
11. Tuan, W. H. & Brook, R. J., The toughening of alumina with nickel inclusions. *J. Eur. Ceram. Soc.*, **6** (1990) 31.
12. Tuan, W. H. & Brook, R. J., Processing of alumina/nickel composites. *J. Eur. Ceram. Soc.*, **10** (1992) 95.
13. Suh, N. & Fillion, P., Optimization of cutting tool properties through the development of alumina cermet. *Wear* **62** (1980) 123.
14. Cho, S.-A., Puerta, M., Cols, B. & Ohep, J. C., Sintering behaviour of Al_2O_3–Cr and Al_2O_3–$Cr(NO_3)_3$ mixtures. *Powder Metall. Int.*, **12** (1980) 192.
15. Newkirk, M. S., Urquhart, A. W. & Zwicker, H. R., Formation of Lanxide ceramic composite materials. *J. Mater. Res.*, **1** (1986) 81.
16. Wahi, R. P. & Ilschner, B., Fracture behavior of composites based on Al_2O_3–TiC. *J. Mater. Sci.*, **15** (1980) 875.
17. Borom, M. P. & Lee, M., Effect of heating rate on densification of alumina–titanium carbide composites. *Adv. Ceram. Mater.*, **1** (1986) 335.
18. Ishigaki, T., Sato, K. & Moriyoshi, Y., Pressureless sintering of TiC–Al_2O_3 composites. *J. Mater. Sci. Lett.*, **8** (1989) 678.
19. Anstis, G. R., Chanticul, P., Lawn, B. R. & Marshall, D. B., A critical evaluation of indentation techniques for measuring fracture toughness. *J. Am. Ceram. Soc.*, **64** (1981) 533.
20. Powder Diffraction File, Inorganic Phases. International Centre for Diffraction Data, Swarthmore PA, USA, 1987.
21. Davidge, R. W. & Green, T. J., The strength of two-phase ceramic/glass materials. *J. Mater. Sci.*, **3** (1968) 629.
22. Koester, R. D. & Moak, D. P., Hot hardness of selected borides, oxides and carbides to 1900°C. *J. Am. Ceram. Soc.*, **50** (1967) 290.
23. Niihara, K. & Hirai, T., Hot hardness of CVD-Si_3N_4 to 1500°C. *Powder Metall. Int.*, **16** (1984) 223.
24. Lankford, J., Comparative study of the temperature dependence of hardness and compressive strength in ceramics. *J. Mater. Sci.*, **18** (1983) 1666.
25. Krell, A. & Blank, P., Inherent reinforcement of ceramic microstructures by grain boundary engineering. *J. Eur. Ceram. Soc.*, **9** (1992) 309.
26. Trumble, K. P. & Ruehle, M., Microstructural studies on the Ni–Al_2O_3 interface. *Mater. Res. Soc. Symp. Proc.*, **138** (1989) 551.