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Sol–gel prepared Ni–alumina composite materials

Part I *Microstructure and mechanical properties*

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The sol–gel method has been utilized for the preparation of dense, homogeneous ceramic–metal composites with up to 50% Ni in Al_2O_3. Examination by SEM and TEM shows that the materials consist of micrometre-size Al_2O_3 with metallic Ni in isolated regions from ~50 μm down to nanometre size. The density ranges from ~97% (10% Ni) to ~74% (50% Ni) of the theoretical number. The hardness decreases from ~18 GPa for pure alumina to ~10 GPa for alumina containing 50% Ni. The fracture toughness increases significantly from K_{1c} = 3–4 MPa $m^{1/2}$ to K_{1c} = ~8.5 MPa $m^{1/2}$. The elastic and shear moduli decrease from E = ~400 GPa and G = ~160 GPa for pure alumina to E = ~320 GPa and G = ~135 GPa when containing 50% Ni. The electrical resistivity is ~10^6 Ωm with 10 to 40% Ni but decreases drastically at 50% Ni content.

1. Introduction

The idea of combining a ductile metallic phase with a strong (but brittle) ceramic is not new. This type of ceramic–often called a cermet–has been produced by dry mixing of ceramic and metallic powder into a preform followed by hot pressing. This process is difficult to control, though, and often results in non-uniform dispersion of the metallic phase along the grain boundaries. For many utilizations the important properties are wear resistance and fracture toughness, for which reason the optimum structure is a continuous ceramic phase containing isolated nanometre-size metal inclusions.

The fine-scale homogeneity that can be obtained using the sol–gel technique would be advantageous in the metal–ceramic composite materials [1–5]. In an earlier study [3] a Ni–Al_2O_3 ceramic was prepared through the dispersion of colloidal alumina in a solution of nickel nitrate. The sol chemistry was adjusted to adsorb Ni cations to the AlOOH (boehmite) surfaces, and then the sol was gelled, dried and fired to full density in a reducing atmosphere. This method had two severe shortcomings. The amount of Ni which could be introduced was limited because a stable dispersion of the boehmite could not be achieved in the presence of high nickel nitrate concentrations; and although small gel fragments could be sintered to full density, the gel did not provide a processable powder that could be sintered or hot-pressed to full density. One of the objectives of this study was to prepare monolithic ceramic–metal composites with a low content of pores and with a well-dispersed metal phase from 10 and up to 50 wt %. In this case, the gel was prepared using an alkoxide precursor, and was densified by hot pressing. The other purpose of the study was to evaluate the physical properties of these materials.

2. Experimental procedure

2.1. Synthesis

The alumina sol was synthesized by a procedure similar to that of Yoldas [6]. Hydrolysis of aluminium sec-butoxide was achieved by mixing aluminium sec-butoxide in isopropyl alcohol with 70 °C water in the molar ratio 1 to 4. The solution was stirred for 15 min at 70 °C and the pH was then adjusted to 2 by addition of HNO_3. Under continuous stirring for 1 h at 80 °C, 1 M $Ni(NO_3)_2 \cdot 6H_2O$ was added in different amounts so that the final product would have an Ni/Al_2O_3 ratio from 10 up to 50 wt %. After drying, the gels were subjected to a 500 °C heat treatment in air to remove organic and nitrate residuals. A subsequent heat-treatment for 4 h at ⩽ 1000 °C in H_2 converted the nickel oxides to metal. The porous fragmented material was then ground to < 250 mesh to obtain a powder that could be cold-pressed at 1 MN, followed by a hot pressing for 1 h at 1460 to 1850 °C (heating 10 °C min^{-1}, cooling 15 °C min^{-1}) and 17 MPa (pressure increase 0.5 MPa min^{-1}, decrease 0.2 MPa min^{-1}). In one experiment cold pressing and sintering was performed without hot pressing, and a few attempts of hot pressing at temperatures < 1450 °C were made, but only the materials hot-pressed at temperatures > 1460 °C were considered successful and therefore characterized in detail.

0022–2461

2.2. Physical properties

The density was determined by weighing and measuring rectangular-shaped specimens. The same pieces were used for determination of the resistivity. The hardness and fracture toughness were found by indentation techniques [4, 7] while the elastic and shear moduli were measured using the ultrasonic through-transmission method in an immersion tank [8–10]. The elastic modulus was measured using the ultrasonic through-transmission method in the immersion tank. Five sets of non-focused immersion-type transducers with central frequencies of 1, 5, 8, 10 and 15 MHz were used to send ultrasonic waves into the sample through the water medium. The received signal was then sent to a Data 6000 waveform analyser to calculate speed and attenuation. A pair of 2 MHz, 1 cm diameter transducers made by Panametrics were also used to measure the speed of shear waves through the material. For the shear transducers, a special ultrasonic couplant with high viscosity was used to efficiently transmit the shear wave. Since the nickel phase was well distributed in the alumina matrix, elastic isotopy could be assumed.

2.3. Structural characterization

The microstructures were determined by X-ray diffraction of a smooth and polished surface. The same surface was observed in the optical and scanning electron microscopes in order to image the millimetre to micrometre scale microstructure. For transmission electron microscopy (TEM) investigations, discs of 3 mm diameter and $\sim 100\,\mu m$ thickness were polished, dimpled and ion-beam thinned. These were observed in the TEM at 120 kV; the elemental composition was evaluated by energy-dispersive spectrometry (EDS). The distribution of phases were determined by bright-field and dark-field imaging and by electron diffraction. The gel-derived powders that were hot-pressed to fabricate the ceramics were also examined by TEM.

3. Results

The powder used for hot pressing ranged from nanometre-size up to a few hundred nanometres. No grain larger than 500 nm was ever observed in TEM. The metal phase was of 1 to 10 nm size and appeared extremely well dispersed on the surface of the much larger alumina grains.

A specimen that was only cold-pressed and sintered is shown in Fig. 1. It was found that the Ni phase de-wets and separates out during sintering, and so it was necessary to hot-press the gel powder to obtain dense ceramics for property studies and further characterization. For the hot pressed specimens it was found that there was surprisingly little difference in the structure between the specimens containing 10 and 50% Ni. The X-ray diffraction revealed large amounts of Ni and Al_2O_3 in all specimens and the SEM and TEM investigations showed that Ni particles of size $\sim 50\,\mu m$ down to ~ 20 nm were present. Fig. 2 (SEM micrographs) shows the distribution on the micrometre scale. Ni appears light and the Al_2O_3 dark on

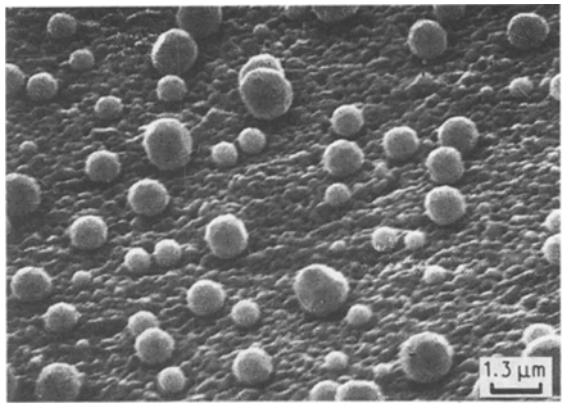

Figure 1 SEM micrograph of a dewetted and ex-soluted Ni–Al_2O_3 composite produced by sintering without hot pressing.

the polished surface. This figure also shows fractured surfaces where the distribution of the smaller Ni particles can be seen. All the specimens are very homogenous on the millimetre scale, with few pores and an even distribution of Ni inclusions which appear in a range of sizes from $< 1\,\mu m$ up to $\sim 50\,\mu m$. Increasing the content of Ni increased not the size of Ni inclusions but their number. However, there is a tendency to some interconnection of the metal with increasing content of Ni. TEM investigations showed more clearly the presence of Ni inclusions down to ~ 20 nm. Fig. 3 shows an example from the specimen containing 30% Ni but it is representative for all the samples. Many of the nanometre to micrometre size Ni inclusions contained (1 1 1) twins. Again, increasing the content of Ni did not increase the size of the metal inclusions but seemed rather to increase the number, especially of the ~ 20 nm size Ni inclusions.

Table I summarizes the properties of the hot-pressed ceramics. The results of some earlier investigations are also cited here, giving the properties of both single-crystal and polycrystalline Al_2O_3 [4, 13]. The density was found to range from $\sim 97\%$ (10% Ni) to $\sim 74\%$ (50% Ni) of the theoretical density. The hardness decreased from about 18 GPa for pure alumina to about 10 GPa for alumina containing 50% Ni. The fracture toughness increased significantly from $K_{1c} = 3$–$4\ MPa\,m^{1/2}$ to $K_{1c} = \sim 8.5\ MPa\,m^{1/2}$. The elastic and shear moduli decreased from $E = \sim 400$ GPa and $G = \sim 160$ GPa for pure alumina to $E = \sim 320$ GPa and $G = \sim 135$ GPa when containing 50% Ni. The resistivity remained constant at $\sim 10^6\,\Omega m$ from 10 to 40% Ni, but decreased dramatically for 50% Ni.

4. Discussion

This study has revealed that the hydrolysis of aluminium sec-butoxide yields a better precursor for the synthesis of Ni–Al_2O_3 ceramics than colloidal boehmite. In this sol, it was possible to introduce large quantities of Ni metal – up to 50% Ni – whereas in the boehmite sol there was a distinct loss of homogeneity in the presence of high Ni concentrations.

It should be noted that many attempts were made to cold-press or hot-press and then sinter the

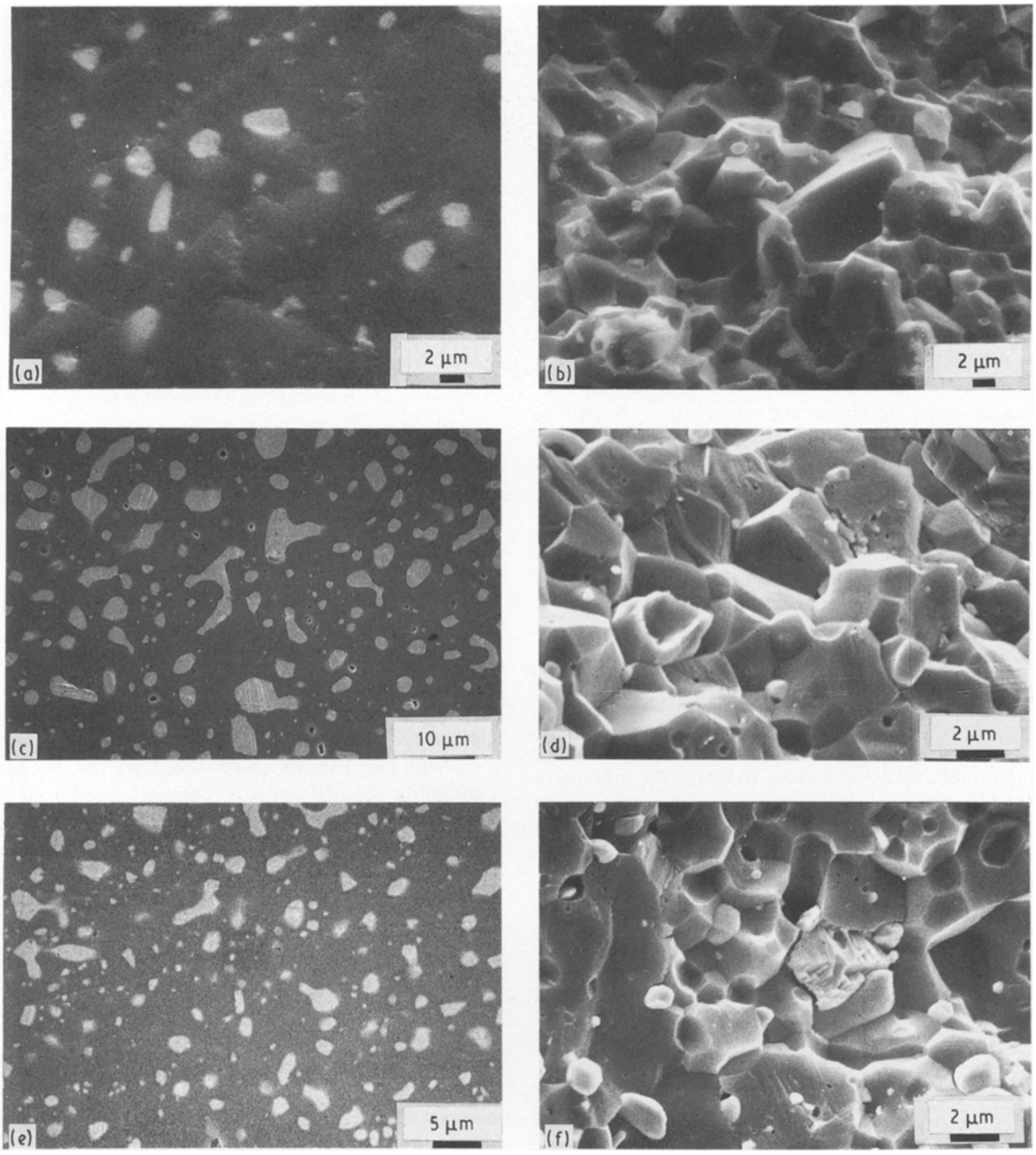

Figure 2 Polished and fracture surfaces of Ni–alumina composites observed in the SEM. 10% Ni: (a) polished, (b) fractured. 30% Ni: (c) polished, (d) fractured. 50% Ni: (e) polished, (f) fractured. On the polished specimens the Ni appears light and the alumina dark. The alumina appears continuous and the Ni as inclusions with a grain size distribution up to $\sim 20\,\mu m$.

Ni–Al_2O_3 powder at temperatures $< 1450\,^{\circ}C$, but densification of the compact could not be achieved. Since it has been shown by others [6] that sol–gel derived aluminas can be readily sintered at $T < 1400\,^{\circ}C$, it can only be concluded that large amounts of the Ni phase interfere with the sintering mechanism. When the sintering was performed at temperatures in excess of $1450\,^{\circ}C$, the Ni phase melted and was exsolved due to dewetting (Fig. 1). This in itself suggests the possible application of this process for the fabrication of supported-metal catalysts; but for the fabrication of dense ceramics, pressure is required.

Even in the case of hot pressing, it was not possible to achieve a fully dense microstructure at $T < 1500\,^{\circ}C$. This suggests that the liquid Ni phase that forms at $T > 1500\,^{\circ}C$ promoted densification of the ceramic composite. The micrographs in Figs 2 and 3 clearly reveal the extensive agglomeration of Ni, and the apparent grain growth in the Al_2O_3 phase. Nevertheless, a finer-scale particulate was retained. This is most clearly evident in the fracture surfaces of Fig. 2 and within the corundum grains of Fig. 3.

The duplex nature of the Ni phase is undoubtedly responsible for the observed mechanical properties of the composites. There is a factor of two decrease in the hardness of the Al_2O_3 due to the presence of the Ni phase (Table I). This decrease is especially evident at high Ni contents because of a percolation of the Ni phase. This is apparent in the micrographs of Fig. 2

TABLE I Physical properties of Ni–alumina composites containing up to 50% Ni

Ni (wt %)	Density (% of theor.)	Hardness, H_V (GPa)	Fracture toughness, K_{ic} (MPa $m^{1/2}$)	Elastic modulus, E (GPa)	Shear modulus, G (GPa)	Poisson's Ratio	Resistivity, ρ ($10^{10}\,\Omega$ cm)
0[a]	[b]	16–20	3–4	401	161	0.326	100
0[c]	94	14.6	3.8	326	132	0.237	0.1–100
10	97	14.5	5.5	385	155	0.237	1.73×10^{-4}
15	90	14.4	6.0	383	152	0.250	1.28×10^{-4}
20	89	15.3	6.3	368	150	0.230	[b]
30	84	13.0	6.7	303	123	0.230	1.18×10^{-4}
50	74	9.6	8.3	318	134	[b]	3.27×10^{-13}
100[d]	[b]			200	76	0.312	7×10^{-18}
Standard deviation	1.0	0.3	0.5	5	3	0.014	~ 5%

[a] Single-crystal Al_2O_3 [5, 11, 12].
[b] Not determined.
[c] Polycrystalline Al_2O_3 [11–13].
[d] Ni metal [12].

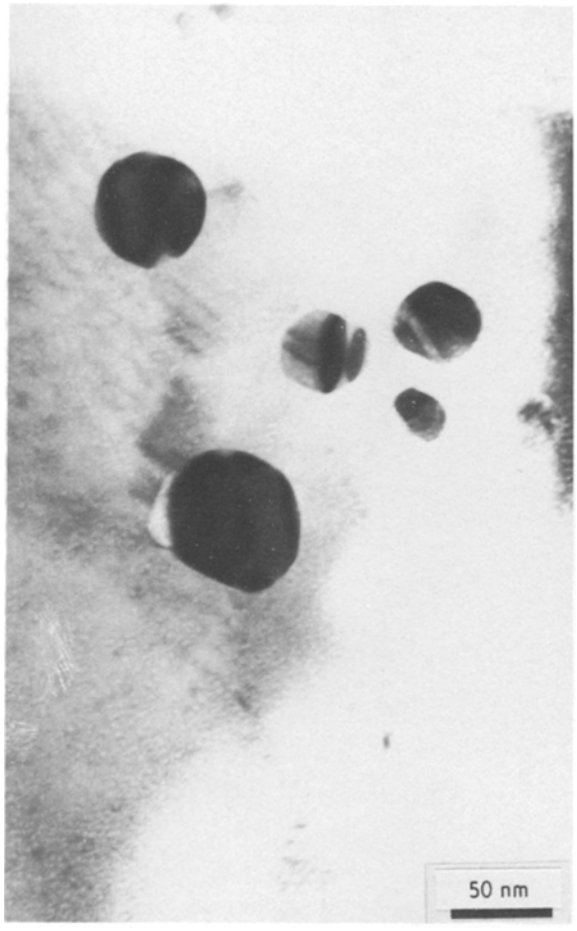

Figure 3 Typical TEM bright-field image of Ni–alumina composite. The image shown is from the specimen containing 30% Ni but is representative for all specimens. The Ni inclusions often contain 1 1 1 twins.

but more so in the dependence of electrical resistivity upon Ni content that is presented in Table I. The large change in conductivity at 50% Ni is a clear indication that the Ni phase has become continuous. The elastic modulus (Table I) obeys the simple law of mixtures for composites [9].

Most significantly, there is a large increase in the fracture toughness of these composites relative to the

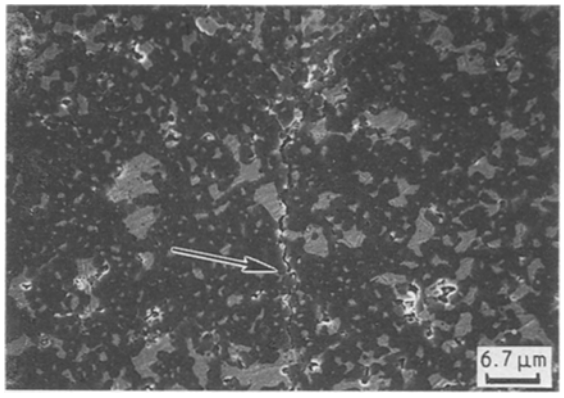

Figure 4 The crack from a hardness indentation passes through the centre of the micrograph from top to bottom. Note the crack deflection which occurs overall and one example of crack bridging (arrowed).

values for 100% Al_2O_3 (Table I). This could be due to any one or more of four mechanisms, namely crack bowing, crack deflection, crack bridging and induced microcracking [14]. Fig. 4 shows an indentation crack on the polished surface of a composite containing 50% Ni. The crack has been deflected by the Ni inclusions. At one place (arrowed) bridging of the crack can be observed. This, together with the fact that the fracture surfaces were quite granular and were extensively decorated with fine particulate Ni phase, suggests crack deflection and crack bridging to be predominant causes.

5. Conclusions

It was found that dense Ni–Al_2O_3 ceramics could be synthesized using a sol–gel derived powder wherein a homogenous dispersion of Ni was simultaneously achieved at the nanometre and micrometre scales. The properties were directly dependent on the Ni content and its distribution within the microstructure. Al_2O_3 was everywhere interconnected, but at around 50% Ni there was also percolation of the Ni phase. The fracture toughness was significantly influenced by the

presence of the Ni phase because of crack deflection and crack bridging.

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