Microstructural characterisation of interpenetrating nickel/alumina composites

D.E. Aldrich, Z. Fan*

Department of Mechanical Engineering, Brunel University, Uxbridge, Middlesex UB8 3PH, UK

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Abstract

Interpenetrating phase composites (IPCs) are a new class of composite materials in which both phases are three-dimensionally (3D) continuous. Such interpenetrating microstructures offer improved combinations of mechanical and physical properties and enhanced damage tolerance. However, identifying those composites containing interpenetrating phases has been a challenge. A study was performed on the microstructures of some nickel/alumina composites that had been produced by hot pressing powder blends of various volume fractions of nickel and alumina. The composite microstructures were characterised in terms of grain size and contiguity to establish the distribution of the phases. Two different techniques, preferential etching and resistivity measurements, were used to determine which compositions displayed interpenetrating phases. © 2001 Elsevier Science Inc. All rights reserved.

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1. Introduction

Advances in composite science and technology have resulted in the design of microstructures for specific purposes. Research has progressed on from traditional composite materials with discrete, dispersed additions and has focused on incorporating larger quantities of second phase reinforcement or the utilisation of processing routes that result in composites with a connected second phase. This new class of composite materials has been termed interpenetrating phase composites (IPCs) and has attracted much interest over the past 10 years. The desire behind IPCs is to deliberately form a material in which each phase will span or percolate throughout the microstructure. This will result in a material with multi-functional characteristics [1], each phase contributing its properties to the macroscopic properties of the composite. Two differing properties such as strength and conductivity can be optimised in the same material. As a result of the three-dimensional (3D) interpenetrating structure, the composite properties will be isotropic and may also lead to significant improvements in fracture resistance.

The processing and properties of metal/ceramic IPCs have been reported by a number of researchers [2–6]. One of the difficulties in producing IPCs is controlling the 3D microstructure that is formed and it is therefore also important to be able to characterise the interconnected nature of the phases in the composite. Most of the investigations have been focused on the mechanical and physical properties of the IPCs produced. Few investigations provide any quantitative information regarding the interconnected nature of the composites that have been formed. Determina-
tion of whether the nature of the phases is interpenetrating is usually based on qualitative judgements from composite micrographs obtained from a two-dimensional (2D) section. This is a consequence of the lengthy and difficult techniques that are necessary to quantify the interconnected nature of both phases.

To enable full characterisation of the composite, visualisation of the microstructures may be useful in appreciating the 3D nature of the phases. This can be achieved using computational image reconstruction from serial sectioning of the microstructure as reported by Li et al. [7]. The technique of X-ray microtomography [8] has also been used to generate 3D images of composite materials. However, this technique is still not widely available in materials laboratories and more importantly the scale of the microstructure also has to be sufficiently large for this technique to be effective. It has become evident that with the advances in IPCs there is a need for simple methods to provide quantitative information on the connected nature of the phases and also more rapid techniques to determine whether the phases are interpenetrating. This study proposes the use of techniques by which the interconnected nature of the composite phases can be quickly determined.

The present study is concerned with the characterisation of various Ni–Al2O3 composites that had been produced by a powder blending and hot pressing route. The composite microstructures were quantified in terms of grain size and the contiguity parameter to establish the distribution of the nickel and alumina phases in the composites produced. Two different techniques were used to establish the interpenetrating nature exhibited by the phases in the IPCs. Electrical resistivity measurements were used to determine whether the nickel phase was continuous and the nickel phase was etched out of the composites with dilute nitric acid to see if a self-supporting continuous network of alumina had formed.

2. Experimental

Composites were produced by hot pressing nickel and alumina powder blends containing nickel volume fractions of 0.075, 0.15, 0.25, 0.35, 0.50, 0.65, and 0.85. The alumina powder used was CT3000SG α-alumina (Alcoa Industrial Chemicals Europe) with an average particle size of 0.7 μm and purity of 99.8%. The nickel powder used was Inco 210 filamentary nickel powder of Fisher subsieve size 0.7 μm supplied by Inco Speciality Powder Products (Swansea, UK). This nickel powder morphology was selected to influence the connected nature of the nickel phase in the composites. A micrograph of the filamentary nickel powder is shown in Fig. 1. The powders were blended by mixing in a glass jar in propan-2-ol on a roller mill at 160 rpm for 1 h prior to drying and then lightly crushed with a mortar and pestle to form a free flowing powder. The powder blends were hot pressed in a graphite die in a flowing argon atmosphere to form dense pellets of diameter 25 mm. Pure alumina and nickel pellets were also produced. Full details of the mixing procedure and the processing conditions used to consolidate the powders can be found in an earlier paper [9]. The bulk density of each composite was measured using the Archimedes technique and X-ray diffraction was performed on each sample to check the compositions.

To allow microstructural observation, all hot-pressed samples were sectioned using a Struers Accutom-5 diamond saw cutting parallel to the pressing direction and then mounted in PMMA cold curing resin. They were then successively ground using P400, P800, P1200, and P2400 Grade SiC paper and polished using 6-μm and then 1-μm diamond paste. A two-stage chemical route was used to etch the composite microstructures. Firstly the nickel in the composites was swab etched for 1–2 min using 8 parts nitric acid, 5 parts acetic acid, and 5 parts distilled water etchant until the grain boundaries were revealed. Micrographs of the grain boundaries were taken using a JEOL JXA840A scanning electron microscope (SEM). The composites were sputter coated with Au/Pd using an E5000 SEM coating unit (Polaron Equipment, UK) at 20 mA and an accelerating voltage of 1.2 kV. The alumina in the composites was etched by immersing the samples in 85% phosphoric acid at 250 °C for 2–3 min. Care had to be taken not to over etch particularly for the low alumina volume fraction composites. The microstructures were again photographed using the SEM.

The concept of contiguity (C) can be used to quantify the connected nature of the phases in a composite. Gurland [10] defined contiguity as the fraction of the internal surface of an α phase shared...
with other \( \alpha \) phase particles in an \( \alpha-\beta \) two-phase mixture. The contiguity of a phase varies between 0 and 1 as the distribution of one phase in the other changes from completely dispersed to a fully agglomerated structure. The interfacial areas can be obtained using a simple method of counting intercepts with grain and phase boundaries on a polished plane of the microstructure and the contiguity can be given by the following equations [10],

\[
C_\alpha = \frac{2N_{\alpha\alpha}^{\alpha\alpha}}{2N_{L}^{\alpha\alpha} + N_{L}^{\alpha\beta}} \quad (1)
\]

\[
C_\beta = \frac{2N_{\beta\beta}^{\beta\beta}}{2N_{L}^{\beta\beta} + N_{L}^{\alpha\beta}} \quad (2)
\]

where \( C_\alpha \) and \( C_\beta \) are the contiguity of the \( \alpha \) and \( \beta \) phases, \( N_{\alpha\alpha}^{\alpha\alpha} \) and \( N_{L}^{\alpha\beta} \) are the number of intercepts of \( \alpha/\alpha \) and \( \beta/\beta \) interfaces, respectively, with random line of unit length, and \( N_{L}^{\alpha\beta} \) is the number of intercepts of \( \alpha/\beta \) interfaces with a random line of unit length. These equations are valid for any particle size, shape, and distribution.

A series of random straight test lines were drawn on the micrographs of the etched nickel and the number of intercepts of the lines with nickel–nickel and nickel–alumina grain boundaries were counted. The same number of test lines was drawn on the micrographs of the etched alumina and the intercepts of the test lines with the alumina–alumina grain boundaries were counted. At least 500 intercept points were counted for each sample. The phase contiguities were calculated using Eqs. (1) and (2).

The mean intercept length method was used to measure the grain sizes of the nickel and alumina phases in the composites from micrographs of the etched composite phases. Point sampling was employed using a simple method of counting intercepts with grain and phase boundaries on a polished plane of unit length, and the mean intercept length measured. A total of 150 intercepts of the lines with nickel–nickel and nickel–alumina grain boundaries were counted. At least 500 intercept points were counted for each sample. The phase contiguities were calculated using Eqs. (3) and (4) proposed by Fan et al. [11],

\[
C_\alpha = \frac{f_\alpha R}{f_\alpha R + f_\beta} \quad (3)
\]

\[
C_\beta = \frac{f_\beta}{f_\alpha R + f_\beta} \quad (4)
\]

where \( R \) is the grain size ratio in a random mixture of equiaxed \( \alpha \) and \( \beta \) particles defined as \( R = d_\beta/d_\alpha \), where \( d_\alpha \) and \( d_\beta \) are the grain sizes of the \( \alpha \) and \( \beta \) phases, and \( f_\alpha \) and \( f_\beta \) are the volume fractions of the \( \alpha \) and \( \beta \) phases. By comparing the calculated contiguity with the measured values, it is possible to get an idea of the randomness of the powder blending route and therefore the distribution of the nickel and alumina phases.

The electrical resistivity of each of the composites was measured to determine the degree of connectivity of the metallic phase and establish at which composition the metal phase percolated. The range of values that the composites displayed was so large that two techniques had to be used to measure the electrical resistivity. For the conductive samples a four-point probe test method was employed [12]. Four sharp needles each 1 mm apart were pressed onto a polished, flat composite surface. All composite surfaces had been polished to a 1-\( \mu \)m finish using diamond paste. The outer two needles injected the current into the sample and the potential difference was measured across the inner two needles. The equipment was calibrated using samples of known resistivity prior to measurements being taken and a constant current of 2 A was used for all measurements on the composites. All measurements were carried out at 20 \( \pm \) 1 °C. The resistivity \( \rho_c \) was calculated using Eq. (5),

\[
\rho_c = 2\pi d \frac{V}{I} \quad (5)
\]

where \( d \) is the distance between the needles, \( V \) is the voltage drop, and \( I \) is the current. For the higher resistivity samples out of the range of the four-point probe technique, an AC impedance analyser was used. The sample contact areas were coated with quick drying silver paint and clamped between two platinum electrodes. A potential difference of 1 V was applied across them while a frequency sweep was performed from 0.1 Hz to 1 MHz via a Solartron SL1255 HF frequency response analyser interfaced to a PC running Z View 2 software. All measurements were performed at 20 \( \pm \) 1 °C. This leads to a direct measure of resistance from a reactance versus resistance plot allowing the resistivity to be calculated from the sample dimensions. The equation (Eq. (6)) was used to calculate resistivity \( \rho_c \):

\[
\rho_c = \frac{RA}{I} \quad (6)
\]

where \( R \) is the resistance, \( A \) is the area of the sample, and \( l \) is the length of the sample between the electrodes.

To investigate the volume fraction of alumina at which a continuous network of alumina was formed, 50% concentrate nitric acid was used to etch out the nickel phase from the composite microstructures. The samples were etched for intervals of 15 s and periodically observed under a light microscope until no
nickel phase remained. This was to see if the remaining alumina had formed a self-supporting continuous skeletal structure.

3. Results and discussion

All the composites produced had relative densities greater than 96.5%. XRD confirmed that they contained only nickel and $\alpha$-alumina phases. The composites formed from the nickel and alumina powders are shown in Fig. 2. The microstructures are quite uniform and the nickel phase in the composites is very finely dispersed. The composite containing 15 vol.% nickel is shown in Fig. 2a. The nickel particles are very fine, of average grain size 1.3 $\mu$m, and are well distributed in the alumina matrix. As the volume fraction is increased to 25 vol.% the nickel morphology becomes more connected with significant contact between nickel particles and the grain size increases to 1.6 $\mu$m. Further addition of nickel results in larger grains and the nickel becomes interconnected. The

Fig. 2. Micrographs of the nickel–alumina composites showing (a) 15, (b) 25, (c) 35, (d) 50, (e) 65, and (f) 85 vol.% nickel composites. (Balance of composition is alumina.) The dark phase is alumina and the light phase is nickel.
measured grain size values are presented in Table 1. There are signs of agglomeration in the alumina phase in some of the microstructures although this would be expected when using a powder metallurgy processing route. The nickel volume fraction was increased up to 85 vol.%, and Fig. 2f shows the nickel as the matrix phase with very fine discretely dispersed alumina inclusions.

The initial filamentary nature of the nickel powder is not clearly visible in the dense composite microstructures. This suggests that attrition of the nickel powder occurs during powder mixing, leading to the branched nickel chains breaking down into smaller particles with a reduced aspect ratio. This results in the finely dispersed microstructures that are shown in Fig. 2. Attrition of the filamentary nickel powder during mixing warrants further investigation to understand the effect of the mixing process and therefore the resulting interconnected nature of the nickel phase in these composites. Refinement of the mixing procedures may also be necessary to reduce agglomeration of the powders, although random mixing is not essential, as the aim is the formation of two interconnected phases.

Table 1 contains all the microstructural data for the alumina and nickel phases in the composites. A graph showing the measured and calculated contiguity for the alumina phase in the composites plotted against volume fraction of alumina can be seen in Fig. 3. Curves are also plotted for the contiguity parameter calculated at different grain size ratios \( \frac{R_N}{R_A} \) when assuming a random mixture of grains. The measured alumina contiguity generally follows the trend of that calculated from the grain size measurements when assuming random mixing although at some volume fractions there is divergence of the curves. For volume fractions of alumina up to around 0.5, the contiguity of the alumina phase is higher than that calculated for a random mixture of grains indicative of alumina agglomeration. Above this volume fraction, the measured contiguity of the alumina phase falls below the calculated value. Fig. 4 shows the measured and calculated contiguity of the nickel phase in the composites plotted against the nickel volume fraction. Overall, there is reasonably good agreement between the curves. This indicates that the mixing in the composites results in a nickel phase that is fairly randomly distributed. At higher volume fractions of nickel, the measured contiguity increases above that calculated from grain size measurements.

It should be noted that the contiguity measurements on the composite phases will be subject to inaccuracies resulting from difficulties experienced in the etching and subsequent measurement of the phase contiguity, as well as being affected by the number of measurements taken. They do however give useful indications of the connected nature of the phases and the randomness of the mixing process.

Fig. 3. Measured and calculated contiguity parameter for the alumina phase plotted against volume fraction alumina for the composites. Also shown here are the theoretically calculated contiguity data for composites with random distributions and different grain size ratios as indicated by the number attached to each dotted line.
A graph of electrical resistivity plotted against volume fraction of nickel for the composites can be seen in Fig. 5. The electrical resistivity of the composite containing a nickel volume fraction of 0.075 was measured as $2.503 \times 10^9 \, \Omega \, m$, slightly lower than that for pure alumina ($4.515 \times 10^9 \, \Omega \, m$). This is a very high resistivity value and shows the composite to be an insulator with the nickel particles/phase isolated within the alumina matrix. The transition from insulating to conducting behaviour occurs between 0.075 and 0.15 volume fraction nickel with the percolation concentration being taken as 0.13. The electrical resistivity of the 0.15 volume fraction nickel composite is $2.270 \times 10^{-4} \, \Omega \, m$ and drops to $2.231 \times 10^{-6} \, \Omega \, m$ when the volume fraction of nickel is increased to 0.25. Therefore, an interconnected network of nickel was said to form at nickel volume fractions of 0.25 or higher as this is the composition at which the composite resistivity starts to become comparable to that of pure nickel. The microstructure of the 0.25 volume fraction nickel composite showing the interconnected nickel phase can be seen in Fig. 2b.

The nickel phase was removed from the composites by etching with dilute nitric acid and it was found that in the 0.35 volume fraction alumina composite a self-supporting networked alumina structure was left upon removal of the nickel phase from the composite sample. Combining the observations of the microstructures of the composite with the nickel phase removed with the electrical resistivity measurements enables the composites that display interpenetrating nickel and alumina phases to be identified. These are those with nickel volume fractions of 0.25, 0.35, 0.5, and 0.65. Micrographs of these composites showing their interpenetrating microstructures can be seen in Fig. 2b–e.

Simple visual inspection of 2D microstructures has generally been the previous method used by researchers of IPC materials to draw conclusions on
the connected nature of the composite phases. However, it is clearly evident that these judgements provide only qualitative information that is based on an investigators own opinion as to whether a phase is interpenetrating. Therefore, the technique outlined here of characterising the microstructures through the use of the contiguity parameter and the use of resistivity measurements and removal of the metallic phase from the composites allows more advanced quantitative conclusions to be reached on the nature of these IPC microstructures.

4. Conclusions

The contiguity data for the nickel/alumina composites formed in this study have been useful in quantifying the microstructures produced. The data had also been helpful in understanding the mixing process and the subsequent distribution of the composite phases. A combination of the two simple techniques of electrical resistivity measurements and dissolving the nickel phase out of the composites enabled those compositions that displayed interpenetrating nickel and alumina phases to be identified. This is a simple and valuable method that can be used for the determination of the phase morphology in this new type of composite microstructure.

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