JOURNAL OF MATERIALS SCIENCE 7 (1972) 427–434

The Strength and Fracture Toughness of Polycrystalline Magnesium Oxide Containing Metallic Particles and Fibres

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The transverse rupture strength of hot-pressed and annealed composites of magnesium oxide and dispersed metallic phases (nickel, iron, cobalt) increases with increasing volume fraction of metal and annealing temperature. The strengthening effect of the metal is attributed to an inhibition of grain growth while flaw healing occurs during the annealing of the composites.

The strength of magnesium oxide hot-pressed with nickel fibres is not affected by the volume fraction of fibre or the annealing temperature, and is comparable to the strength of porous magnesia. However, the work of fracture, though insensitive to heat-treatment, increases by at least two orders of magnitude for a moderate volume fraction of randomly oriented fibres. Mechanisms of energy absorption during the fracture of composites containing weakly bonded, non-aligned fibres are discussed. They include the work done in plastically deforming the fibre as it is withdrawn from its socket. It is concluded that this mechanism may be of importance in composites containing very weakly bonded ductile fibres.

1. Introduction

The inherently brittle nature of ceramic materials leads to the conclusion that the most hopeful method of enhancing the toughness of a ceramic is to incorporate within it a second phase which will interfere with the propagation of a crack in the ceramic matrix. For this purpose the use of a metallic second phase is particularly attractive, because of the possibility of exploiting its inherent toughness.

In a previous study [1] it was found that the incorporation of small volume fractions of metallic phases in single crystal magnesium oxide does not substantially increase the effective surface energy for crack propagation.

The effect of higher volume fractions of metal is the subject of the present work. Because of the difficulty of incorporating high volume fractions of metal in a single crystal, composites of magnesium oxide and metal have been fabricated by hot-pressing. Metal in the form of both wire and powder has been used. The relation between the microstructures developed and the strength, fracture toughness and work of fracture of the composite have been studied.

2. Experimental Procedures

2.1. Hot-pressing

The hot-pressing was carried out in a graphite die 1.25 in. in internal diameter, suitably mounted in a water-cooled mild steel vacuum chamber. A cylindrical furnace with Kanthal windings was used to heat the die, and the top furnace covers were also used as a rough guide for the thrust rod which was connected to a hydraulic press. Pt-Pt 13% Rh thermocouples were placed near the windings and in the walls of the graphite die.

Composites with metallic particles were made by mixing Fisher M-300 grade magnesium oxide powders with Johnson and Matthey 300 mesh metal powders, together with small amount of M-300 grade LiF. The amount of LiF used in all cases did not exceed a few percent. The mixed powders were then transferred to a clean graphite die and hand-pressed before inserting in the furnace. Composites containing short nickel

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fibres 3 to 5 mm in length of different diameters were fabricated by mixing the fibres with MgO powders, together with 1% by weight of LiF. The hot-pressing was carried out in two stages, following the technique used by Miles and Sambell [2] for vacuum hot-pressing of dense polycrystalline magnesium oxide: 750 psi at 600°C for $\frac{1}{2}$ h and 1500 psi at 900°C for 1 h at about 10^{-3} torr. The composites were usually free from gross cracking, as would be expected from the fact that the metals have somewhat higher coefficients of expansion than MgO. A partially translucent fibre composite is shown in fig. 1. The graphite die and punches were changed after several runs. The addition of LiF greatly facilitates the densification of the composites apparently acting as a high-temperature lubricant. Most of the LiF came out as small beads at the bottom of the graphite die. Several densification mechanisms have been discussed by Hart *et al* [3] and will not be further discussed here.

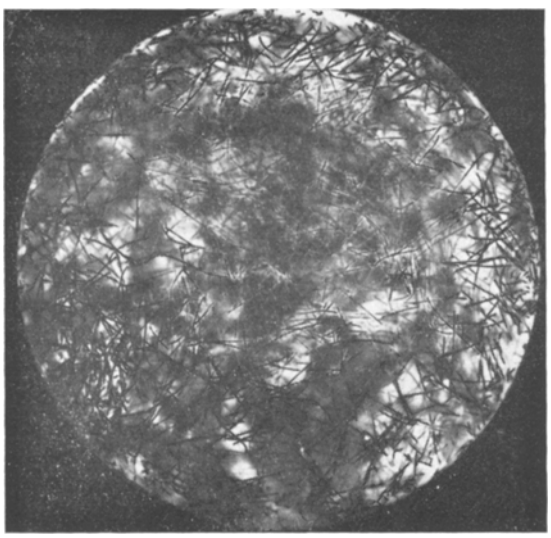

Figure 1 As-pressed composite of MgO with nickel fibre showing partial translucency (× 2.4).

2.2. Specimen Preparation and Mechanical Testing

The composites were machined into rectangular bars 22 × 4 × 3 mm. Several bars were placed on an alumina crucible separated by thin slices of single crystal magnesium oxide and heat-treated in a molybdenum-wound furnace at 0.10 torr for 10 h at 1000, 1200 and 1400°C respectively. (The residual gas in the annealing atmosphere was probably hydrogen, which leaked through the alumina furnace tube from the chamber containing the windings.) The furnace was slowly cooled down to 200°C and the specimens were then removed. The as-pressed and heat-treated slabs were mechanically polished on 600 grit paper. Specimens for determining fracture toughness and work of fracture were prepared by notching annealed slabs, using a diamond slitting-disc 350 μm in thickness. The notched and unnotched specimens were fractured at room temperature on a three-point bending jig with a 19 mm span between the outer knife edges on an Instron machine, at a cross-head speed of 0.02 cm/min. Specimens were designed such that the force is either applied parallel or perpendicular to the direction of pressing of the composite to check for anisotropy. As far as possible three specimens were used for each observation. The mechanical tests performed were similar to those reported by Davidge and Tappin [4], and Evans and Davidge [5]. The density was determined by a displacement method and the volume of pores was calculated from the observed density. The interparticle mean free path λ was determined by the intercept method [6], i.e.

$$\lambda = \frac{1 - V_f}{N_f} \tag{1}$$

where V_f is the volume fraction of the second phase and N_f the number of intersections of particles by a straight line of unit length.

The determination of modulus of rupture, work of fracture and effective surface energies will be briefly described. The modulus of rupture of a rectangular bar in three point bending is given by

$$\sigma_f = \frac{3P_fL}{2bd^2} \tag{2}$$

where P_f is the load at fracture, L is the distance between the knife edges, b the width and d the thickness of the bar. Brown and Srawley [7] have expressed σ_f in terms of a modified Griffith equation given by

$$\sigma_f = \frac{1}{Y}\left(\frac{E(2\gamma_I)}{c}\right)^{\frac{1}{2}} \tag{3}$$

where E is the Young Modulus, γ_I, the effective surface energies for crack initiation, c the crack length, Y is the constant depending on the geometry of the specimen and testing condition. γ_I can be evaluated if the nominal fracture stress

of a bar having a crack of known length c and the Young's Modulus E of the composite are known. The effective Young's Modulus can be approximated by a law of mixtures

$$E^* = E_1V_1 + E_2V_2 \quad (4)$$

where E_1 and E_2 are the Young's Modulus of dispersed phase and matrix respectively, V_1 and V_2 are the corresponding volume fractions. Equation 4 overestimates the modulus, mainly by not allowing sufficiently for the effect of porosity, but the accuracy of the results hardly justifies a more exact estimate.

It should be noted that equation 3 applies strictly to a sharp notch. The applicability for a machined notch has been justified by Evans and Davidge [5] by comparing the fracture stress of a sharp crack and machined notch of equivalent depth in theoretically dense magnesium oxide. They found that the surface energy for crack initiation for a sharp crack is about 10% less than that of machined notch. This led them to conclude that the stress concentration associated with a sharp crack is not very different from an array of penny-shaped cracks which are formed at the base of the machined notch. Assuming that a similar situation exists at the root of the machined notch in our composites, the effective surface energies for crack initiation, γ_I, can be computed by combining equations 2 and 3 giving

$$\gamma_I = \frac{9}{8}\frac{P_f^2L^2Y^2c}{Eb^2d^4} \quad (5)$$

where P_f here refers to the fracture load of the notched bar. The work of fracture, γ_f is given by the total work done under the load-deflection curve, divided by the area of the unnotched part of the beam [8].

3. Results

3.1. Magnesium Oxide containing Metallic Particles

Composites were found to have porosities ranging from 3 to 7%, these values not being significantly affected by annealing. The spacing of the metal particles was on the order of 10 μm, varying from 11 μm at a volume fraction of nickel of 0.16 to 6 μm at a volume fraction of 0.36. Fig. 2 shows the trends in fracture stress for MgO-Ni composites. The results for MgO-Fe and MgO-Co were essentially similar and are not included.

The fracture stress increases with increasing volume fraction of metal, after annealing the composite. The effective surface energy for crack initiation γ_I and the work of fracture γ_f show broadly similar trends to the fracture stress, but the value of γ_f is in the range 260 to 740 Jm^{-2} while the values of γ_I lie in the range from 10 to 60 Jm^{-2}, i.e. γ_f is an order of magnitude larger than γ_I.

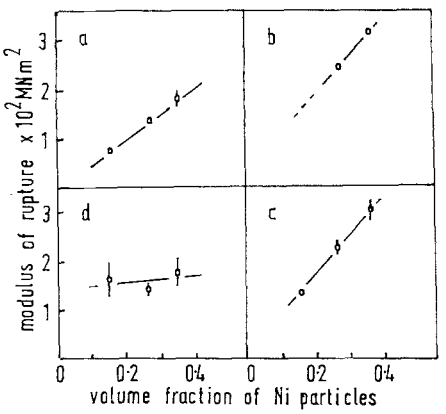

Figure 2 Modulus of rupture of composites containing different volume fraction of nickel particles (a) annealed at 1000°C; (b) annealed at 1400°C; (c) annealed at 1200°C; (d) as-pressed.

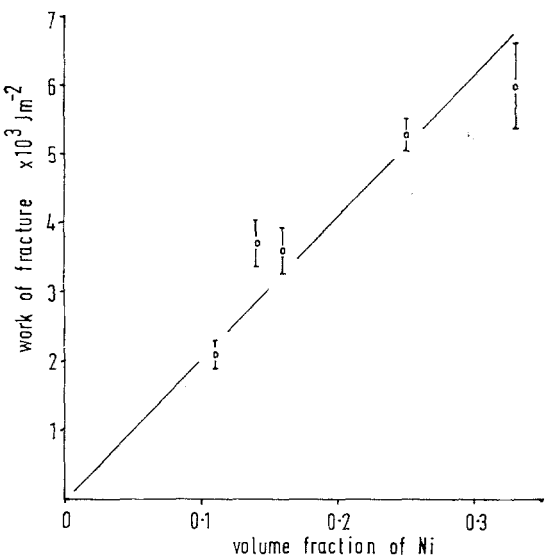

Figure 3 Work of fracture for different volume fractions of nickel fibres.

3.2 Magnesium Oxide containing Random Ni Fibres

The strength is not significantly affected by volume fraction and heat-treatments, and is generally lower than the strength of theoretically

TABLE I

Volume fraction of nickel fibre	Diameter of fibre μm	Volume fraction of pores	Mean work of fracture $\times 10^3$ Jm^{-2}	Mean modulus of rupture MNm^{-2}
0.33	89	0.07	6.0 $\pm$ 0.63	82 $\pm$ 2.3
0.25	89	0.02	5.3 $\pm$ 0.25	79 $\pm$ 5.7
0.16	89	$\sim$ 0 (translucent)	3.6 $\pm$ 0.36	88 $\pm$ 1.7
0.14	89	$\sim$ 0 (translucent)	3.7 $\pm$ 0.36	95 $\pm$ 6.0
0.11	89	$\sim$ 0 (translucent)	2.1 $\pm$ 0.22	93 $\pm$ 7.0
0.05	38	$\sim$ 0 (translucent)	0.5 $\pm$ 0.1	83 $\pm$ 3.5

dense polycrystalline magnesium oxide, but comparable to the strength of commercial magnesia. The work of fracture is not significantly affected by heat-treatments, but is generally at least two orders of magnitude higher than dense polycrystalline magnesium oxide. Since neither strength nor work of fracture were changed by annealing, the results averaged over all heat treatments are presented in table I together with the standard deviations. The trend of work of fracture with volume fraction for 89 μm diameter fibres is shown in fig. 3.

4. Discussion

4.1. Magnesium Oxide with Metallic Particles

Since the morphologies of the metallic particles do not alter appreciably with annealing temperatures, the improvement in the strength with volume fraction of metal, which occurs only after annealing, cannot be directly attributed to a decrease in interparticle spacing.

Grain growth during the annealing of powder composites was observed in regions of relatively pure MgO which arose due to incomplete mixing of the powders, an initial grain size of the order of 1 μm increasing to one of the order of 10 μm after annealing at 1400°C. It is probable that grain growth was inhibited in regions of higher metal concentration although the difficulty of measuring the MgO grain size in such regions prevented us from confirming this. The density of the composites did not increase significantly during annealing. However a reduction in the sharpness of flaws in the as-pressed material, together with an inhibition of grain growth by the metal particles may account for the combined effects of annealing temperature and volume fraction of metal.

The strength of composites with the highest volume fraction of metal, 0.36, annealed at 1400°C is matched by pure and theoretically dense MgO only when the grain size of the latter is small ($\sim$ 5 μm) and the surface finish good [5, 9].

The surface energy for crack initiation, γ_I has values similar to those which have been observed in similar tests of pure MgO polycrystals [5], and other polycrystalline ceramics [4].

However the work of fracture γ_f is an order of magnitude larger than γ_I. Davidge and Tappin [4] observed that in polycrystalline alumina, $\gamma_f \approx 1.5\gamma_I$ for initial crack depths similar to those used in the present work. A relatively high γ_f/γ_I ratio of approximately 2.5 in graphite was attributed to a tortuous crack path. In our composites, the crack path through the MgO was mainly intergranular (fig. 4) and a considerable amount of subsidiary cracking was observed, which may go some way towards explaining the high value of γ_f. Although the metal MgO interface is believed to be weak (from the observed weakness in the case of fibre composites – see below), some plastic deformation of metal particles can be expected to occur where they are

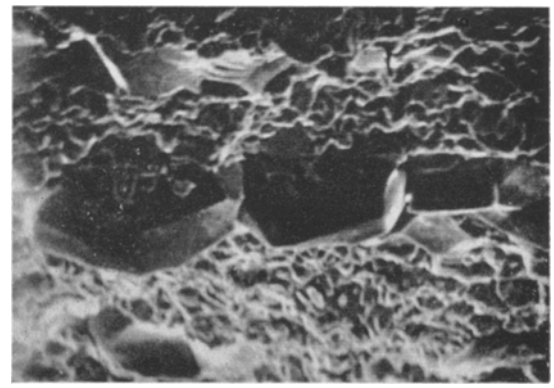

Figure 4 Scanning micrograph of fracture surface of magnesium oxide containing iron particles, volume fraction 0.39, annealing temperature 1400°C (× 650).

mechanically trapped between separating MgO surfaces. It is difficult to estimate the magnitude of this effect, but it is tentatively suggested that it contributes significantly to γ_f.

4.2. Fibre composites

The strength of the fibre composites is not dictated by the grain size or inter-fibre spacing but by the severity of the flaws introduced during the fabrication of the composites as a result of the microstresses due to the difference in the thermal coefficients of expansion between the matrix and fibres. The critical flaw size in the composites using equation 3 is found to be $\sim 82\,\mu m$, close to the diameter of the fibre, if the nominal fracture stress σ_f is taken to be 10^2 MN m^{-2}, $\gamma_I \sim 10$ J m^{-2}, $E^* \sim 2.8 \times 10^5$ MN m^{-2} (for a volume fraction of 0.16 nickel fibre), $Y = 2.5$. Flaws of this dimension can be formed at the interface between the fibre and the matrix, since the higher coefficient of expansion of the nickel fibre sets up a tangential compression and a radial tension in the matrix close to the fibre. The flaw size is further magnified if several fibres are bundled together. The fracture of fibre composites is likely to be initiated at these flaws.

Examination of the fracture surfaces, fig. 5, shows that both pull-out and rupture of fibres take place. Fibres rupture some distance away from as well as near to the crack plane. The incidence of fibre rupture appears to be more frequent with fibre of smaller diameter. The magnesium oxide fractures intergranularly. In some instances, grains of MgO can be seen sticking on the fibres, fig. 6, suggesting that some bonding has occurred. The longer fibres which have been pulled out are often bent. To account for the high work of fracture, the individual contributions due to pull-out, deformation and rupture of the fibre and debonding between the fibre and matrix are discussed.

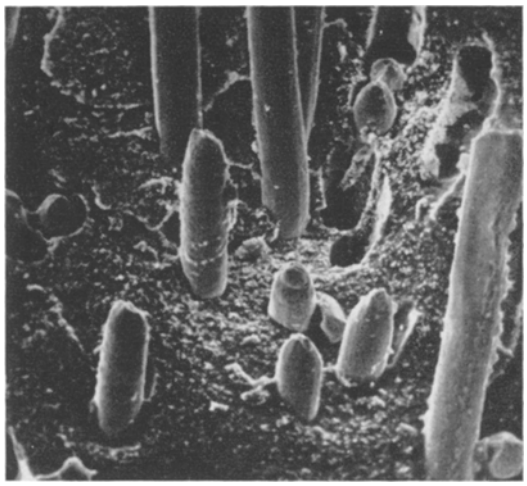

Figure 5 Fracture surface of fibre composite showing pull-out and rupture of nickel fibres (× 150).

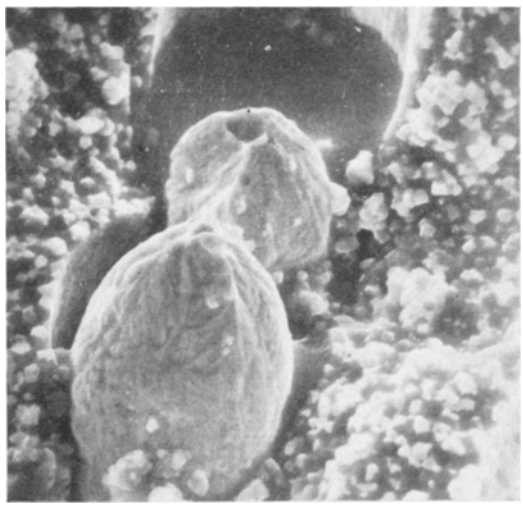

Figure 6 Enlarged view of ruptured fibres (× 600).

4.2.1. Contribution due to rupture of fibres

It is found that the work to fracture an extracted fibre of 89 μm in diameter (1.6×10^{-4} J) was an order of magnitude less than the as-received fibre (2×10^{-3} J). The reduction in the fracture stress and ductility of the extracted fibre indicate that the fibres are damaged during fabrication and possibly hydrogen embrittled since the composites were annealed in a dilute atmosphere of hydrogen. The degradation in the mechanical properties of nickel wires annealed in hydrogen has been reported by Windle and Smith [10]. For specimens containing 0.16 volume fraction of nickel fibres of 89 μm diameter, the contribution to the work of fracture due to rupture of 20% of the approximately 10^7 fibres intersecting 1 m^2 is 2.5×10 Jm^{-2}. This is at least an order of magnitude less than the total work of fracture.

4.2.2. The contribution due to debonding

The work due to debonding [11, 12] is found to be given by $3(\sigma_f)/E_f \,.\, W_p$, where σ_f is the fracture stress of the fibre, E_f the Young Modulus of the fibre and W_p the work of fracture due to pull-out of fibre. The contribution to the total

work of fracture due to debonding can be neglected since $\sigma_f/E_f \simeq 10^{-3}$.

4.2.3. Contribution due to pull-out on assumption of aligned fibres

It is known that during fibre pull-out whether in a ductile or a brittle matrix, a shear stress τ acting at the fibre-matrix interface resists the pull-out. The fibre breaks with a fracture stress σ_f when the load transfer length reaches a limiting value, giving [13, 14]

$$l_c = \frac{r\sigma_f}{\tau} \tag{6}$$

where l_c is the critical length of the fibre which must be exceeded before the fibre will break, τ the interfacial shear stress, and r the radius of the fibre. τ can be estimated from equation 6 if the fracture stress σ_f and the critical length l_c are known. Because the crack will always intersect some fibres at a distance less than $l_c/2$ from their ends, some pull-out must always be observable. A method of estimating $l_c/2$ is to take it equal to the largest pulled-out length of fibre observed. If $l_c/2 = 1.5$ mm, $\sigma_f = 1.97 \times 10^8$ Nm^{-2}, $r = 44.5 \times 10^{-3}$ mm, τ is then 3 MNm^{-2}. This argument is not seriously affected by the fact that the fibres are not aligned. Because many fibres are intersected by the fracture surface, there will be a considerable number which do in fact intersect the fracture surface at an angle close to 90°. However, because of the possibility that l_c is underestimated, the value of 3 MNm^{-2} can be regarded as an upper limit for τ. The work of fracture which would arise if the number of fibres which are observed to have been pulled out of unit area of fracture surface were pulled out from an aligned composite can now be estimated. The density of pulled-out fibres observed for the specimen having a volume fraction 0.16 of fibres was approximately 10^7 fibres/m^2. The work of pulling out an aligned fibre of length l is on average [13]

$$W_p = \frac{\pi r \tau l^2}{12} \tag{7}$$

Substituting the known values of r and l and the estimated value of τ into equation 7 gives a work of fracture of approximately 3×10^3 Jm^{-2}. This is of the same order of magnitude as the observed work of fracture (fig. 4). However, the physically distinct nature of the pull-out process for randomly oriented fibres requires further consideration.

4.2.4. The effects of misaligned fibres

The fact that the pulled-out fibres are often bent and some fragmentation of the matrix is always observed during pull-out suggest that some additional mechanisms for energy absorption must occur during pull-out of fibres not normal to the fracture plane. The following mechanisms may be proposed. (1) enhancement of friction stress near the exit point of the hole from which the fibre is being withdrawn, (2) plastic bending which must be propagated along the fibre as it is being withdrawn from its hole. The effects are shown in fig. 7. If the fibre is at a small enough angle to the fracture plane it will not be able to pull out and will either break, fig. 7c or break through the brittle matrix, fig. 7d. The occurrence of the latter leads to the fragmentation of MgO near the fracture surface.

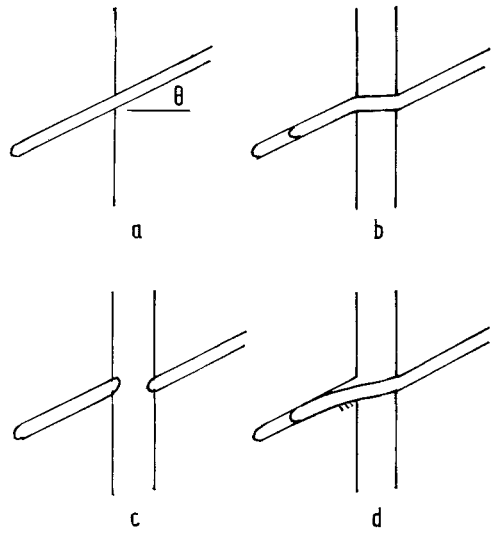

Figure 7 Effects occurring when a matrix crack intersects a non-aligned fibre. (a) initial crack; (b) pull-out with bending; (c) fracture of wire; (d) fracture of matrix.

The contributions to the work of fracture due to enhanced friction and fragmentation of the matrix are difficult to estimate. The plastic deformation of the fibre during pull-out can be discussed more quantitatively.

Consider a rather rigid matrix with ductile fibres randomly distributed in a plane. The initial deformation of the fibre as the crack faces move apart appears to approximate a shear through the angle θ. Assume then that the material between the crack faces has been subjected to a

shear of tan θ. The work done per unit volume is then

$$w_s = \tau_f \tan \theta \tag{8}$$

where τ_f is the shear flow stress of the fibre (neglecting work hardening). As this work must be supplied by the tensile force σA in the fibre moving through a distance A^{-1}, where A is the cross-section, then

$$\sigma = \tau_f \tan \theta \tag{9}$$

If the tensile fracture stress $\sigma_f = 2\,\tau_f$, for example, the wire will break if $\tan \theta > 2$ or $\theta > 64°$ even in the absence of interfacial friction. In practice the constraint of the matrix may not enforce a shear except perhaps initially, and the fibre will rather bend into alignment. The shearing mode must give an upper limit to the plastic work.

This upper limit is easily calculated for the case of zero interfacial shear stress, and $\sigma_f = 2\,\tau_f$. From equation 8, the work done to pull out a fibre length l at an angle θ to the crack plane normal is on average (assuming that the shorter segment always pulls out)

$$w = \frac{\pi r^2}{4} \cdot l \cdot \tau_f \tan \theta \tag{10}$$

For a volume fraction V_f of fibres randomly oriented within a plane, the total work is

$$W = \int_0^{1.12} w \cdot N(\theta)\, d\theta \tag{11}$$

where $N(\theta)\, d\theta$ is the number of fibres intersecting unit area of the fracture surface at angles to the fracture plane normal within the range from θ to $\theta + d\theta$. The upper limit of integration is set by the value of θ at which fibres fracture rather than pull out. Since the volume fraction of fibres within the range of angles from θ to $\theta + d\theta$ is given by $2\,V_f\, d\theta/\pi$, equating area and volume fractions gives

$$N(\theta) = \frac{2V_f \cos \theta}{\pi^2 r^2} \tag{12}$$

From equation 11,

$$W \simeq \frac{V_f\, \sigma_f\, l}{22} \tag{13}$$

Comparing equation 13 with the maximum work of fracture due to the pull out of aligned fibres of critical length [13]

$$W = \frac{V_f\, \sigma_f\, l}{12} \tag{14}$$

it is clear that the works of fracture which can be achieved by plastic deformation alone during the pull-out of randomly oriented fibres are less than those obtainable from interfacial shear in aligned fibre composites. The assumption of a bending mode of deformation, rather than shearing, gives a lower plastic work. If the radius of curvature of the bent zone is R, a volume $\pi r^2\, R\theta$ of fibre is bent through the angle θ, and subsequently straightened. The work done on this volume is then

$$w = 2M\theta \tag{15}$$

where M is the plastic bending moment. Neglecting work hardening, this gives

$$w = \frac{16}{3} \cdot \tau_f \cdot r^3\, \theta \tag{16}$$

where r is the radius of the wire. The work done per unit volume is then

$$w_s = \frac{16}{3\pi} \cdot \tau_f \cdot \frac{r}{R} \tag{17}$$

Equation 17 shows that the wire will not fracture unless the radius of bending is of the order of the radius of the wire, or less. It is not possible to estimate the total work of fracture since the value of R and its dependence on θ are not known.

The interesting feature of the work of fracture due to pull-out of nonaligned fibres is that substantial values can be obtained with fibres which are too weakly bonded, or too short to give high works of fracture when aligned. In our case however, the work of fracture appears to be similar in magnitude to that which would have been obtained with aligned fibres.

5. Summary and Conclusions

1. The strength of the composites with a volume fraction of 0.36 of dispersed metallic particles, nickel, iron or cobalt, annealed at 1400°C is matched by pure and theoretically dense magnesium oxide only when its grain size is small ($\sim$ 5 μm) and surface finish good. The increase in the strength with annealing is attributed to a reduction in the severity of flaws, the role of the metal particles being to inihbit grain growth.
2. The work of fracture, γ_f, is higher than the effective surface energy for crack initiation, γ_I, by an order of magnitude. This is attributed to plastic deformation of the dispersed metal during the opening of the crack.
3. The strength of the composites containing nickel fibres is comparable to strength of com-

mercial magnesia. The work of fracture is, however, increased by at least two orders of magnitude for a moderate volume of fraction of nickel fibres. The mechanisms of shearing or bending of misoriented fibres during pull-out have been outlined to account in part for the energy absorption during the fracture of misoriented fibre composites.

4. The results obtained suggest that the strength of the fibre composites could be improved by incorporating metal powder in addition to the fibre, particularly if the fibres are aligned in the tensile stress direction to reduce the effect of the flaws introduced by the fibres.

Acknowledgements

The authors are grateful to the Atomic Energy Research Establishment, Harwell, for financial support and to R. A. J. Sambell for useful discussions on vacuum hot-pressing techniques.

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Received 28 October and accepted 14 December 1971.