

The Microstructure and Fracture Properties of MgO Crystals containing a Dispersed Phase

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MgO crystals containing up to 40% by volume of magnesioferrite and up to 2% by volume of iron and nickel were produced by a diffusion technique followed by appropriate heat treatments. Magnesioferrite precipitate did not significantly change the effective surface energy of a crack as measured by the double cantilever beam technique. Iron and nickel precipitate was produced in the form of platelets lying on $\{100\}_{\text{MgO}}$ planes whose orientation relationships were $[001]_{\text{MgO}} \parallel [001]_{\text{Fe}}$, $[110]_{\text{MgO}} \parallel [100]_{\text{Fe}}$ with a spread of $\pm 10^\circ$, approximately, and $[001]_{\text{MgO}} \parallel [001]_{\text{Ni}}$, $[010]_{\text{MgO}} \parallel [010]_{\text{Ni}}$ with negligible spread. Despite the crystallographic orientation relationships, the metal-MgO interface appeared to be very weak; the reasons for this are discussed. The effect of the metal precipitate on crack propagation was to markedly increase the density of cleavage steps. For a volume fraction of precipitate of 0.02, this led to a small increase in the effective surface energy, on the order of 1 Jm^{-2} .

1. Introduction

In recent years, considerable effort has been devoted to the study of the mechanical properties of pure ceramic materials. A conclusion which can be drawn from this work is that ceramics are brittle at low temperatures because of the fundamental factors of lack of dislocation mobility and insufficiency of slip systems [1]. It therefore appears that any improvement in the mechanical properties of ceramics at low temperatures must lie in the direction of interfering with crack initiation or propagation in an inherently brittle matrix. From this point of view, it was decided to study the effect of second phase particles on crack propagation in MgO single crystals. Previous work on the precipitation strengthening of oxides has dealt mainly with the effect on yield stress or hardness [2, 3]. However, Hsu, Kobes, and Fine [4] reported that the precipitation of a titanium-rich phase in sapphire increased the load at which cracking occurred during indentation hardness testing. Amongst previous work on precipitation in alkali halides, a study of the interaction of cracks with gold particles in NaCl crystals [5, 6] is of particular

relevance to the present work. In this study, a dispersion of gold particles, associated with voids, was found to reduce the velocity of a propagating crack. This was linked to the observation of cleavage steps introduced by the inhomogeneities. A calculation relating the change in crack velocity to a change in the effective surface energy of the crack [6] led to the suggestion that this latter quantity was increased by a factor of between 10 and 100. In the present work we have directly measured the effective surface energy of cracks in MgO crystals containing second phase particles.

2. Experimental Procedure

MgO crystals were doped with iron or nickel by putting metal powder in contact with both sides of a cleaved slice of crystal and heating in air. In the case of iron a temperature of 1400°C was normally used; to obtain a similar penetration of nickel, a higher temperature of about 1700°C was necessary. Magnesioferrite precipitate was produced in iron-doped crystals by cooling to 1100°C and ageing for various periods. The phase diagram for the system Mg-Fe-O in air is

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shown in fig. 1. This treatment produces large dendritic precipitates (fig. 2), in contrast to the octahedral particles which are formed by ageing at 800 to 1000°C after rapidly cooling to room temperature [7]. The average volume fraction of magnesioferrite was determined from density measurements.

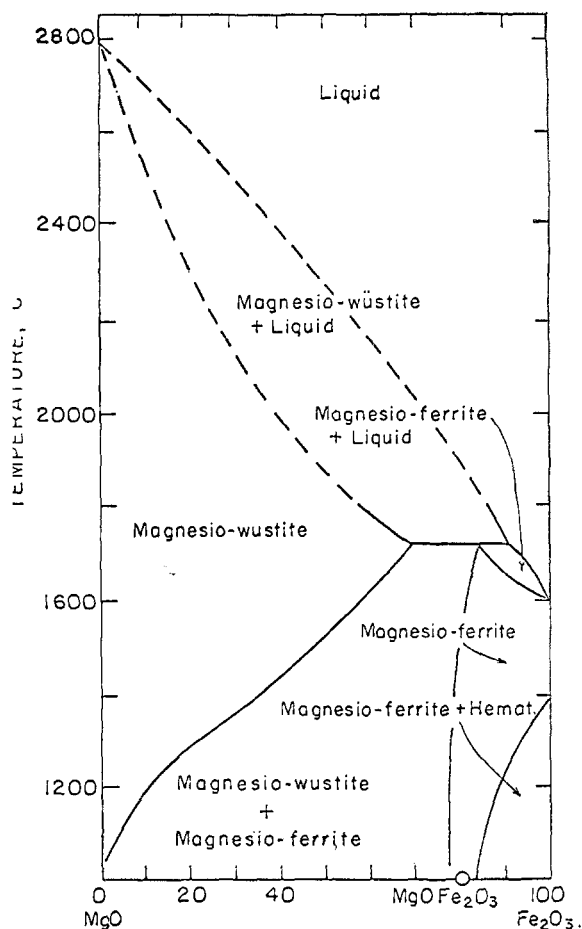


Figure 1 Phase diagram for the system Mg-Fe-O in air, which shows the regions of existence of magnesioferrite. (After Phillips *et al* [18].)

Following the procedure of Davidge [8], a precipitate of metallic iron was formed by reducing a crystal containing iron in solid solution or as magnesioferrite in an atmosphere of hydrogen, usually at 1400°C. The same technique was found to produce nickel particles in crystals containing nickel in solid solution. An alternative technique of introducing the metal directly by high temperature diffusion in vacuum or under

hydrogen was found to be unsuitable because of the limited penetration which could be obtained. By diffusing the metal in the form of oxide, a fairly uniform composition could be obtained in slices about 1 mm thick. The surfaces of the crystal were somewhat damaged by the diffusion anneal but were readily smoothed by chemically polishing in hot orthophosphoric acid.

To measure the effective surface energy of cracks, slices of crystal were partially cleaved to make double-cantilever cleavage specimens [9]. To ensure that the crack propagated in a plane of constant composition it was made parallel to the surfaces from which the diffusion had occurred. In some cases partially doped specimens were prepared so that the crack ran from an undoped into a doped region. By loading the specimens on a hard Instron machine it was possible to obtain several crack propagations and arrests in the same crystal [10].

The theory of the double-cantilever technique for measuring effective surface energies has been discussed and developed by various authors [11-13]. In this work we used the expression for the surface energy due to Gross and Scrawley [13],

$$\gamma = \frac{6 F^2 L^2}{E w^2 h^3} \left[1 + 1.335 \left(\frac{h}{L} \right) + 0.446 \left(\frac{h}{L} \right)^2 \right]$$

where F is the force needed to propagate a crack of length L , E is the Young's modulus and w and h are the width and height respectively of the arms of the crack.

Fracture surfaces were examined by optical and scanning electron microscopy.

3. Results and Discussion

3.1. Microstructure

a. Crystals containing magnesioferrite. The precipitate took the form of dendrites (fig. 2), often very extensive, with arms lying in $\langle 100 \rangle$. The lattice of the magnesioferrite (spinel structure) is parallel to that of the MgO matrix, with double the lattice parameter, i.e. an essentially continuous sublattice of oxygen ions runs through both precipitate and matrix. Rarely, dendrites with arms lying in $\langle 110 \rangle$ were observed. These were always in regions of a very high magnesioferrite concentration; otherwise no explanation was found for their occurrence.

b. Crystals containing iron. The iron takes the form mainly of platelets lying on $\{100\}$ with edges parallel to $\langle 110 \rangle$ as reported by Davidge [8]. Other forms are occasionally observed, such

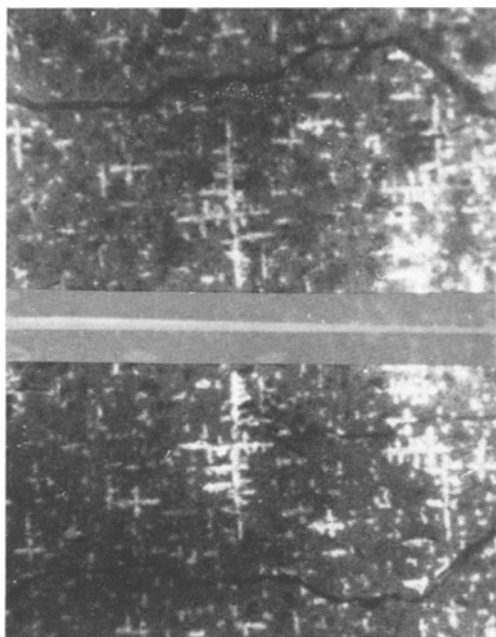


Figure 2 Matching fracture surfaces of a MgO crystal containing dendritic precipitates of magnesioferrite ($\times 900$).

as triangular platelets; the simplest morphology of square platelets is shown in fig. 3. The surfaces of the platelets are by no means smooth, as seen in fig. 4. X-ray rotation photographs show a preferred orientation based on the relationship reported by Davidge [8], i.e.

$$[001]_{\text{MgO}} \parallel [001]_{\text{Fe}}, [110]_{\text{MgO}} \parallel [100]_{\text{Fe}}.$$

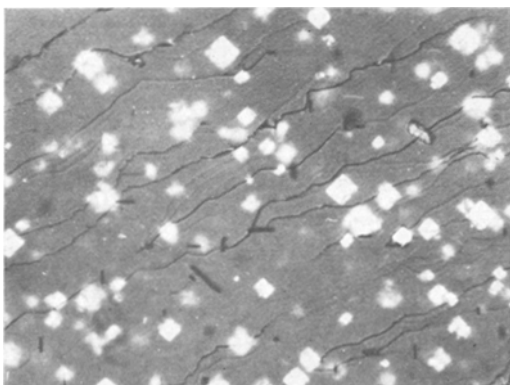


Figure 3 Platelets of iron precipitate in a MgO crystal ($\times 350$).

However, it should be emphasised that there is a large spread of approximately $\pm 10^\circ$ about this

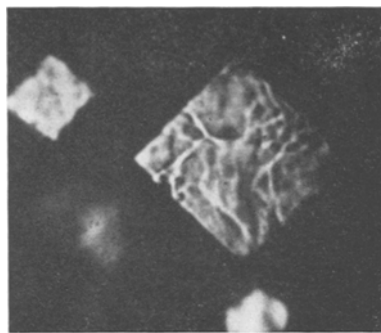


Figure 4 Surfaces of iron platelets in a MgO crystal ($\times 1200$).

ideal relationship, the bcc iron scattering being in the form of non-uniform Debye-Sherrer rings rather than single crystal reflections. In view of this it appears doubtful whether the good atomic fit across (100) MgO for this orientation relationship noted by Davidge is more than coincidental, especially in view of the fact that the iron produced at 1400°C presumably precipitates in the fcc form. Some evidence of retained fcc iron was found in the form of weak extra spots on the X-ray rotation photograph which could be indexed as (002) and (111) reflections from fcc iron. It is suggested that some particles, by virtue of their small size or their perfection, fail to transform to bcc iron on cooling. The positions of the reflections show that the fcc iron forms with its crystal axes parallel to the crystal axes of the fcc MgO matrix.

c. Crystals containing nickel. The morphology of the nickel precipitate is very similar to that of iron, but X-ray photographs show sharp single-crystal nickel reflections with the crystal axes of the nickel parallel to those of the MgO matrix. This result supports the tentative identification of similarly oriented fcc iron described above and suggests that the bcc iron acquires its spread of orientation in the phase transformation $\text{fcc} \rightarrow \text{bcc}$ which occurs in the majority of particles on cooling. It is interesting to note that the orientation of the fcc phase is related to the ideal orientation of the bcc by the Bain lattice correspondence.

3.2. Crack Propagation

a. Crystals containing magnesioferrite. Table I lists the effective surface energies for cracks in crystals containing various volume fractions of magnesioferrite. The standard deviations refer to the set of values obtained from successive crack

TABLE I

Volume fraction of Magnesioferrite	Effective surface energy Jm^{-2}
0.02	2.13 ± 0.33
0.25	1.42 ± 0.11
0.30	2.34 ± 0.08
0.40	1.58 ± 0.15

propagations in the same crystal. The effective surface energy shows no significant correlation with the volume fraction of magnesioferrite and the values are all within the range of values obtained for nominally pure MgO crystals by the same technique [10]. The fracture surfaces show no more cleavage steps than is usual in pure MgO, and the cracks pass through the magnesioferrite particles with very little disturbance, as shown in fig. 2. Cleavage steps show some tendency to run along the interface between the precipitate and matrix, otherwise the magnesioferrite has no effect on the form of the crack. An attempt was made to compare propagations in doped and undoped regions of the same crystal; however, a crack initiated in the undoped region advanced without an arrest in a band containing 6% by volume of magnesioferrite. Since the width of the band was several times larger than the usual distance between arrests it is probable that the effect of the doping was to reduce somewhat the effective surface energy for crack propagation. When the fracture surface was etched, slip lines were observed in the undoped region, but not in the doped, suggesting a reduction in the amount of plastic deformation at the crack tip in the doped region.

b. Crystals containing iron or nickel particles. Initial experiments showed that the effective surface energies of crystals doped to contain ~ 2% by volume of metal were of the same order of magnitude as those of pure MgO crystals. To make a more sensitive measurement of the effect of the dispersed metal a crystal partially doped with approximately 2% by volume of iron was tested. The first crack propagation took place in the undoped region at an effective surface energy of 1.68 Jm^{-2} ; subsequent propagations in the doped region occurred at values of 2.80, 3.83, 3.57, and 2.61 Jm^{-2} . This gives some indication of a small increase in effective surface energy, of the order of magnitude of 1 Jm^{-2} . The fracture surface is shown in fig. 5. The roughness of the fracture surface is dramatically increased in

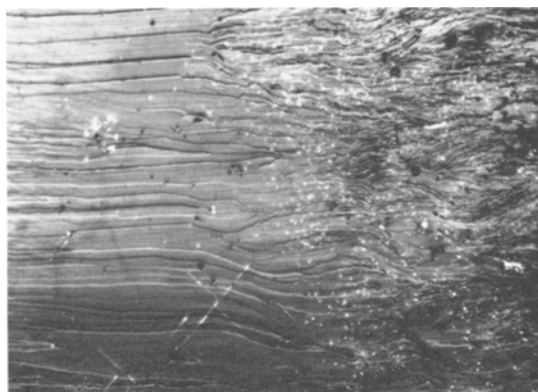


Figure 5 Fracture surface of a MgO crystal partially doped with iron ($\times 25$).

the doped region. Cleavage steps are frequently generated at particles and existing cleavage steps assume a tortuous path as they run from one particle to another. Ruptured particles are not observed, indicating that the metal-oxide interface is weak. The fracture surfaces of crystals containing nickel particles are very similar. Fig. 6 shows that nickel particles also are pulled out of the fracture surface rather than ruptured. It is clear that the plasticity of the metal is not brought into play and that any increase in effective surface energy must be attributed to the increased roughness of the fracture surface. The contribution of cleavage steps to the energy of crack propagation has been the subject of considerable discussion [5, 14, 15], the essential



Figure 6 Scanning electron micrograph of the fracture surface of a MgO crystal containing nickel particles, taken at an angle of 10° to the surface.

difficulty being to determine the amount of plastic work associated with the propagation of the step. In our case the additional cleavage steps have a small effect, not more than of the order of the true surface energy. This is much less than the estimate of a 10 to 100 fold increase in effective surface energy in the similar system of NaCl crystals containing weakly bonded gold particles [6], suggesting either that much greater plasticity is associated with the disturbance of the crack path in NaCl, or that there is some inadequacy in the theory which was used to link crack velocities to effective surface energies.

To determine whether the weakness of the metal-MgO interfaces was due to the greater thermal contraction of the metal during cooling from the reduction temperature, sessile drops of iron and nickel were formed on cleaved surfaces of MgO. The solidified drops were found to be strongly attached to the MgO, despite the fact that the thermal contraction difference led to plastic deformation of the MgO substrate. Shear stresses of 68 MNm^{-2} and 57 MNm^{-2} were needed to detach drops of nickel and iron, respectively [16]. If one face of a $10 \times 10 \times 1 \mu\text{m}$ platelet in a MgO crystal had a similar interfacial shear strength, it would be ruptured rather than pulled out by a large proportion of cracks intersecting it. It is concluded that the weakness of the platelet interfaces is a result of the mechanism of reduction by which it forms rather than a consequence of differential thermal contraction.

4. Conclusions

Dispersed second phases have little effect on the effective surface energy for crack propagation in MgO crystals. Brittle magnesioferrite particles have no significant effect on crack propagation.

A small volume fraction ($\sim 2\%$) of iron or nickel platelets with weak interfaces while producing a spectacular increase in the density of cleavage steps, produce only a very minor increase in the effective surface energy for crack propagation. It appears that small-scale perturbations of the crack path are ineffective com-

pared to the large-scale changes in orientation of cracks in polycrystalline MgO where the effective surface energy is an order of magnitude greater than in single crystal MgO [17]. A weak interface, together with a simple morphology, prevent iron or nickel particles produced by reduction of a mixed oxide crystal from contributing any plastic work to the effective surface energy.

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References

1. G. W. GROVES, *Proc. Brit. Ceram. Soc.* **15** (1970) 103.
2. M. E. FINE, *Trans. Japan Inst. Metals* **9** (1968) 527.
3. G. W. GROVES, "Strengthening Methods in Crystals", ed. A. Kelly and R. B. Nicholson (Elsevier, Amsterdam, 1971) p. 403.
4. S. E. HSU, W. KOBES, and M. E. FINE, *J. Amer. Ceram. Soc.* **50** (1967) 149.
5. C. T. FORWOOD and A. J. FORTY, *Phil. Mag.* **11** (1965) 1067.
6. C. T. FORWOOD, *ibid* **17** (1968) 657.
7. G. W. GROVES and M. E. FINE, *J. Appl. Phys.* **35** (1964) 3587.
8. R. W. DAVIDGE, *J. Mater. Sci.* **2** (1967) 339.
9. J. J. GILMAN, *J. Appl. Phys.* **31** (1960) 2208.
10. D. A. SHOCKEY and G. W. GROVES, *J. Amer. Ceram. Soc.* **51** (1968) 229.
11. P. P. GILLIS and J. J. GILMAN, *J. Appl. Phys.* **35** (1964) 647.
12. S. M. WIEDERHORN, A. M. SHORB, and R. L. MOSES, *ibid* **39** (1968) 1569.
13. J. E. SCRAWLEY and B. GROSS, *Mat. Res. Std.* **7** (1967) 155.
14. J. J. GILMAN, *J. Appl. Phys.* **27** (1956) 1262.
15. F. F. LANGE and K. H. D. LAMBE, *Phil. Mag.* **18** (1968) 129.
16. C. D. R. LANGTON, B.Sc. Thesis, Oxford 1969.
17. A. G. EVANS, *Phil. Mag.* **22** (1970) 841.
18. B. PHILLIPS, S. SOMIYA, and A. MUAN, *J. Amer. Ceram. Soc.* **44** (1961) 167.

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