Boundary segregation of Ca, Fe, La and Si in magnesium oxide

Changes in the composition of oxide materials at and near boundaries have been reviewed by Kingery [1]; the surface and grain boundary segregation of aluminium in MgO crystals resulting from spinel precipitation has been reported [2, 3]. Johnson *et al.* investigated grain boundary segregation in magnesium oxide by Auger electron spectroscopy and reported that segregation of calcium, silicon and titanium occurred [4]. Black and Kingery [5] have reported surface segregation of ferric iron, chromium and scandium in single crystal MgO. In the present study we have investigated grain boundary segregation in a sample of magnesium oxide, prepared by W. Coblenz, which contained small amounts of iron, calcium, silicon and lanthanum with the use of a "dedicated" scanning transmission electron microscope.

A sample of high purity magnesium oxide, prepared by autoclave oxidation of magnesium metal at the General Electric Co. Glass Research Laboratory in Cleveland, and an admixture of ferric oxylate were calcined at 700° C for 1 h. Samples were pressed with oleic acid and isopropyl alcohol and subsequently sintered at 1700° C for 5 h, annealed at 1100° C for 19 h and air quenched by dropping from the furnace onto a bed of sand.

The samples were mechanically thinned by grinding to a final thickness of about 2 μm and then prepared for electron microscopy by ion thinning with argon ions accelerated through a potential of 6 kV. Conductivity in the electron beam was assured by coating the samples with a layer of evaporated carbon.

The samples were observed and X-ray microanalysis was carried out in a VG HB5 scanning transmission electron microscope manufactured by Vacuum Generators Microscopes Ltd, East Grinstead, England. A sample of a grain boundary was examined in which the bright-field image showed no indication of precipitation at a magnification of × 200 000. High spatial resolution X-ray microanalysis was used to examine solute segregation. The spatial resolution is determined by the initial probe size, by the amount of beam spreading in the sample and by specimen stability during measurements. We estimate that sample stability and beam broadening limited the X-ray spatial resolution to about 50 Å.

For analysis, specimens were held in a graphite-nosed cartridge which allowed translation and tilting and the analysis was performed with a probe of about 25 Å diameter with a current of about 10^{-8} amps, which was manually stepped along a line perpendicular to the boundary. The foil was tilted such that the boundary was parallel to the electron beam. A 30 sec count time was used for each point and after collection a computer generated semi-empirical background was subtracted from the spectrum.

Spectroscopic absorption analysis indicated that this sample contained 1570 p.p.m. by weight Fe and 20 p.p.m. by weight Ca. Emission spectroscopic analysis indicated the presence of 10 to 50 p.p.m. by weight Si and less than 50 p.p.m. by weight La. In Fig. 1 the projected grain boundary image is seen to be precipitate-free and about 40 Å wide. As illustrated in Fig. 2, there is a substantial enhancement in concentration at the grain boundary over a region less than about 200 Å in width for each of the cations present. The relative enhancement of Si, Ca, and La is greater than that for Fe. This probably results because there is a greater strain energy contributing to segregation for these materials.

With experimental data now indicating segregation of aluminium [3, 4], ferric iron (this work and [5]), scandium [5], titanium [4], silicon (this work and [4]), calcium (this work and [4]), and

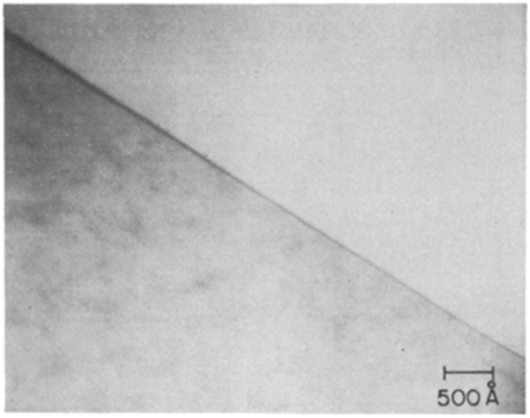

Figure 1 Grain boundary in MgO doped with about 1500 p.p.m. by weight Fe and quenched from single-phase region.

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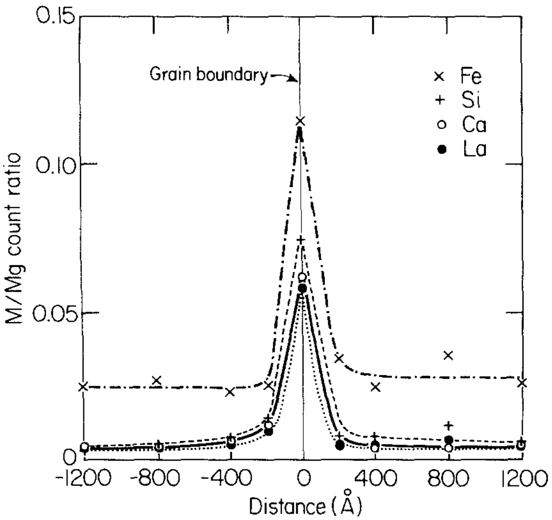

Figure 2 Results of X-ray microanalysis across boundary shown in Fig. 1. Results are given in X-ray count ratios versus position.

lanthanum (this work), it seems clear that segregation of solutes at grain boundaries in ionic oxides such as MgO is very common indeed, and that this factor must generally be taken into account in discussing properties and behaviour of this class of materials.

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Factors affecting the stress dependence for creep of polycrystalline magnesia

During high temperature creep of polycrystalline ceramics, the variation of the secondary creep rate, $\dot{\epsilon}_s$, with applied stress, σ, at a constant temperature, T, can be expressed as

$$\dot{\epsilon}_{s|T} \propto \sigma^n.$$

When creep occurs by the generation and movement of dislocations the stress exponent, n, is usually found to be within the range 3 to 5. Indeed, in the dislocation creep regime, it has been proposed [1] that ceramics can be classifed into two groups depending on whether the stress exponent is approximately 5 (e.g. NaCl, LiF, UO_2) or close to 3 (e.g. MgO, BeO, Al_2O_3). Alternatively, it has been suggested that a specific n value of 3 or 5 should not be assigned to each ceramic [2] since evidence is available which indicates that the stress exponent can depend on the fabrication procedures used to produce the material [3]. In the present work, a study has been made of the effects of changes in the method of sample preparation on the stress exponent for creep of polycrystalline MgO.

Specially prepared $Mg(OH)_2$ was calcined at either 1273, 1373 or 1473 K. The resulting material was then pressed into bars (6.4 mm x 6.4 mm x 32 mm) and sintered at 2073 K in air. The detailed analysis (wt%) was therefore the same for all samples, namely, 99.85% MgO, 0.1% SiO_2, 0.02% CaO, Al_2O_3 and Fe_2O_3 and 0.012% B_2O_3. Moreover, irrespective of the calcination temperature used, samples were produced having 93 to 95% theoretical density and having a uniform grain diameter in the range 10 to 14 μm. Cylindrical testpieces, 4.25 mm diameter and 6.4 mm long, were ultrasonically trepanned from the bars and compression creep tests were carried out over a range of stresses at 1596(± 1) K. The constant

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