Mobility of cations in magnesium aluminate spinel

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Transport of cations in magnesium aluminate spinel due to an applied electric field at approximately 1000 °C has been measured by observing changes in elemental concentrations near the cathode and anode surfaces using ion backscattering techniques. The results indicate that magnesium ions are the mobile species at 1000 °C and that these ions combine with ambient oxygen at the cathode surface to form a MgO layer. Quantitative interpretation of the data leads to the conclusion that the ionic transference number of spinel becomes approximately 0.5 after treatment in an electric field.

I. INTRODUCTION

The transport properties of magnesium aluminate spinel at elevated temperatures have been investigated in recent years by a variety of techniques. A number of interdiffusion studies between MgO and Al_2O_3 ceramics have been performed[1,2] and self-diffusion of oxygen has been measured in single crystals.[3,4] However, few direct measurements of cation diffusion in spinel have been performed.[5] The electrical properties have been measured in stoichiometric and aluminum excess material[6−8] and ionic transference numbers have been determined as a function of temperature and oxygen pressure.[9] These electrical measurements indicated that charge transport was predominantly ionic. But since $MgAl_2O_4$ spinel is made up of two cations, Mg^{2+} and Al^{3+}, it is of interest to determine the degree to which ionic current is carried by Mg^{2+} or Al^{3+}.

In the present work ion motion was induced at temperatures near 1000 °C by moderate electric fields. The resulting rearrangement of ions was determined by measuring the composition of the crystal near the electrodes using Rutherford backscattering (RBS) techniques.[10]

II. EXPERIMENTAL PROCEDURES

Magnesium aluminate spinel was grown[11] by pulling crystals from a stoichiometric $MgAl_2O_4$ melt in iridium crucibles. Disks, 10−16 mm in diameter, were cut from the crystal ingots and were polished with successively finer SiC abrasive papers and 0.3-μm alumina powder. One set of three samples was annealed at 1016 °C in air, in an electric field of 460 V/cm for intervals of 1.5−18 h. These samples were held between solid-disk platinum electrodes. Other samples were treated similarly except that the ambient gas was 95% ^{18}O enriched. Solid-disk and Pt gauze (for better contact with the ambient gas) electrodes were tried for these samples; it was found that more consistent results were obtained with the solid electrodes.

The electric field applied to the test sample was held constant and the current was measured by a digital microammeter. At the end of each anneal the furnace was shut down and the sample was cooled inside the furnace.

The electric field remained on until the sample had cooled a few hundred degrees below the treatment temperature.

RBS analysis[10] of the cathode and anode surfaces was performed using 2-MeV ^{4}He. Scattered particles were detected and energy analyzed by a silicon surface barrier detector. The scattering angle was 150° and the detector was situated 90 mm from the target. A molybdenum plate with a 2-mm-diam hole covered the samples during analysis in order to reduce the accumulation of charge. The ion beam, 1 mm in diameter, was centered on the hole in the Mo plate.

III. QUALITATIVE RESULTS AND CONCLUSIONS

In RBS helium ions of fixed initial energy (2 MeV) are scattered from atoms in the near-surface region of the sample. At a fixed angle the energy of the scattered particles will depend on two variables: the mass of the target nucleus and its depth below the surface of the sample. Heavier elements in the sample scatter the α particles with higher energies, while scattering at greater depths increases the energy loss during penetration and return and thus gives rise to scattered particles with lower energies. The data shown by circles in Fig. 1 for untreated spinel exemplify the effects of scattering center mass and depth. The heaviest element present in spinel is Al and the step at 1.15 MeV reflects the onset of scattering from Al ions at the sample surface. If no other elements were present the curve would remain essentially smooth at energies below the 1.15-MeV step due to scattering from Al at increasing depth in the sample. However, since spinel is made up of Mg and ^{16}O as well as Al, additional steps due to these elements are present, at 1.08 and 0.86 MeV, respectively. The 1.08-MeV "step" due to scattering from Mg is rather broad due to the fact that natural magnesium is made up of three isotopes.

Subjecting the sample to an electric field of 461 V/cm in an $^{18}O_2$ atmosphere for $7\frac{1}{4}$ h at 995 °C produces changes in the spinel that give rise, at the cathode surface, to the data indicated by plus signs in Fig. 1. Clearly the step at 1.15 MeV is gone, indicating an absence of Al at the cathode surface. The step at 1.08 MeV is due to a
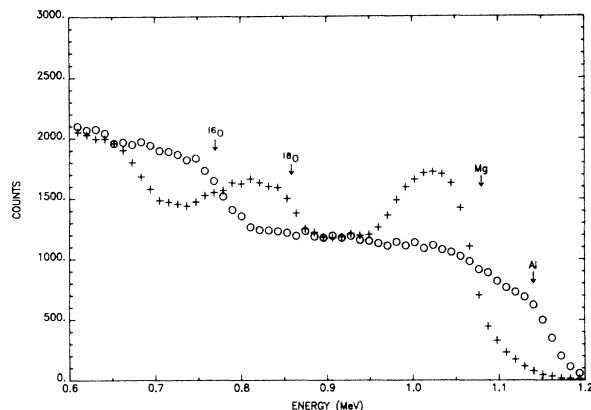
FIG. 1. Energy spectra of 2-MeV ^{4}He ions scattered from MgAl$_2$O$_4$ spinel for untreated material (○), and from the cathode surface of a sample annealed at 995 °C in an electric field of 461 V/cm (+). The arrows indicate energies at which ^{4}He would scatter from the indicated elements at the surface of the sample.

FIG. 2. Ion scattering spectra, expressed as depth distributions of Al, for MgAl$_2$O$_4$ treated at 1016 °C for 1.5 h (□) and 18 h (△). The arrows indicate depths below the surface at which scattering from Al is observed.

combination of Mg scattering from the surface and Al scattering from approximately 0.1 μm within the sample. The fact that the count rate between 1.08 and 0.98 MeV is much greater than in untreated spinel indicates that there exists a surface layer, approximately 0.1 μm thick, of MgO, for which the scattering from Mg is greater than in spinel due to the greater density of Mg in MgO. The combination of this greater scattering from the surface layer of MgO and the beginning of Al scattering from below the 0.1-μm layer produces the peak. The coincidence of the two curves near 0.9 MeV is due to scattering from Al and Mg ions of normal spinel composition for both samples (i.e., below the MgO layer in the treated sample the composition is the same as in the untreated spinel).

The rise at 0.85 MeV corresponds to scattering from ^{18}O ions at the surface of the treated sample. It is clear from the depression between 0.77 and 0.70 MeV that the ^{18}O scattering is limited to a surface layer and that the normal ^{16}O scattering, which occurs for the surface at 0.77 MeV, does not take place, but begins only at lower energy (0.70 MeV) corresponding to depths greater than approximately 0.1 μm.

These RBS results which show excess Mg and ^{18}O but no Al at the cathode surface lead to the definitive conclusion that a layer of MgO has grown on the cathode surface during electric field treatment. Such a layer should increase in thickness for longer treatment times. To demonstrate this increase in MgO-layer thickness more clearly we show in Fig. 2 RBS spectra for two samples, treated, respectively, for 1.5 and 18 h in air. In this figure the horizontal scale has been converted to scattering depth for Al in the MgO layer. It is clear that for both samples there is no Al present at the sample surface. For the sample treated for 1$\frac{1}{2}$ h (no. 312) scattering from Al is observed at a depth of $\sim$0.1 μm, while for the sample treated for 18 h (no. 313) the Al is observed to be considerably deeper ($\sim$0.5 μm). The decrease of scattering intensity in each spectrum that follows the onset of

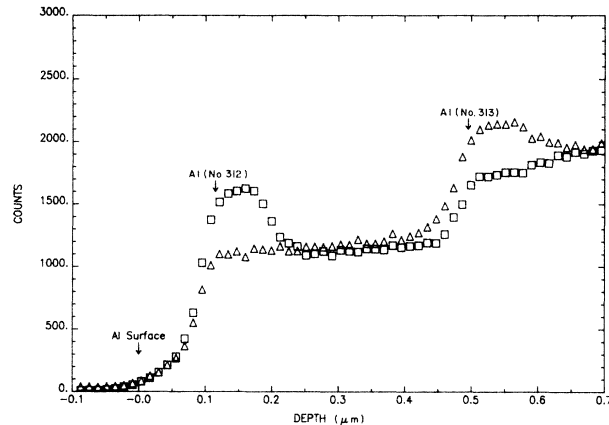scattering from Al has been explained previously in connection with Fig. 1 and corresponds to the decrease in Mg density at the transition from MgO to spinel. The fact that the two Al peaks occur near the scattering edges of Mg (no. 312) and ^{16}O (no. 313) is coincidental. The quantitative relationship between treatment time and MgO-layer thickness that is illustrated here will be discussed more fully in Sec. IV.

It is interesting to note that between 0.25 and 0.45 μm the scattered intensity for the two samples is approximately the same, even though this scattering is from MgO for one sample (no. 313) and from MgAl$_2$O$_4$ for the other (no. 312). This is due to the fact that these two materials have similar scattering cross sections and stopping powers.

An example of results for the anode side is presented in Fig. 3, where the RBS spectrum of sample no. 313, treated 18 h in ^{16}O$_2$, is compared with that of an untreated sample. Only a slight difference in the spectra is evident; between approximately 1.07 and 1.13 MeV the spectrum of the treated sample indicates the presence of a slight excess
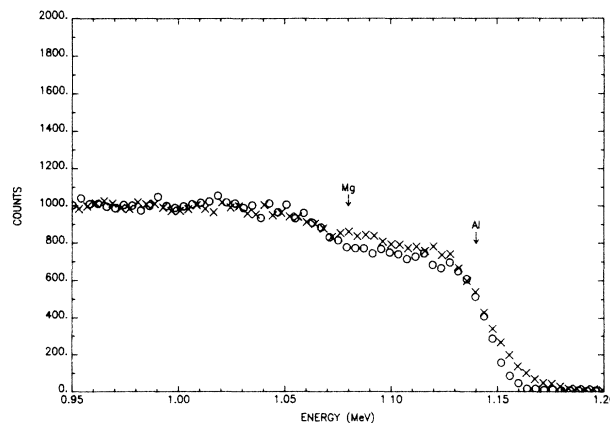

FIG. 3. Energy spectra of ^{4}He scattered from MgAl$_2$O$_4$ spinel for untreated material (○), and for the anode surface of a sample annealed at 1016 °C in an electric field of 461 V/cm (×).

of Al for some distance below the anode surface. However, this difference was not observed for all anode surfaces. In samples treated in $^{18}O_2$ there was no evidence of ^{18}O at the anode surfaces. Clearly, there is no Al_2O_3 layer at the anode. From these results we conclude that the Mg that makes up the MgO layer at the cathode is compensated by a small change in stoichiometry throughout a deep portion of the sample below the anode and not by a thin, magnesium-depleted layer.

IV. QUANTITATIVE RESULTS AND DISCUSSION

It is possible from RBS spectra such as those of Fig. 1 to calculate the thickness of the surface layer. The displacement of the Al step to lower energy (or the ^{16}O step in samples treated in $^{18}O_2$) provides the most reliable measure of the thickness of the non-aluminum-containing layer (or ^{18}O-containing layer). An estimate of layer thickness can also be made from the width of the ^{18}O peak in samples where that peak is resolved from other structure. In Table I we list what we believe are fairly reliable determinations of layer thicknesses. All the samples listed in Table I were treated with flat electrodes. For two of the samples, spectra were obtained for multiple (1 mm diam) spots on the cathode surface and the differences between these values are an indication of the layer-thickness variation over the cathode region. For the samples treated in $^{18}O_2$ it is evident that the layer thicknesses of Mg (column 4) and those of ^{18}O (columns 5 and 6) correspond well and differ less than the variation from spot to spot. Thus the surface layer is indeed Mg ^{18}O. Table I does not include values obtained from two samples that had been treated with Pt-mesh electrodes. For these there is a large uncertainty in the electrode area, i.e., whether it should be only the points of contact between the mesh and the sample or the whole area covered by the mesh. Moreover, even though these samples exhibited the same qualitative behavior as those treated with flat electrodes, the results were much more variable and the thicknesses of the ^{18}O layers appeared to be less than those of the excess Mg layers.

If it is assumed that the current I passing through the crystal during treatment is uniform over the electrode area A and is carried by Mg^{2+} ions, an expression for the layer thickness δx of MgO can be derived. In the equation,

$$\delta x = (M/ZedN_0)\int(I/A)dt , \qquad (1)$$

M and d are the atomic mass and density of MgO, Ze is the ionic charge, and N_0 is Avogadros's number. A comparison between thicknesses calculated from Eq. (1) and values measured and recorded in Table I allows us to assess the validity of the above assumptions. Figure 4 is a plot of the calculated versus measured MgO-layer thicknesses. If the above assumptions are valid then points in Fig. 4 should fall on a line of slope 1. A line drawn through the data of Fig. 1 has a slope of 0.46 and does not intersect the origin. The implication of Fig. 4 is that after the MgO layer exceeds 0.1 μm not all the current is carried by Mg^{2+} ions. As implied earlier in this paper, Al^{3+} carries little current; otherwise there would be aluminum present in the surface layer at the cathode. The extra current is therefore carried by electrons, either through the bulk of the MgO/spinel sandwich, or by short circuiting along the sample surfaces or through the gas in the sample chamber. If the electron current is passing through the bulk, then the cationic transference number is 0.46 rather than the unity measured in an oxygen concentration cell.[9] There may not be a contradiction, however, since in an electrochemical cell no current flows and, as the dashed line of slope 1 through the origin of Fig. 4 indicates, the present data are not inconsistent with unity transference number when little current has passed through the spinel.

Recent measurement[12] of the conductivity of spinel at 1100 °C as a function of treatment time in electric fields of the same order as those used here showed that rather large increases of conductivity occurred. Such increases would be difficult to account for purely in terms of ionic conduction and therefore also support the idea that electronic conduction becomes significant after some magnitude of charge has passed through spinel.

The uniformity of current flow should also be dis-

TABLE I. Layer thickness calculated from RBS spectra.

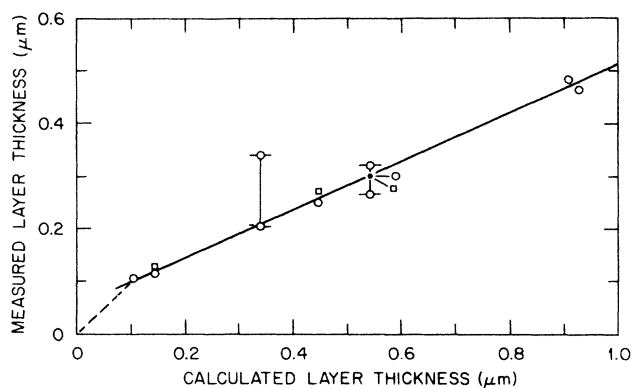| | Treatment | | | Layer thickness (μm) | | |
Sample	Temperature (°C)	Time (h)	Gas	Al edge displacement	^{16}O edge displacement	^{18}O peak width
1010	1016	$4\frac{1}{2}$	$^{16}O_2$	0.341		
				0.208		
312	1016	$1\frac{1}{2}$	$^{16}O_2$	0.107±0.007		
313	1016	18	$^{16}O_2$	0.486±0.010		
				0.269	0.262	
607	995	$20\frac{1}{2}$	$^{18}O_2$	0.321	0.338	0.306
				0.300	0.306	
611	995	$7\frac{1}{4}$	$^{18}O_2$	0.114	0.129	0.124
612	995	$41\frac{1}{4}$	$^{18}O_2$	0.251	0.277	0.267
617	995	169	$^{18}O_2$	0.467		

FIG. 4. Thickness of MgO layer at cathode. Comparison of calculated with measured values determined from the scattering edges of Al (O) and O (□).

cussed. The data points joined by vertical lines in Fig. 4 indicate the range of variation when different spots within the electrode area of a sample were measured. For the sample with the largest variation it was observed, after removal of the electrodes, that the slight marks normally left behind at the rim of the circular electrode were, on one surface, smaller than the electrode and irregular in shape. On the basis of these observations we suggest that current flow through the spinel was not completely uniform over the electrode area.

From ion-drift measurements such as these reported here it is possible to determine diffusion coefficients for the mobile ions using the expression[13]

$$D = \frac{fkTFd_s}{M_sZe_2N_{Mg}} \frac{\delta x(\text{measured})}{E\delta t} .$$ (2)

In Eq. (2), f is the diffusion correlation factor, k the Boltzmann constant, F the Faraday constant (96 500 C), and d_s and M_s the density and molecular weight, respectively, of spinel. N_{Mg} is the density of magnesium ions per cm^3 of spinel, E the electric field, and δx and δt are the measured layer thicknesses and treatment times.

On the assumption that the field through the sample is

uniform and equal to V/x, where V is the applied voltage and x the sample thickness, we calculated diffusion coefficients from our data and obtained values from 4×10^{-14} to 1×10^{-13} for 1016 °C and from 2×10^{-14} to 8×10^{-14} cm^2/s for 995 °C, with the highest values corresponding to the shortest treatments and the lowest diffusion coefficients corresponding to the longest treatments. The dependence of these results on the time of treatment and the fact that the current decreased during the experiments indicates that significant polarization developed during treatment, so that for the longer times only a fraction of the applied voltage produced the electric field within the spinel. Therefore the values for diffusion coefficients quoted above must be considered lower limits.

Diffusion coefficients of the order of 1×10^{-13} cm^2/s for spinel at 1000 °C are about a factor of 5 smaller than values obtained by extrapolation of measurements reported[1,5] for polycrystalline spinel. In view of the uncertainties associated with extrapolating diffusion coefficients from $T > 1300$ °C, the assumptions made in our interpretation, and the fact that previous diffusion experiments were made with polycrystalline samples with large concentration gradients, the present and previous results are in surprisingly good agreement.

V. SUMMARY

RBS measurements of the composition of surface layers of spinel heated in an electric field show clearly that Mg^{2+} is the predominant ionic current carrier. An MgO layer grows at the cathode surface and is compensated by a slight reduction in the [Mg]/[Al] ratio in the bulk of the sample rather than by a pure Al_2O_3 layer at the anode. After current has flowed for some time it appears that only half is carried by Mg^{2+} ions, with the remainder being electronic.

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