

CRYSTALLITE GROWTH IN MAGNESIUM OXIDE UNDER APPLIED ELECTRIC FIELDS

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ABSTRACT

An electrolysis cell is described for use in conjunction with a high-temperature X-ray furnace, which permits X-ray diffraction studies to be made of solids during the course of their high temperature electrolysis. The technique is applied to an investigation of the effect of electric fields on crystallite growth in MgO at 600°C in air, argon and reducing atmospheres. In all cases crystallite growth is greatest at the positive electrode face, suggesting that the charge carriers are anions. The efficiency of the electrolysis process depends both on the concentration of charge carriers and on the concentration of anion vacancies by which the charge carriers migrate. The defect concentration is increased under reducing conditions. In MgO samples containing a high concentration of protons, the conduction is protonic, with the greatest crystallite growth occurring at the cathode due to the catalytic action of the water vapour formed in that region by recombination of protons with hydroxyl ions.

INTRODUCTION

The subject of crystallite growth in metal oxides has received considerable attention because of its practical significance, particularly in ceramic technology. One of the more important refractory oxides is MgO; crystallite growth in this material and the associated phenomena of sintering and densification have been studied extensively^{1–4}.

During a study⁵ on the effect of electric fields on the dehydroxylation of Mg(OH)₂, differences were observed in the crystallite sizes at the positive and negative electrode regions of the resulting oxide. The flow direction of the gas atmosphere with respect to the electrodes appeared also to influence the crystallite size of the product, and since the TG electrolysis cell in which those experiments were carried out⁵ produced an inherent vapour gradient in the sample, the matter was not investigated further. The recent construction of an electrolysis cell for use with an X-ray furnace under controlled atmospheres has made possible a further investigation of the effect, the results of which are reported here.

EXPERIMENTAL

Materials

The magnesium oxide used in this study was obtained by calcining B.D.H. reagent grade $\text{Mg}(\text{OH})_2$ in a laboratory muffle furnace at 450°C for 0.5 h. The product, which was shown by X-ray diffraction to be MgO of small crystallite size (80–90 Å) was stored in sealed bottles until required.

Electrolysis cell

The electrolyses were carried out in a cell designed for use in conjunction with a Stone XR-6 X-ray furnace (or any other X-ray furnace employing a flat plate heating element). In the present furnace, the ceramic-covered heating plate was replaced by a home-made heavy-duty Kanthal element encased in zirconia because the platinum winding supplied by the manufacturer is fragile and burns out easily. The specimen holder was fabricated from a 2 mm thick stainless-steel sheet into which a central hole 10 mm square was cut; its purpose was solely to confine the powder sample and prevent it spreading sideways. A chromel–alumel thermocouple was spot-welded on to the specimen holder and connected to the thermocouple lead-out terminals provided on the furnace (Fig. 1). It was found necessary to strap

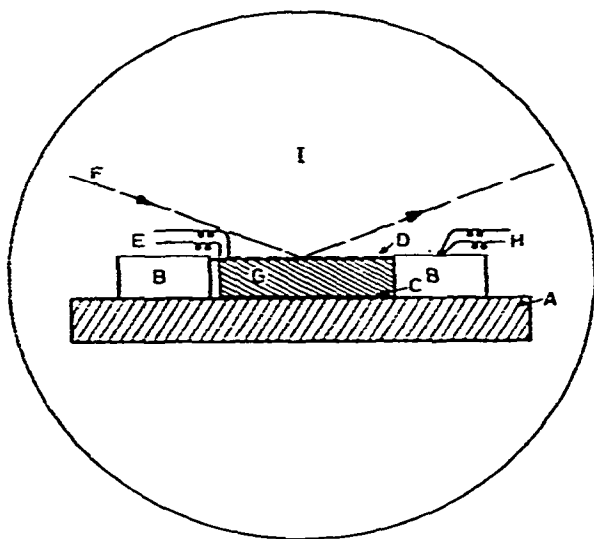


Fig. 1. Schematic diagram of cell for simultaneous high-temperature electrolysis and X-ray diffraction. Not to scale. A = Heating element, Kanthal winding in zirconia; B = stainless steel sample holder; C = bottom electrode (platinum foil); D = top electrode (platinum mesh); E = platinum lead-out wires; F = incident X-ray beam; G = powder sample; H = chromel-alumel thermocouple; I = back plate of furnace.

the whole assembly down to the ceramic heating block with 28 gauge Nichrome wire, since movement of the specimen cannot be tolerated in line-broadening experiments

and can lead to spurious results. The sample powder is packed directly on to the lower platinum foil electrode which is placed on the ceramic heating plate. The upper electrode is platinum mesh, made of 28 gauge wire with a 1 mm mesh opening. This is placed on top of the powder sample and pressed down into it to present a flat, plane surface to the X-ray beam. By this means, only one electrode face can be monitored per run, but the effect of electrolysis can be continuously observed over a period of time. The use of a mesh electrode presupposes that electrode reactions will occur in the powder immediately adjacent to the mesh; this assumption should become increasingly valid with decreasing mesh size, which, however, also diminishes the intensity of the sample diffraction pattern. The present choice of mesh size represents a compromise between these two effects.

The cell was aligned in the goniometer by using a standard silicon powder, and the thermocouple calibrated by measuring the d-spacing of the 410 peak of MgO, the temperature dependence of which is accurately known⁶. Large temperature gradients (of the order of 50°C) often occur between the heating plate and sample face in diffractometer furnaces having flat heating blocks. This well-known difficulty was minimised here by calibrating the thermocouple directly against the temperature of the sample face presented to the X-rays, as deduced from the d-spacing measurements.

Electrolysis procedure

At the start of each run, the accuracy of the sample packing and placement of the top electrode gauze was checked by making a room-temperature measurement of the initial particle size. (Such precautions would be unnecessary in qualitative work but for quantitative line-broadening measurements, correct disposition of the sample face in the beam is critical if reproducible results are to be obtained.) The furnace was then quickly brought to the reaction temperature (600°C) and the electrolysing voltage applied from a Philips PW4022 E.H.T. power supply. The goniometer was set to oscillate over the 200 MgO peak at $d = 2.11 \text{ \AA}$ ($42.82^\circ 2\theta$, Cu $K\alpha$ radiation) at a scan speed of $\frac{1}{4}^\circ 2\theta \text{ min}^{-1}$. Mean crystallite sizes calculated from the line-width measurements by standard procedures⁷ were recorded as a function of elapsed electrolysis time, as measured from peak to peak on the recorder trace. With practice in the initial setting-up procedures, the reproducibility of all measurements of equilibrium crystallite size was within 5%; the reproducibility of the measurements on the positive face was better than that of the negative face at all field strengths. The equilibrium crystallite size is defined here as the value attained when the growth curve levels off (under the present experimental conditions this was taken as the mean of the values recorded in the time interval 90–120 min of elapsed reaction time).

The majority of electrolysis experiments were performed in an atmosphere of dry flowing air (25 ml min^{-1}), but to investigate the effect of oxygen partial pressure on the electrolysis, several runs were made in argon and a reducing gas (95% N_2 , 5% H_2) at the same flow-rate. Flushing the cell with argon results in a marked decrease in measured X-ray intensity due to interaction between the heavy gas atoms and the X-rays. For comparison purposes, runs were made in all three atmospheres

with the gauze in place, but without the electrolysing voltage. Several electrolysis runs were also made using the parent hydroxide material.

RESULTS AND DISCUSSION

Electrolysis in air

The results of a typical electrolysis experiment in air at 600°C are shown in Fig. 2. As in all experiments in air the equilibrium crystallite size (as previously defined) is significantly greater at the positive than at the negative electrode, the crystallite size at the latter being smaller than the unelectrolysed value.

The effect of field strength on the equilibrium crystallite sizes at the positive and negative electrodes in air at 600°C is shown in Fig. 3. At all field strengths investigated here the crystallite size at the positive electrode is always greater than the unelectrolysed value, but the size at the negative electrode dips sharply below the unelectrolysed value at lower field strengths and approaches the unelectrolysed value only at the highest field strengths.

As a starting point in explaining these results, it is necessary to consider the nature of the charge carriers in the system, a matter about which there is some disagreement in the literature. Mitoff⁸ interpreted his conductance studies in terms of electronic conduction, as did several earlier workers^{9,10}. On the other hand, more recent work by Mitoff¹¹ indicates that conduction is ionic below 1300°C and electronic above this temperature. This is supported by electrochemical cell measurements¹². On the basis of measurements on polycrystalline samples, Davies¹³ has suggested that the nature of the charge carriers depends on the oxygen partial pressure, the carriers being O²⁻ and Mg²⁺ at higher and lower pressures, respectively. This appears to be supported by the most recent single crystal measurements at 900–1200°C on samples containing small amounts of NiO¹⁴; in that particular system the change-over in carrier type occurred at $P_{O_2} = 10^{-4}$ – 10^{-3} atm. It thus appears likely that under the conditions of the present electrolysis experiments the charge carriers are ions, the nature of which may depend on the atmosphere. This is also supported by calculations of the electrical mobility μ of O²⁻ and Mg²⁺ ions which are related to their diffusion coefficients D by

$$\mu = De/kT \quad (1)$$

where e is the electronic charge and k is Boltzmann's constant. Substituting the diffusion data of Lindner and Parfitt¹⁵ for magnesium in MgO and that of Oishi and Kingery¹⁶ for oxygen in MgO, the electrical mobilities at the electrolysis temperature are very similar, having the values 1.27×10^{-13} and 1.72×10^{-14} cm sec⁻¹/V cm⁻¹ for Mg²⁺ and O²⁻, respectively. These calculations are only approximate, since they depend on the validity of an extrapolation of higher temperature diffusion data to the lower electrolysis temperature. Nevertheless they imply that at 600°C, conduction by cations and anions is equally possible, the exact nature of the current-carrying ions being determined by such factors as the defect structure of the oxide. The latter is in

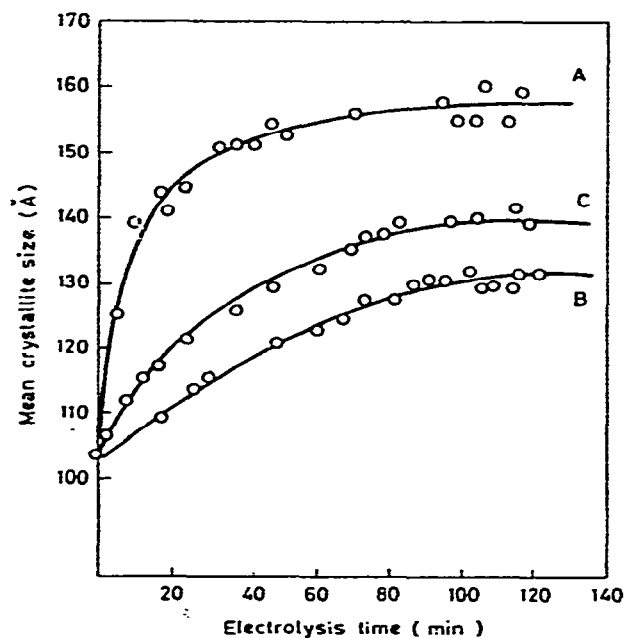


Fig. 2. Typical growth curve of MgO crystallites in air, 600°C, field strength $3 \times 10^5 \text{ V m}^{-1}$. A = Anode face; B = cathode face; C = unelectrolysed sample.

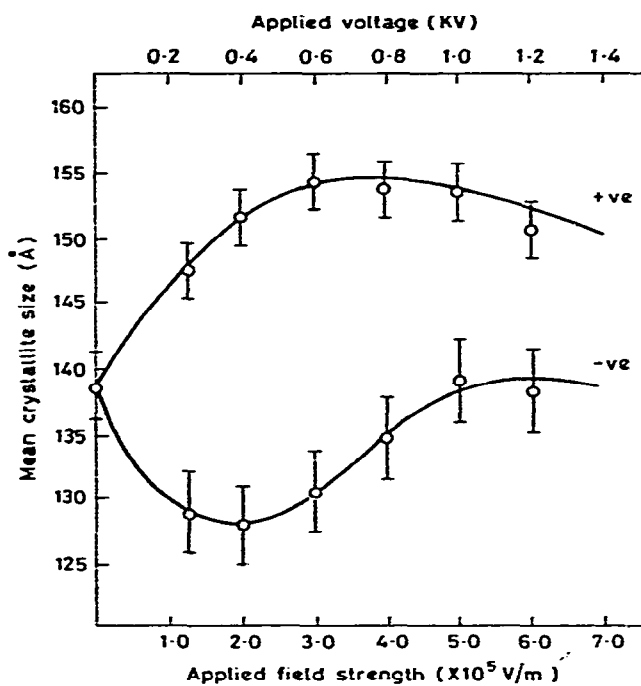


Fig. 3. Effect of applied field strength on mean crystallite size of MgO in air, 600°C.

turn determined by the nature of the impurities present and by the reaction atmosphere. If oxide ions are taken to be the charge carriers at atmospheric oxygen pressure, these will migrate via anion vacancies to the positive electrode. The presence of anion vacancies argues a metal-excess structure¹⁴, and recombination of these excess metal ions with oxide ions at the anode should produce oxide crystallites of increased size at that electrode, as is experimentally observed.

The experimental arrangements under which the present measurements were made (Fig. 1) impose upon the system the condition that only the upper electrode face is exposed directly to the ambient atmosphere. This situation may be used to gain additional mechanistic evidence, since if the charge carriers in air are indeed oxide ions, two electrode reactions can be envisaged between the sample and the atmosphere. These are



at the cathode, and the reverse reaction at the anode. Thus, in experiments where only the cathode surface is exposed to oxygen, electrode reaction (2) will ensure an ample supply of current-carrying oxide ions, but such will not be the case when the anode surface is exposed. Indeed, in the latter case the electrode reaction will remove the current carriers, which will not be replenished because under these conditions the cathode region will be starved of oxygen. Thus, if the current carriers are oxide ions, the current flowing through the cell should be greater when the cathode face is uppermost than when the anode face is uppermost. This was found to be the case at all field strengths, typical equilibrium current values at $4 \times 10^5 \text{ V m}^{-1}$ being 0.18 mA (cathode uppermost) and 0.06 mA (anode uppermost). Moreover, the current flowing with the cathode uppermost was field dependent, whereas with the anode uppermost the equilibrium current values were independent of the field strength at all but the highest fields. This anode behaviour is typical of a system in which there is depletion of charge carriers.

Electrolysis in argon and reducing atmospheres

The foregoing discussion of the charge carrier mechanism suggests that at lower oxygen partial pressures the electrolysis results should be different from those in air. However, for a comparison of electrolysis results in other atmospheres to be meaningful, account must be taken of the possible effect of the atmosphere on grain growth in the unelectrolysed sample (for example, hydrogen atmospheres significantly increase the rate of grain growth in MgO ¹⁷). The results were therefore expressed in terms of a parameter δ , defined by

$$\delta = D_{\text{electrolysed}} - D_{\text{unelectrolysed}} \quad (3)$$

where D is the mean crystallite size in a particular atmosphere. Plots of δ for air, argon and 95% N_2 /5% H_2 are shown in Fig. 4, from which the following points emerge:

(i) At all oxygen partial pressures, including reducing conditions, grain growth is greatest at the positive electrode.

(ii) Grain growth due to electrolysis is greatest in reducing conditions and decreases with an increase in oxygen partial pressure.

(iii) The behaviour at the negative electrode varies from grain growth suppression in air (negative δ) to a significant enhancement of grain growth in H_2/N_2 (positive δ). In argon, which contains 2% O_2 according to the maker's specifications, and therefore represents an intermediate case, δ is zero for the negative electrode.

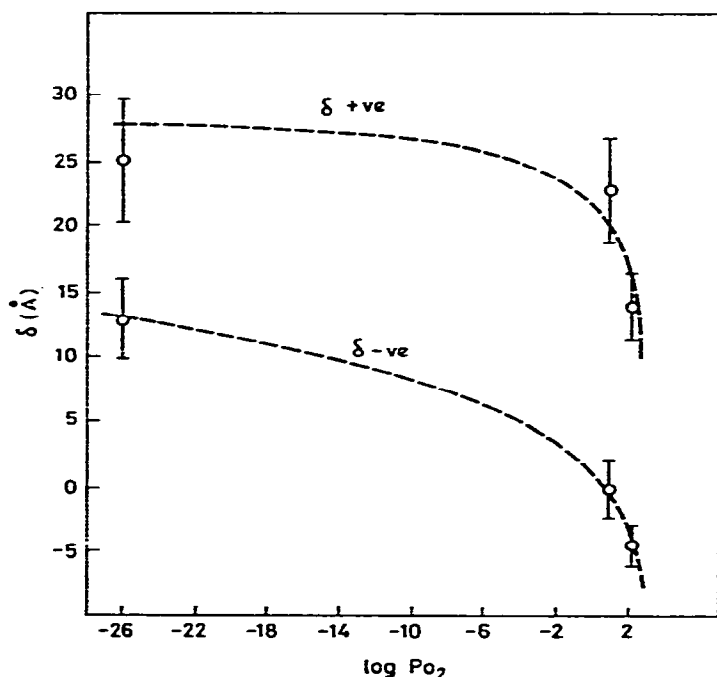


Fig. 4. Plot of δ (as defined in text) as a function of oxygen partial pressure for MgO at 600°C, field strength $4 \times 10^5 \text{ V m}^{-1}$.

The currents carried by the samples under different atmospheres are shown in Fig. 5. The similarity between this and Fig. 4 shows clearly a relationship between the effect of electrolysis on crystallite growth and the current flowing, which in turn depends on the reaction atmosphere. In reducing atmospheres, the increased current may be due to an increase in the concentration of anion vacancies resulting from surface reduction of the oxide as suggested by Dell and Weller¹⁸; the defects introduced into MgO by hydrogen are, however, thought to favour volume diffusion rather than surface diffusion¹⁷.

The results of the atmosphere experiments suggest that over the range of oxygen partial pressures investigated here, the charge carriers are in all cases anions. The amount of crystallite growth due to electrolysis apparently depends both on the number of charge carriers and on the number of anion defects which provide the

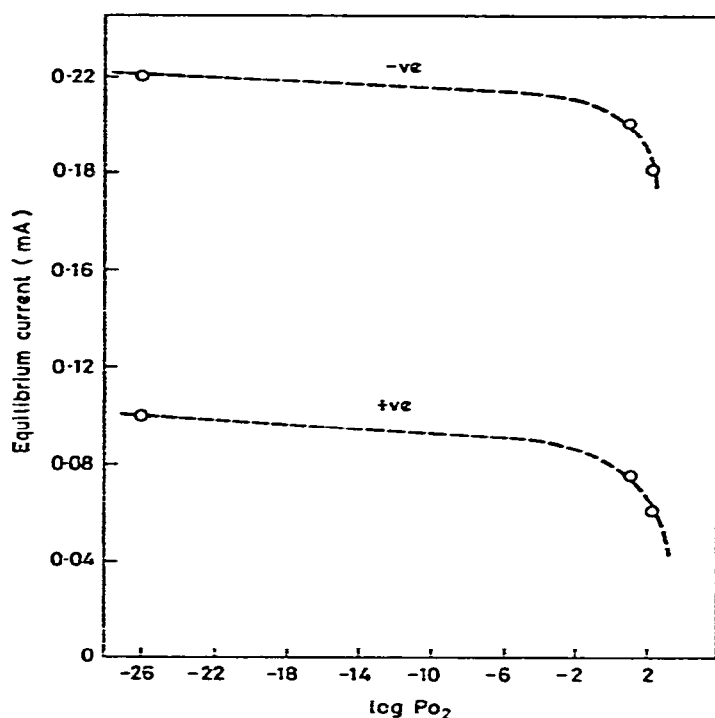


Fig. 5. Plot of equilibrium electrolysis current as a function of oxygen partial pressure for MgO at 600°C, field strength $4 \times 10^5 \text{ V m}^{-1}$.

transport mechanism. At higher oxygen partial pressures the concentration of charge carriers is large, particularly where the cathode surface is in contact with the atmosphere, and the factor which ultimately limits the electrolysis efficiency is the defect concentration. The reverse is the case in reducing conditions.

The effect of protons on electrolysis

Since all the foregoing experiments indicate charge transport by negative ions, it is of interest to know how the electrolysis results would differ if the current was carried by positive ions. Since at the temperature of the present experiments the proton is the most mobile positively charged ion, a few electrolysis experiments were made using $\text{Mg}(\text{OH})_2$. Since this hydroxide was the same material from which the oxide had been prepared for the previous experiments, the impurities in both materials were identical. Although dehydroxylation of the hydroxide will have occurred during the rapid heat-up of the X-ray furnace, mass spectrometric studies have shown that an appreciable concentration of protons still remains in such materials up to much higher temperatures¹⁹. Thus the difference between this material and the oxide used previously is a much higher proton concentration in the former.

The results of a typical experiment are shown in Table 1, which includes for comparison analogous electrolysis data for the oxide. Table 1 shows that by comparison with the oxide, the electrolysis behaviour of $\text{Mg}(\text{OH})_2$ is completely the

TABLE 1

ELECTROLYSIS DATA FOR Mg(OH)_2 AND MgO IN AIR, FIELD STRENGTH $4.0 \times 10^5 \text{ V m}^{-1}$

<i>Material</i>	$\delta + \tau e$	$\delta - \tau e$	<i>Equilibrium current (mA)</i>	
			<i>Anode uppermost</i>	<i>Cathode uppermost</i>
Mg(OH)_2	-2.8	+22.1	0.22	0.18
MgO	+14.0	-4.5	0.06	0.18

reverse; the maximum crystallite growth is now at the negative electrode, although the actual magnitude of the effect is comparable. By contrast with the oxide, current flow in the hydroxide is greater when the anode is uppermost, although differences between the anode and cathode currents are much less than for the oxide, and may not be significant. These results are consistent with the electrolysis behaviour of protons in other systems²⁰ in which the electrolysis product is water vapour which forms at the cathode by recombination of protons with hydroxyl ions. The increase in crystallite size at the cathode is attributable to the effect of this water vapour, which is known to catalyse grain growth in MgO ¹⁷.

CONCLUSIONS

1. Electric fields induce an increase in mean crystallite size of MgO in air at the anode face, due to the transport of oxide ions to that region and their subsequent reaction with magnesium ions.
2. Similar results are obtained even in reducing conditions, suggesting that the charge carriers are oxide ions in all cases. No evidence was found for conduction by Mg^{2+} in the present system.
3. The electrolysis efficiency depends both on the number of available charge carriers and on the number of anion defects, which provide a path by which the former migrate. The current carried is limited by the charge carrier concentration at low oxygen partial pressures and by anion defects at higher oxygen partial pressures.
4. In MgO containing a high concentration of protons, the greatest crystallite growth occurs at the cathode face. This can be explained in terms of proton migration to the cathode, where the subsequent formation of water vapour catalyses crystallite growth.

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