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Cavity growth in neutron-irradiated magnesium oxide

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The growth of cuboidal cavities in neutron-irradiated magnesium oxide after annealing in the temperature range 1475 to 1775° C has been followed using the techniques of transmission electron microscopy and electron spin resonance. Microscopic examination has shown that, while cavities are nucleated on annealing at about 1500° C, most of their growth does not occur until a temperature approaching 1625° C is exceeded. Electron spin resonance spectra from the same samples annealed in the temperature range 1475 to 1575° C indicate that some of the vacancies, which are released to the lattice when cavities are nucleated, are used in the formation, from iron present at impurity level in the crystals, of Fe^{3+} in octahedral symmetry at magnesium sites. This corresponds to the region of negligible cavity growth. For annealing treatments at and above 1625° C however, the fractional volume of crystal occupied by cavities increases by a factor of ten and simultaneously the octahedral symmetry Fe^{3+} transitions disappear. The role of iron in controlling vacancy movement and cavity growth is discussed.

1. Introduction

The growth of cavities bounded by low index crystallographic planes is a feature of irradiation damage occurring in ionic single crystals. To nucleate these defects and to sustain their growth it is necessary to create a sufficient number of vacancies with a mobility high enough to allow agglomeration. For this to occur in magnesium oxide, MgO, Morgan and Bowen [1] have shown that it is necessary to irradiate to a dose exceeding 10^{20} nvt and subsequently to anneal in argon at a temperature greater than 1500° C for 1 h. In addition to the production of vacancies, exposure to such irradiation results in the transmutation of magnesium and oxygen nuclei thereby producing mainly inert gas atoms of neon and helium [2]. Morgan and Bowen demonstrated that the cavities in annealed material contained these gases at low pressure.

In the case of the alkali halides, it has been shown that impurity atoms often play an important role in radiation damage processes. The MgO studied by Morgan and Bowen was known to contain a relatively large impurity concentration of about 500 ppm which was chiefly Fe, Al, Ca and Si. Thus it is expected that at least some of these impurities may be involved in the cavity growth process, especially as Bowen's density measurements, made on similarly treated samples, suggested that cavity growth was a two stage process [3]. However, to date, no evidence for the correlation between impurity content and cavity growth has been reported and the aim of this study was to investigate if any such relationship existed. Transmission electron microscopy (TEM) on its own was inadequate to identify impurities, so a complementary technique was necessary. Such a technique is that of electron spin resonance (esr) which is not only capable of detecting very low levels of certain impurities, but is also useful for monitoring changes in local environments. Esr has already been used extensively in the study of neutron irradiation damage in MgO and of the effect of annealing at temperatures below that necessary to nucleate cavities [4]. Thus it was intended in this work to extend the use of this technique to the study of samples containing cavi-

ties and to correlate the results with TEM of the same samples.

2. Experimental

The single crystals of MgO used for this study were obtained from Semi-Elements Inc, Saxonburgh, Pa. Cleaved specimens having dimensions of about $10 \times 4 \times 0.5\,mm^3$ were given a heat-treatment for 18 h at 1300° C in an ambient of hydrogen before being irradiated to a dose of 3.66×10^{20} nvt in the Harwell Dido reactor. The irradiation temperature was about 150° C.

Post-irradiation annealing treatments, each of 1 h duration, were carried out over a range of temperatures at 50° C intervals between 1475 and 1775° C in an atmosphere of argon. The heating and cooling periods were short compared with the 1 h annealing time; to achieve the latter, the samples were air-cooled.

Esr spectra in the region of magnetic field corresponding to the *g*-value of the free electron were obtained from each of the annealed samples. All measurements were made with a 35 GHz spectrometer using 160 kHz phase-sensitive detection at 77 K. Measurements were made with the magnetic field in a {1 0 0} plane of each specimen. Calibration of this field was made using a trace of D.P.P.H., the *g*-value of which was taken to be 2.0037, supplementing the electromagnet calibration obtained employing the proton/lithium resonance technique.

After examination by esr the samples were cleaved and the flakes so produced were further reduced in thickness by chemical polishing using phosphoric acid at about 150° C (see, for instance, Washburn *et al.* [3]). The thinned samples were examined in a JEM 120 electron microscope. To determine the size distribution of the cavities, a number of micrographs were recorded from different areas for each annealed specimen. The sample orientation was close to a ⟨1 0 0⟩ direction in all cases.

3. Results

3.1. Transmission electron microscopy

Examination by TEM showed that the sample annealed at 1475° C contained interstitial dislocation loops and tangles as seen in Fig. 1. This damage is similar to that described and discussed by Groves and Kelly [6] and by Bowen and Clarke [7]. In all of the samples annealed above 1500° C cuboidal cavities as seen in Fig. 2a and b were

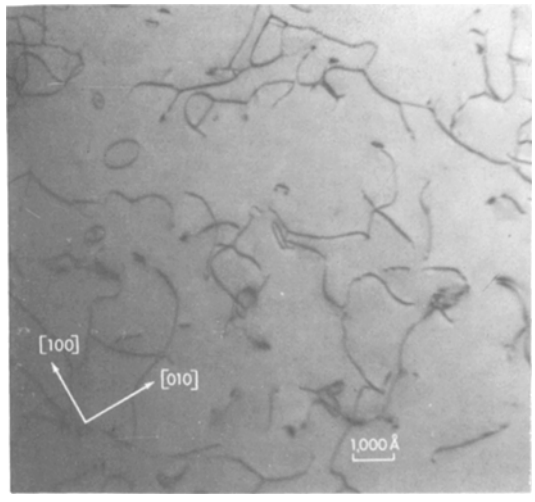

Figure 1 Interstitial dislocation loops and tangles in the sample annealed at 1475° C for 1 h.

present. These figures, which were recorded from the sample annealed at 1675° C, show that the cavities range in size from about 50 to 300 Å and are bounded by {1 0 0} faces. The dislocations which were still present in those samples annealed at temperatures greater than 1500° C were often associated with cavities. This observation is in agreement with that of Morgan and Bowen [1] but we would further point out that dislocations frequently appeared to be pinned by the cavities as at A in Fig. 2a. This pinning was such that the orientation of the dislocations close to the cavities was near to a ⟨1 1 0⟩ direction, as at A in Fig. 2b.

The histograms in Fig. 3 show the size distributions of the cavities as a function of annealing temperature. They were derived from at least ten micrographs taken from different areas for each annealed sample. The main observation to be made from these size distributions is that the mean cavity size increases dramatically on annealing at a temperature exceeding some value between 1575 and 1625° C. Annealing at higher temperatures than this does not appear to produce any further increase in cavity size or significant change in the size distribution.

The total cavity volume per unit crystal volume and the concentration of cavities for each annealed sample have also been estimated and are given in Table I. For the purpose of these calculations a mean specimen thickness for the total area from which the size distributions were obtained was taken to be 1000 Å, a typical sample thickness for transmission microscopy. Accepting the crudeness

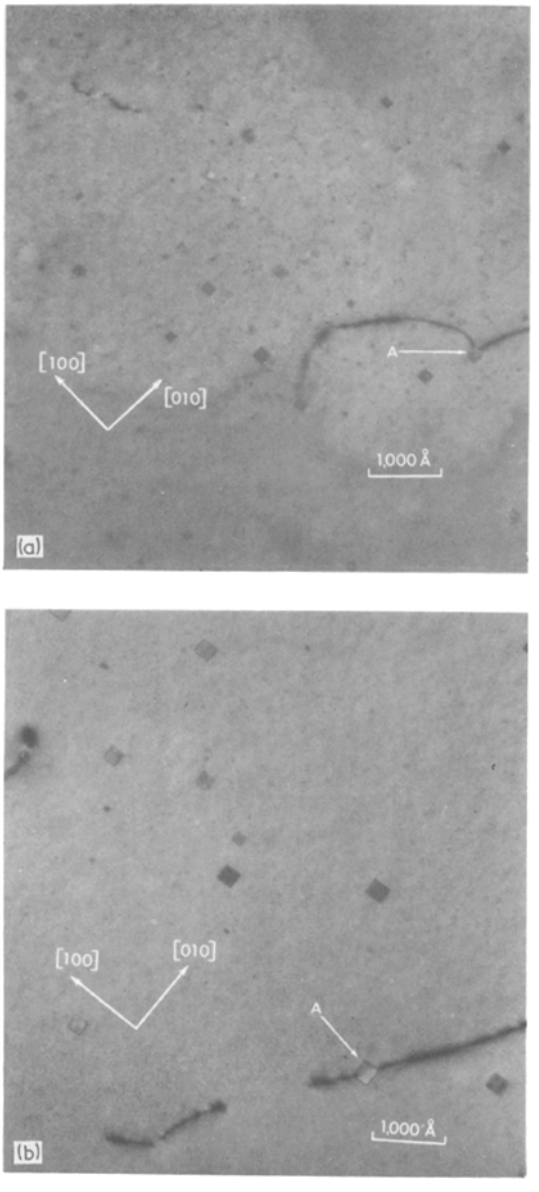

Figure 2 The pinning of dislocations at cavities in the sample annealed at 1675° C. In (a) both sections of the dislocation at A are approximately in the plane of the foil, while in (b) one section of the dislocation at A is almost perpendicular to this plane.

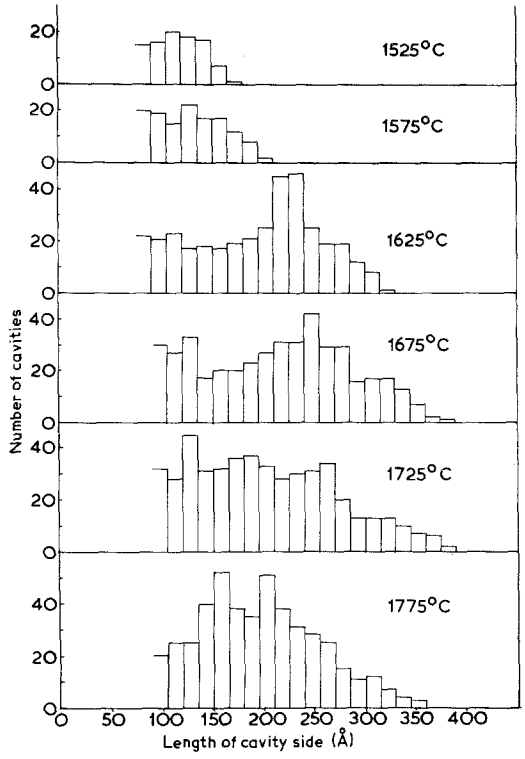

Figure 3 Histograms showing the size distributions of cavities as a function of annealing temperature.

of this approximation, Table I shows that the large increase in cavity size which occurs at 1625° C (see Fig. 3) is accompanied by a large increase in the ratio of the total cavity volume to crystal volume. The cavity concentration remains more or less unchanged.

3.2. Electron spin resonance

The main results of the esr studies are illustrated by the spectra obtained from the specimens annealed at 1475, 1575 and 1625° C, respectively. In examining these it is to be noted that, although detailed analyses of the particular specimens used were not available, data on other MgO crystals made by the same supplier (Semi-Elements Inc)

TABLE I

	Temperature of anneal (°C)					
	1525	1575	1625	1675	1725	1775
Ratio of cavity volume/ crystal volume ($\times 10^4$)	1.8	1.4	13.5	11.2	11.9	16.2
Number of cavities per cm^3 ($\times 10^{-14}$)	0.95	0.51	1.38	0.83	1.00	1.64

has been given by Martin [8] whose results showed that the major paramagnetic impurity was iron at about 100 wt ppm; it is also generally accepted from analytical evidence on other MgO crystals that both manganese and chromium are often present at low trace levels.

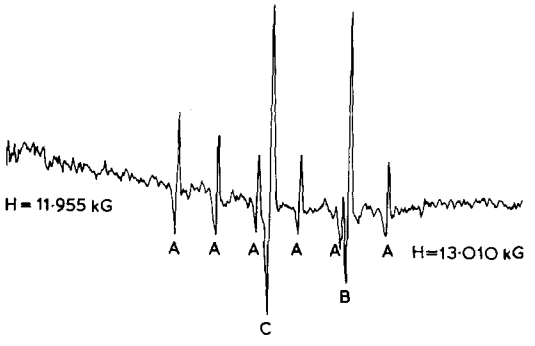

Figure 4 An esr spectrum of the sample annealed at 1475° C.

Fig. 4 shows the spectrum obtained with the magnetic field parallel to ⟨1 0 0⟩ for the specimen annealed at 1475° C which contained interstitial loops but no cavities (cf. Fig. 1). The prominent features are (a) six lines marked A, (b) a line B having $g = 1.9785$ and (c) a line C having $g = 2.0034$. Features A and B were identified by comparison with Henderson and Wertz's data [9] as arising from the $+\frac{1}{2} \rightarrow -\frac{1}{2}$ transition of Mn^{2+} and from Cr^{3+}, respectively. The origin of line C is in some doubt. Further measurements showed that it was isotropic, indicating that it could not be ascribed to an interstitial atom with an associated vacancy; although the g-value is reasonably close to that of the $+\frac{1}{2} \rightarrow -\frac{1}{2}$ transition of Fe^{3+} in octahedral symmetry, this interpretation is precluded because the $-\frac{3}{2} \rightarrow -\frac{1}{2}$ and $+\frac{3}{2} \rightarrow +\frac{1}{2}$ Fe^{3+} transitions are absent; and finally the g-value does not fit with any of those of the impurities listed in the review by Henderson and Wertz. Evidence given later suggests that line C may arise from an electron trapped in a vacancy to form a centre persistent even at the annealing temperatures used.

In the spectra obtained from specimens annealed at both 1525 and 1575° C, i.e. just above the temperature necessary to nucleate cavities, new features were observed. These are shown in Fig. 5 which refers to a specimen annealed at 1575° C. The most important change is the occurrence of the new lines marked D and E; the g-value of 2.0031 for the D transition, together with the

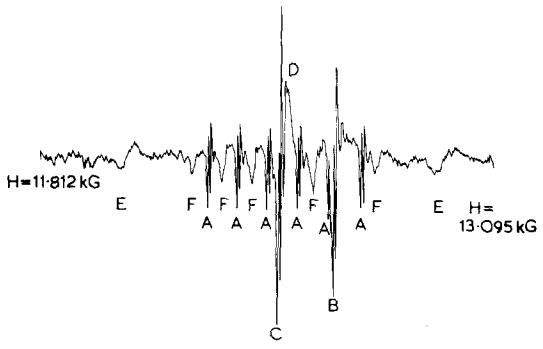

Figure 5 An esr spectrum of the sample annealed at 1575° C.

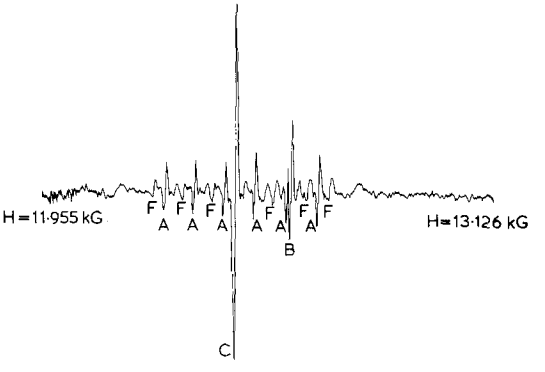

Figure 6 An esr spectrum of the sample annealed at 1625° C.

observed anisotropy of the E lines, fit well with reported data on Fe^{3+} [9, 10] and enable them to be identified as the $-\frac{1}{2}$ to $+\frac{1}{2}$ and $\pm\frac{3}{2} \rightarrow \pm\frac{1}{2}$ transitions, respectively, of Fe^{3+} in octahedral symmetry, i.e. Fe^{3+} occupying a magnesium site. The other differences appear to be associated with localized detailed changes in the manganese environment; they include additional transitions close to each of the six A lines and also transitions F situated midway between the A lines. The transitions F are of low intensity and have the same separation as the A lines.

The spectra of specimens annealed above 1575° C (e.g. Fig. 6) differ from those just described in two major respects. In the first place there is no indication of the D and E lines corresponding to Fe^{3+} in octahedral symmetry; secondly, the additional lines in Fig. 5 which were attributed to Mn^{2+} are much less pronounced. Comparison of all the spectra shows that the intensity ratio of the Mn^{2+} hyperfine and Cr^{3+} lines remained approximately constant throughout all the annealing treatments and consequently the

hyperfine components of Mn^{2+} could be used as an intensity reference, (cf. [11]). On this basis it appears that in Fig. 6 the intensity of line C has increased by approximately twice, indicating that annealing at 1625° C produces a two-fold increase in the number of centres responsible for line C.

4. Discussion

An important conclusion of Morgan and Bowen [1] from their studies of neutron-irradiated and annealed MgO was that to nucleate cavities it was necessary to anneal samples irradiated to a dose in excess of 10^{20} nvt at a temperature greater than 1500° C in an ambient of argon. This minimum critical temperature was attributed to the activation energy associated with vacancy mobility. In addition, the results of our annealing studies concerning the nucleation and growth of cavities would suggest that another critical temperature for the growth exists in the temperature range of 1575 to 1625° C. While annealing above some temperatures within this range does not produce any significant change in the concentration of cavities, the ratio of total cavity volume to unit volume of crystal increases by an order of magnitude. This must similarly be accounted for by the movement of vacancies and consequently we propose that, following the nucleation of cavities, some mechanism exists which impedes further growth of these defects until another critical temperature (for 1 h annealing period) is exceeded. An indication of the nature of this mechanism can be inferred from the results of our esr measurements as will be discussed later.

One feature of cavities which was noted by Morgan and Bowen [1] was that they were often located at cusps in dislocation lines. In our studies we have found that these cusps correspond to two sections of a dislocation each pinned to a corner of a cavity and lying close to a ⟨1 1 0⟩ direction in the immediate proximity of the cavity (see Fig. 2a and b). The reason why no cusp is observed in the dislocation associated with the cavity at A in Fig. 2b is attributed to the orientation of this dislocation with respect to the direction of observation. Its short length and oscillatory contrast on one side of this cavity is indicative of this section having a large component perpendicular to the plane of examination. Conversely, the section on the other side of this cavity is relatively long showing that it lies approximately parallel to the plane of the foil in the region shown. The cusp at A in Fig. 2b consequently lies in a plane perpendicular to the plane of the sample. Thus the association of cavities with dislocations is interpreted as follows. When an interstitial loop, which is still present in a sample at an annealing temperature greater than 1500° C, moves through the crystal it is probable that the interaction with the cavities present will result in partial annihilation of the loop by vacancies from the cavities. The movement of the parts of the loop near cavities will consequently be impeded. It is further suggested that the observed ⟨1 1 0⟩ orientation of dislocations in the region of cavities is related to a favourable configuration for the above annihilation process to occur. This is attributed to the fact that in the NaCl structure the uninterrupted rows of anions and of cations in ⟨1 1 0⟩ directions makes diffusion of vacancies of either type more likely in these directions than in others.

The esr results show that the nucleation of cavities, in the samples annealed at 1525 and 1575° C, is accompanied by the appearance of Fe^{3+} in octahedral symmetry. As mentioned earlier, analysis of material made by the same supplier has shown that iron was present in the specimens [8]. Owing to the pre-irradiation heat-treatment in hydrogen it is most likely that any iron present will be in divalent state (cf. [12]); this view is supported by the absence of Fe^{3+} lines in specimens annealed at temperatures below 1500° C (Fig. 4). As the post-irradiation annealing took place in an inert atmosphere the cation vacancies necessary for the conversion of Fe^{2+} into Fe^{3+} on increasing the annealing temperature from 1475 to 1525° C must have come from within the crystal. An adequate supply of vacancies is known to be produced when the vacancy clusters, which are about 7 Å in diameter and which are present in similarly treated specimens, suddenly collapse on annealing at about 1500° C [13]. The disappearance of the Fe^{3+} lines at temperatures above 1625° C could be explained either by a reduction of Fe^{3+} into Fe^{2+} by the outward diffusion of cation vacancies or by the trapping of vacancies near the Fe^{3+} sites, creating an Fe^{3+}-vacancy complex [14] whose esr would probably fall in the low magnetic field region outside the present range of measurement. Since the subsequent growth of the cavities indicates that a large number of vacancies are retained in the crystal the outward diffusion explanation appears unlikely and the trapping mechanism more probable.

In view of the esr evidence, we envisage the cavity nucleation and growth proceeding by stages as follows. On annealing just above 1500° C, a critical vacancy mobility is exceeded and small cavities are nucleated in the manner described by Morgan and Bowen [1]. Simultaneously there is a conversion of iron to Fe^{3+} in octahedral symmetry at magnesium sites; this conversion uses vacancies released when clusters collapse at about 1500° C which then form charge compensating centres for the Fe^{3+} ions. After nucleation, negligible cavity growth occurs until an annealing temperature of 1625° C (for 1 h) is reached, see Fig. 3. This behaviour is attributed to mobile vacancies being trapped near the Fe^{3+} sites in preference to condensation at cavities. A calculation, based on the observed cavity growth between the annealing temperatures of 1575 and 1625° C and an iron impurity level of 100 wt ppm, shows that the number of vacancies required to associate with all the Fe^{3+} is some two orders of magnitude less than the number required to account for the cavity growth. When this stage is complete, cavity growth can proceed. It is suggested that the presence of iron is not expected to alter the magnitude of ultimate growth significantly. However, the extent to which growth is impeded, and hence the annealing temperature necessary for the last growth stage, would be expected to increase with iron concentration. Further evidence which indicates that cavity growth is incomplete when annealing at 1500° C is provided by the measurements of Bowen [3], who recorded the density variation with annealing temperature for similarly treated MgO. These show a discontinuity at about 1625° C and consequently his results suggest that cavity formation is a two-stage process, as our studies using a different technique (TEM) have confirmed to be the case. In addition, the high precision X-ray measurements of Briggs and Bowen [15] showed that complete recovery of the lattice parameter to the unirradiated value did not occur until the annealing temperature reached about 1750° C. However, interpolation of their data would suggest that most of the recovery had occurred at about 1650° C. So, allowing for the fact that their material was irradiated to more than twice the dose of that used in this study, it is concluded that there is a reasonable correlation between the minimum temperature at which we have found it necessary to anneal to produce most of the cavity growth and that reported by Briggs and Bowen to obtain almost complete recovery of the lattice parameter. To the authors' knowledge the influence of an impurity on the movement of vacancies and cavity growth has not previously been reported. Here it appears that iron plays a significant role. It is possible that other impurities may act in a similar way, but this remains to be established.

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