JOURNAL OF MATERIALS SCIENCE 17 (1982) 2939–2946

Magnesioferrite formation in low-concentration Fe/MgO single crystals

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Single crystals of MgO containing iron in concentrations from 310 to 12900 ppm have been examined by magnetic resonance and reflection electron diffraction before and after ageing in oxygen in the temperature range 600–800° C. Before ageing, only the e.s.r. spectrum of isolated Fe^{3+} ions in cubic sites was seen and the diffraction patterns revealed MgO alone. After ageing, a strong anisotropic line, centered near $g = 2.00$ and exhibiting the characteristics of ferrimagnetic resonance, was found and its presence was coupled with the appearance of a spinel pattern superimposed on that of the MgO. Analysis of the variation of anisotropy field with ageing time gave estimates of the room-temperature magnetization, first anisotropy constant and Curie temperature of 258 emu cm^{-3}, -2.7×10^{-3} J cm^{-3} and 500 ± 10 K, respectively, which, in view of the close agreement with published data, suggested magnesioferrite formation even at very low iron concentrations. In the initial stages of ageing a strong isotropic resonance line was observed which appeared to be a precursor of the anisotropic ferrimagnetic line.

1. Introduction

In our previous work on Fe/MgO [1, 2] we have been primarily concerned with the feature of the electron spin resonance (e.s.r.) spectrum in as-grown single crystals in order to characterize the material prior to making studies of the role of the impurity in determining the electrical and dielectric properties of the doped crystal [3, 4]. The earlier work showed that the linewidths of the $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition of Fe^{3+} in cubic sites were substantially independent of the total iron content. In the later work, (which included measurements both on as-grown crystals and on crystals which had been solution treated [5, 6] to maximize conversion to Fe^{3+} and induce homogeneous dispersion) estimates of the numbers of spins contributing to the Fe^{3+} line were made; it was then shown that while the highest measured Fe^{3+} concentrations gave linewidths comparable with those predicted from Kittel and Abraham's dipolar broadening theory, most samples gave linewidths considerably broader than those predicted. Even at extremely low concentrations very little of the iron was present as isolated Fe^{3+} ions and it was suggested that this was partly caused by clustering. It is well known that at iron concentrations above a few thousand ppm, magnesioferrite precipitates may be formed in magnesium oxide after heat treatment (e.g. Groves and Fine [7], Davidge [8]) and recently de Biasi and Devezas [9, 10] have studied the ferrimagnetic resonance (f.m.r.) behaviour of such precipitates. We have now explored these effects in a range of low iron concentration Fe/MgO single crystals after ageing them by heating in oxygen at temperatures between 600 and 800° C and subsequently using a combination of magnetic resonance and reflection electron diffraction (RED) techniques to correlate changes in the resonance spectrum with the development of a new structural phase.

2. Experimental details

Single crystals of magnesium oxide containing iron in a range of concentrations from 310 to 12900

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ppm by weight were obtained from W. and C. Spicer Ltd. The crystals had been grown by arc-fusion and analysed (by Johnson, Matthey and Co) for iron content using X-ray fluoresence. Samples having {100} faces and measuring about 8 mm × 8 mm × 0.3 mm thick were cleaved from these crystals for investigation.

Magnetic resonance spectra were first obtained from these samples both in the as-grown state and after solution treatment [2] using a Varian V-4502 spectrometer system operating at 9 GHz. The samples were then aged for different periods of time, at various temperatures in the range 850 to 1073 K. The ageing treatments were carried out in flowing oxygen, in an electric furnace lined with silica glass. The samples were loaded in a platinum basket in a silica boat and at the end of the ageing period – which varied from a few minutes to tens of hours – were quenched by pushing the boat rapidly clear of the furnace into the inflowing stream of oxygen. Between each of the ageing periods the samples were examined by magnetic resonance and RED.

The e.s.r. spectra were obtained at various temperatures in the range 80–500 K with the aid of V-4502 variable temperature unit, the sample in the cavity being surrounded by a silica glass liner and bathed in a continuous stream of dry nitrogen gas, pre-heated or -cooled as required. The temperature of the sample was monitored by means of a copper–constantan thermocouple, one junction of which was placed in the cavity immediately adjacent to the sample. Spectra were recorded for various orientations of each crystal, the static field being applied always in a {100} plane. The magnet sweep was calibrated with a Newport Instruments Type P2 proton magnetometer (the probe being placed in the magnet gap alongside the cavity), and the klystron frequency was determined using a Hewlett–Packard X532B frequency meter.

For study by reflection electron diffraction the samples were cleaned in acetone and air-dried before being etched for 5 min in fuming nitric acid. This etching treatment preferentially dissolves the MgO leaving impurity precipitates exposed at the top of the etch hillocks on the surface [11]. The advantage in producing such a surface is that the electron beam, at grazing incidence, samples a higher volume-ratio of precipitate to host material than it would otherwise do, so enhancing the contribution to the diffraction pattern from the precipitates relative to that from the bulk material. The etched samples were mounted on a goniometer stage situated below the projector lens of a JEM 120 electron microscope. This stage allowed for 360° rotation of the sample about an axis perpendicular to the electron beam, for tilt of up to 10° about a second horizontal axis perpendicular to the first, and for translation in two mutually perpendicular directions in the horizontal plane. Charge which accumulated on the samples was neutralized by means of an electron beam of a few hundred electron volts energy, directed at the sample.

3. Results

3.1. General features of magnetic resonance

As far as magnetic resonance was concerned the principal effect of ageing was to modify the e.s.r. Fe^{3+} cubic site isolated ion spectrum by the addition of either one or two very intense lines, each situated near $g = 2.0$. These spectral lines were observed after ageing at temperatures from 850 K upwards, and were seen in all the samples, i.e. at total iron concentrations from 310 ppm upwards. The two lines which could be resolved when occurring simultaneously were quite different in behaviour, the one being isotropic and the other anisotropic. The general picture which emerged, however, was that the isotropic line appeared first, being replaced gradually by the anisotropic line as ageing progressed. The greater the initial concentration of iron in the sample or the higher the ageing temperature then the faster this sequence of events occurred.

Fig. 1 shows the early stages of the appearance of the isotropic line (B) in a sample containing 4300 ppm iron and aged at 973 K for consecutive periods of 5 mins. After the first period (Fig. 1a) the Fe^{3+} $\frac{1}{2} \rightarrow -\frac{1}{2}$ e.s.r. line is overlapped by an intense line (B) which spreads widely in the wings, reaching as far as the fine structure (A and C) of the e.s.r. line. After a further 5 min ageing (Fig. 1b) the new line swamps the central Fe^{3+} spectrum completely, only the Fe^{3+} cubic site fine structure still being visible in the wings of the new line. The line is so intense compared with the original Fe^{3+} $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition that, at this gain the peaks have been cut off. The additional e.s.r. line (D) which appears at this stage (in Fig. 1b) is thought to be due to Fe^{3+} vacancy associates [12]. Reducing the gain, Fig. 1c reveals that the line is symmetrical having a

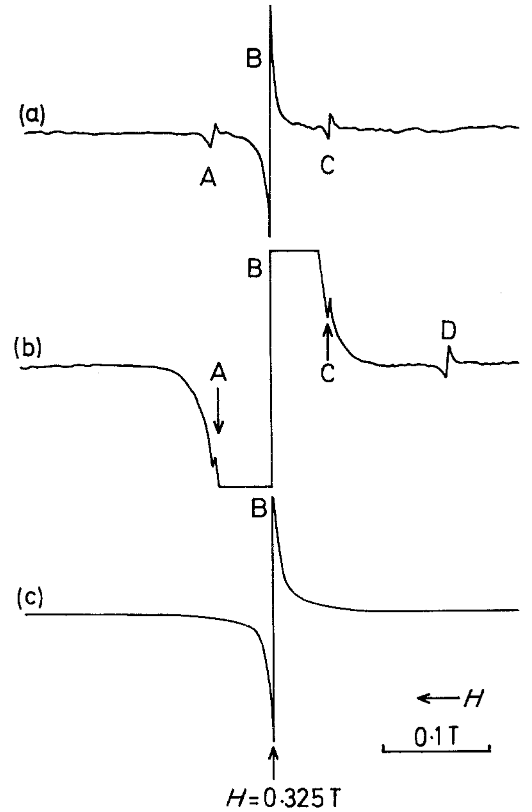

Figure 1 Growth of the isotropic line during the initial stages of ageing at 973 K, (a) after 5 min, (b) after 10 min, same gain as for (a), (c) as (b) but signal gain reduced by × 100.

relatively narrow peak-to-peak linewidth but spreading quite widely in the wings.

The formation of the anisotropic line is illustrated by the pair of spectra shown in Fig. 2. At temperatures of 973 K, a few hours ageing was required before the anisotropic line (E) could be clearly detected. On the other hand, when the ageing was carried out at 1073 K, both the isotropic and anisotropic lines were present in the spectra from the higher iron concentration samples after only 15 min ageing (Fig. 2a). Further ageing of the same sample caused a large increase in the intensity of the anisotropic line relative to that of the isotropic line, which however still showed (Fig. 2b) as a distortion near the centre of the anisotropic line. Considerably longer ageing times were required, particularly for the lower concentration samples, before the spectrum showed only the anisotropic line (Fig. 3).

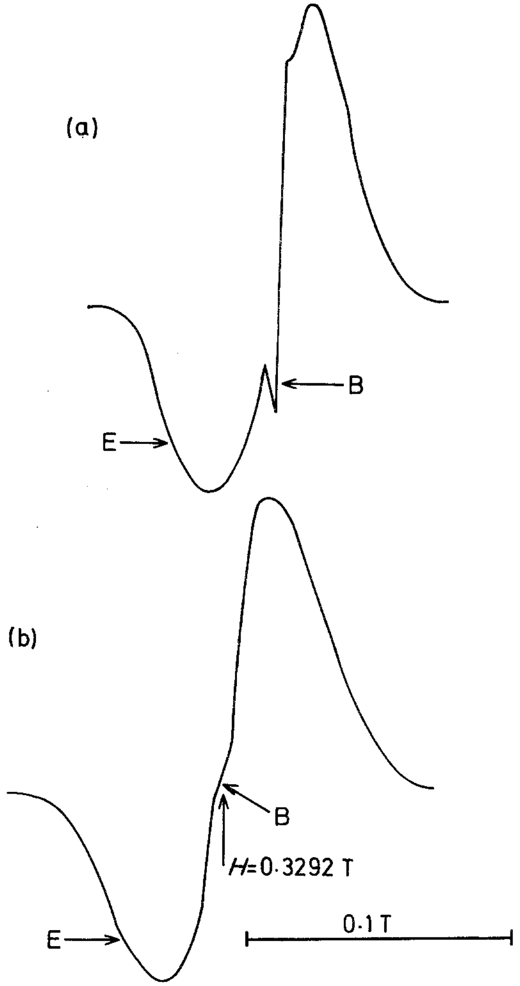

Figure 2 Formation of the anisotropic line in a 11 900 ppm Fe/MgO sample aged at 1073 K (a) after 15 min, (b) after 1 h.

3.2. The isotropic line

The isotropic line is neither Gaussian nor Lorentzian in shape, being more sharply spread in the wings than would be expected from a typical Lorentzian derivative line. The g-value is temperature independent in the range 293 to 466 K, being measured as g = 2.000 ± 0.003. This line is considerably narrower than the anisotropic line, measured values of ΔH_{ms}, (the width from peak-to-peak of the derivative of the line) all lying in the range 1 to 3 mT. The linewidth variation with temperature is illustrated in Fig. 4 which refers to a sample containing 12900 ppm iron and aged at 1073 K for 15 min. There is a decrease in width as temperature is increased and the difference between the widths of the lines recorded with static field in the ⟨100⟩ and ⟨110⟩ directions (about 0.3 mT at 300 K) decreases similarly. The linewidth shows some variation from sample to sample, but for "long" ageing times the lower concen-

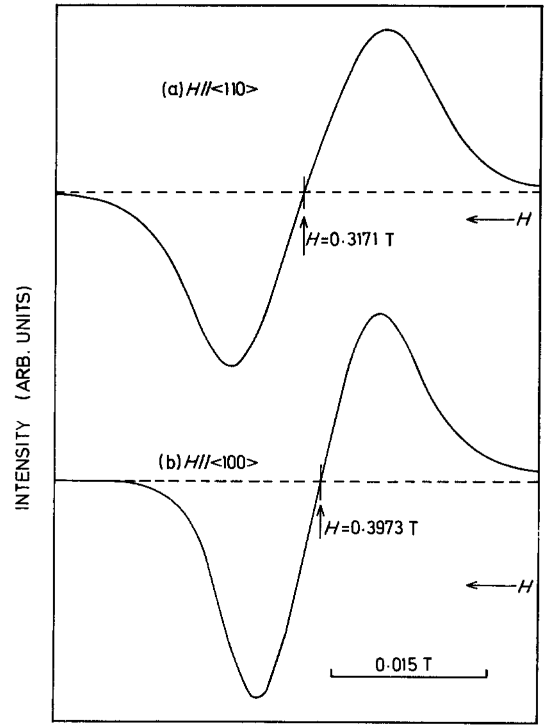

Figure 3 Anisotropic line produced after ageing 4300 ppm Fe/MgO at 1073 K for 24 h.

tration samples give broader lines, as indicated by Table Ia. It was also found that in the early stages the line narrowed with continued ageing. Some typical values of linewidths are given in Table Ib, for various samples aged at 973 K for different periods.

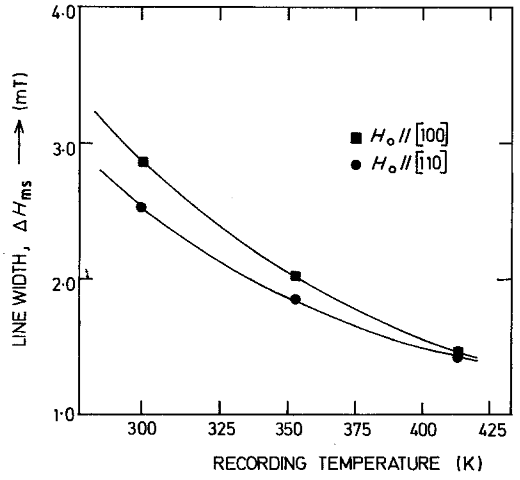

Figure 4 Variation in the peak-to-peak linewidth of the isotropic line with recording temperature for a 12 900 ppm Fe/MgO sample aged at 1073 K for 15 min.

TABLE Ia Variation of linewidth with iron concentration, isotropic line (aged for 15 min at 1073 K; recorded at various temperatures, $H_0 \parallel \langle 100 \rangle$)

Iron concentration (wt ppm)	Linewidth, ΔH_{ms} (mT)		
	296 K	353 K	413 K
8500	3.44	2.33	1.82
11900	2.86	2.22	1.69
12900	2.52	1.84	1.43

3.3. The anisotropic line

From the measurements made in the $\langle 100 \rangle$ and $\langle 110 \rangle$ directions, values of the anisotropy H_a^{sp} were obtained. These were found to increase with ageing time, being temperature-dependent after all ageing times as shown in Fig. 5. This temperature-dependence could be fitted to the empirical relationship

$$|H_a^{sp}|^{1/2} = D\theta + C \tag{1}$$

where θ is the absolute temperature, D is a sample independent constant of value $D = -(4.5 \pm 0.4)10^{-4}\ \mathrm{T}^{1/2}\ \mathrm{K}^{-1}$, C is a constant which varies slightly from sample to sample and H_a^{sp} is in Tesla.

The linewidth was found to be narrower in the $\langle 110 \rangle$ than the $\langle 100 \rangle$ orientation at all temperatures after ageing for up to an hour at 1073 K. After 10 h ageing at the same temperature, the line was still narrower in the $\langle 100 \rangle$ direction when measured at room temperature, but this situation was reversed when the measurements were made at 353 or 413 K, and was also reversed for all measurement temperatures when the ageing was extended to 24 h at 1073 K. The difference between the linewidths for the two orientations was found to be virtually constant after 24 h ageing, being between 1 and 2 mT over the range 113 to 413 K. This was in marked contrast to the behaviour at short ageing times, where differences of as much

TABLE Ib Variation of linewidth with ageing time, isotropic line (aged at 973 K; recorded at room temperature, $H_0 \parallel \langle 100 \rangle$)

Ageing time (min)	Linewidth, ΔH_{ms} (mT)		
	8500 ppm	11900 ppm	12900 ppm
5	2.97	3.01	2.53
10	2.89	2.97	3.07
15	2.82	2.97	3.03
20	2.65	2.74	2.49
25	2.51	–	–
30	2.55	2.38	2.07

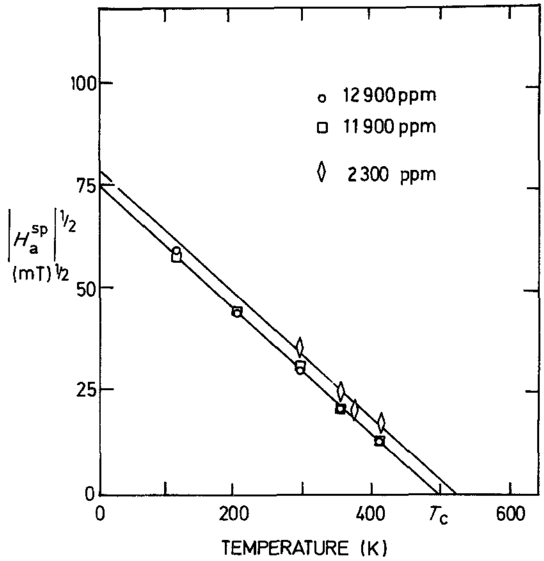

Figure 5 Variation of anisotropy field with temperature for samples containing different concentrations of iron.

as 10 mT were obtained at room temperature, reducing with increased measurement temperature.

The variation of linewidth with ageing time is plotted in Fig. 6 for three samples, where the linewidths were recorded at a variety of temperatures between 113 and 413 K. The linewidths seem to be independent of initial iron concentrations.

3.4. Reflection electron diffraction

The electron diffraction patterns were of two distinct types. The first of these, shown in Fig. 7a and b, arose from the magnesium oxide lattice alone and the second, shown in Fig. 8a and b, contained additional reflections from the ferrimagnetic precipitates. The ⟨100⟩ and ⟨110⟩ patterns in Fig. 7a and b were recorded from an etched sample which contained 4500 ppm Fe which had not received any heat treatment. Patterns like these were obtained from all doped samples in the as-grown state and after solution

The ⟨100⟩ and ⟨110⟩ patterns shown in Fig. 8a and b were recorded from an etched sample which contained 4500 ppm Fe and which had been aged at 973 K for a period of 30 min. The streaks associated with the spots, in the ⟨110⟩ directions in Fig. 8a, are an indication of the degree of etching achieved, being a result of electron refraction at the pyramidal faces of the etch hillocks [13]. Patterns such as these were obtained from all samples containing from 310 to 12900 ppm Fe after they had been aged in the temperature range 873 to 1073 K in oxygen for a period exceeding a few minutes. The additional reflections present in these patterns arise from a second cubic lattice in register with the magnesia matrix, but with a lattice parameter very nearly twice that of the host lattice, i.e. a_0 = 0.838 nm. These patterns closely resemble those obtained by transmission electron diffraction of more heavily doped MgO reported by Groves and Fine [7] and by Krawitz and Cohen [14]. These patterns, like those of Groves and Fine were indexed as a spinel structure. Evidence for this assignment is discussed later.

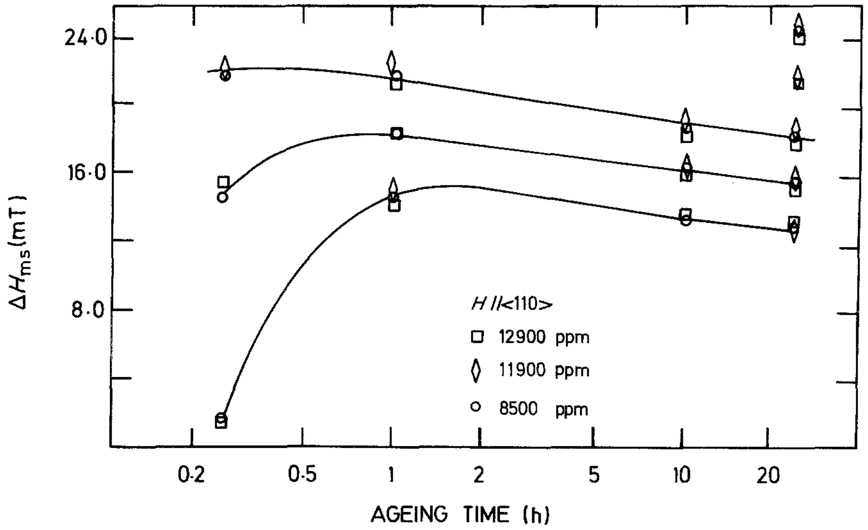

Figure 6 Variation of width of anisotropic line with ageing time at 1073 K.

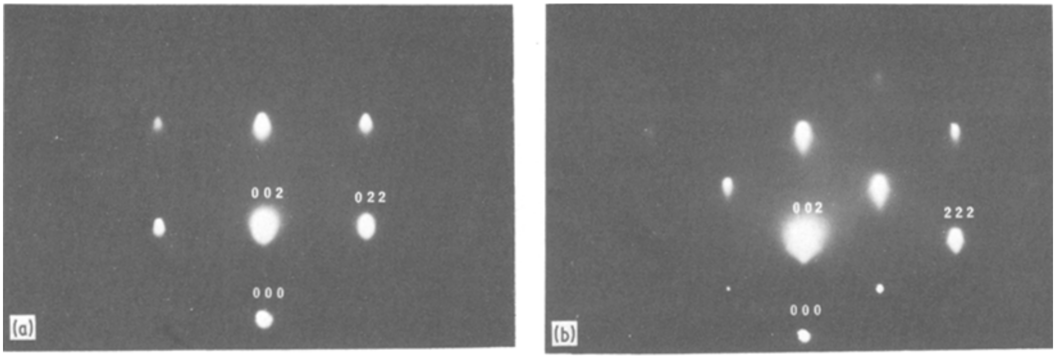

Figure 7 Reflection electron diffraction from etched {100} surface of 4300 Fe/MgO before heat treatment; (a) beam along [100] direction, (b) beam along [110] direction.

4. Discussion

Comparison of the magnetic resonance and reflection electron diffraction data for well-aged specimens showed that the main effect was the formation of a resonance line which exhibited the characteristics attributable to ferrimagnetic behaviour coupled with the presence of a new crystallographic phase having a spinel structure, with a lattice parameter twice that of the MgO host lattice. In view of the published results of Wirtz and Fine [15], de Biasi and Devezas [9, 10] and others [16–18], it seems reasonable to suggest that this represents the formation of magnesioferrite particles precipitated within the MgO matrix.

An attempt to obtain more precise characterization of the precipitate was made by analysis of the variation of measured anisotropy field with ageing time. Here the approach of de Biasi was adopted and computer curve fitting to the expected relation between the anisotropy field for small particles and the corresponding value for bulk material enabled estimates of the room temperature magnetization (I_s) and the first anisotropy constant (K_1) to be obtained; details have been given by Inglis [19]. For a sample containing 12 900 ppm Fe the estimates for I_s and K_1 were 258 e.m.u. cm^{-3} and -2.7×10^{-3} J cm^{-3}. These values are sufficiently close to those given by de Biasi and Devezas [9] ($I_s = 262$ e.m.u. cm^{-3}) and by Belson and Kriessman [20] ($K_1 = -3.2 \times 10^{-3}$ J cm^{-3}) to make it likely that similar material was being examined. Two other features are of interest. Firstly, if the graph of Fig. 5 (which gives the variation of anisotropy field with temperature) is extrapolated linearly to high temperatures, a value of 500 ± 10 K for the Curie temperature of the 11 900 ppm and 12 900 ppm iron samples is obtained. This compares well with the value of 490 K determined by Wirtz and Fine [15] for magnesioferrite precipitates in sintered polycrystalline spheres of MgO containing approximately 14 000 ppm iron and aged at 800° C. Secondly, reference to Fig. 6 shows that the line-

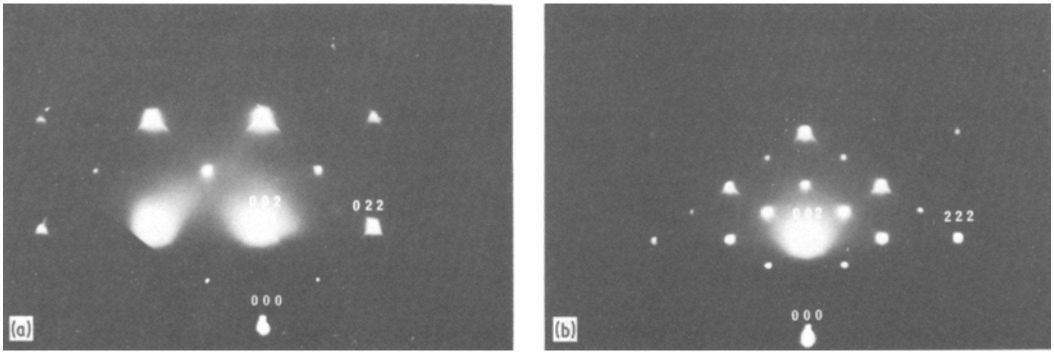

Figure 8 Reflection electron diffraction from etched {100} surface of 4300 Fe/MgO after ageing at 1073 K for 30 min. (a) Beam along [100] direction, (b) beam along [110] direction.

widths initially increase and then show a steady decrease as ageing proceeds. In work on the linewidths of polycrystalline ferrites, Seiden and Grunberg [21] have reported considerable line broadening resulting from porosity. If the precipitates formed here behave like small single crystals with voids (the voids being the interpenetrating regions of MgO) the consequence of continued ageing would be to fill the voids gradually with precipitate so reducing the effective porosity and narrowing the resonance linewidths.

With regard to the reflection electron diffraction results the arguments for indexing the diffraction patterns shown in Fig. 8a and b as spinel structure are as follows. First of all, if one considers the allowed reflections given by the ASTM index for X-ray diffraction by the magnesia–ferrite lattice, then they are either all present or would be present at positions which overlap with the MgO reflections. The systematic absences, given as (200), (420), (600), (640) and (820) in the ASTM index are duly absent or overlap MgO reflections in the (100) reciprocal lattice plane in Fig. 8a. In the (110) reciprocal plane (Fig. 8b), reflections such as the (200) appear, although they should be absent. These cannot be genuine reflections, however, or they would appear in the (100) reciprocal lattice plane as well. They are therefore ascribed to double diffraction [22]. Secondly, the patterns in Fig. 8a and b were consistently detected in those samples which gave an f.m.r. signal, and samples which showed these RED patterns always gave an f.m.r. signal. Furthermore, whilst it is difficult to draw quantitative conclusions from the RED patterns it seems, from the many individual observations made on different samples that the spinel pattern forms most rapidly and with the greatest intensity relative to that of the host lattice, in those samples which have the highest iron concentration, or are subject to the longest ageing times or the highest ageing temperatures – or to any combination of these three factors.

Finally, some comments may be made about the isotropic line observed in the early stages of ageing temperatures – or to any combination of features which we have not yet been able to explain fully. As regards the magnetic resonance results it may be noted that the intensity of the line is too great to allow a paramagnetic origin based on Fe^{3+} on cubic sites even if all the iron were converted to Fe^{3+}. As Fig. 1 shows there is no corresponding increase in the intensity of the Fe^{3+} fine structure lines and the lineshape is unlike that expected from paramagnetic centres in that the wings remain reasonably intense over a field sweep of about 100 mT, although the line centre is narrow. The linewidth, moreover, decreases as the recording temperature is raised, whereas, were the line paramagnetic in origin, one would expect a broadening with increasing temperature. Furthermore, after long ageing times it is noticeable that the samples with the lower concentrations of iron show broader lines than those with the higher concentrations. If the line were paramagnetic and due to isolated Fe^{3+} ions, we would expect the width to be determined largely by dipolar broadening, in which case the linewidth should increase with iron (Fe^{3+}) concentration. An interesting result from the reflection electron diffraction is that the spinel structure phase is clearly observed in the initial stages of ageing; thus samples which exhibit either only the isotropic line or a mixture of the isotropic and anisotropic lines or the anisotropic line alone all give exactly similar patterns. It thus seems that the isotropic line is to be regarded as a precursor of the anisotropic line but the details of its origin in relation to the structural changes in the lattice are not yet clear. It should be noted in conclusion that, over the whole range of iron concentrations, neither the magnetic resonance nor the RED studies gave any evidence of the existence of magnesioferrite precipitation in the as-grown state, or after solution treatment.

Acknowledgements

It is a pleasure to express our thanks to Messrs C. Savage and T. Harcourt for their assistance with specimen preparation.

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Received 17 February
and accepted 15 March 1982