Precipitation (exsolution) in garnet-type oxide

J. Y. LAVAL*

Laboratoire d'Etude et de Synthèse des Microstructures, Centre National de la Recherche Scientifique, Ecole Supérieure de Physique et de Chimie Industrielle, 10 rue Vauquelin, 75231 Paris, Cedex 05, France

The exsolution process of magnetite in a garnet matrix is described. The intragranular nucleation of magnetite in substituted yttrium iron garnets is characterized by a transitional event. Magnetite nucleates in the centre of zones which constitute a transitional phase fully coherent with the matrix. An ionic process model is proposed for this transitional event. This model is in good agreement with the experimental data obtained in electron microscopy. It is shown that the activation energy barrier is lower for nucleation via a transitional phase.

1. Introduction
In oxides, the ionic structure is usually more complex than the atomic structure in alloys. The mechanism for phase transformations is by ionic diffusion and it usually occurs with high activation energy. However, owing to the intricate ionic configuration of the lattice, small ionic displacements may produce a sharp change in the lattice symmetry. Such displacements may lead to a so-called transitional or intermediate phase on which the nucleation of the second phase can occur with a smaller activation energy. Such nucleations have been observed in mineral oxides, for instance in silicates [1].

Our aim is to describe the exsolution process of magnetite from a gadolinium and aluminium substituted yttrium iron garnet.

2. Phase diagram
The Y–Fe–O, Gd–Fe–O, Y–Al–O systems have been extensively studied by Van Hook [2–4]. If we substitute a small amount of Gd and Al for Y and Fe we find that the phase relations in the garnet region are comparable, but because of an increase in the eutectic temperature the main difference will be the appearance of a magnetite and garnet phase. This was confirmed by optical micrography of quenched samples. Fig. 1 gives

a schematic diagram of the phase relation in the garnet region around the eutectic temperature for the pseudo-binary system:

$$(Y_{0.8}Gd_{0.2})_2O_3 - (Fe_{0.92}Al_{0.08})_2O_3.$$
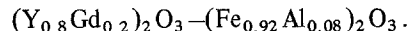
If the specimen contains a slight excess of iron (Δ_{Fe}, Fig. 1) from the composition of the stoichiometric garnet (G) and if we cool the specimen according to the line X, the magnetite will precipitate in M heterogeneously essentially on grain boundaries, where the activation energy for magnetite nucleation will be the lowest. An homogeneous nucleation will need significant undercooling (M'') (the misfit between the two structures is too large to be accomodated coherently) and the creation of an incoherent interface inside a grain will be energy consuming. If there is a transitional phase available which is coherent with the matrix and on which magnetite may nucleate coherently, the activation energy for nucleation will not be so high and nucleation may occur for a smaller undercooling (in M').

3. Experimental
The garnet samples have been prepared from high purity, fine oxide powders. The powder was mixed 2 h in a roller mill of special steel giving a reasonable pick-up in iron [5]. This powder was calcined
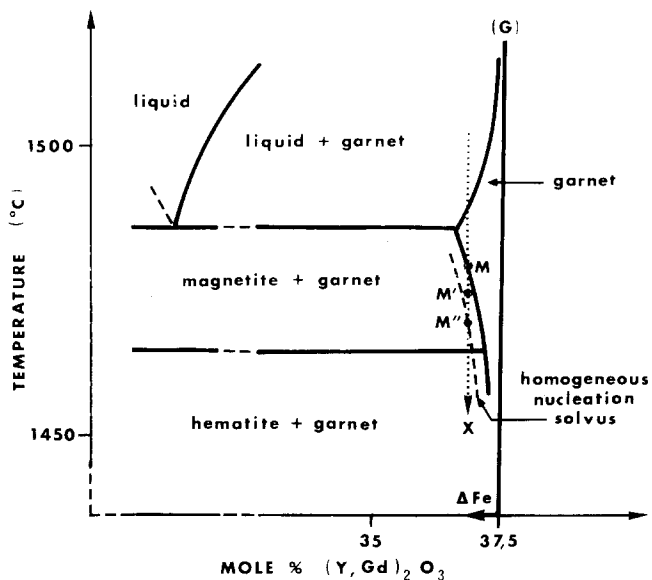
Figure 1 Schematic diagram of stable and metastable phase relations for the pseudo-binary $(Y_{0.8}Gd_{0.2})_2O_3 - (Fe_{0.92}Al_{0.08})_2O_3$ system

at 1235° C, in an oxygen atmosphere, re-milled, pressed (700 N cm^{-2}) and fired in an oxygen atmosphere at around 1480° C. The resistor furnace gives a thermal gradient of 20° C cm^{-1} along the cylindrical samples (length 1 cm).

After water-quenching the cylinders were cut into thin plates which were then mechanically reduced to 50 μm, polished for micrographic observations and then thinned further to electron transparency by ion bombardment [6].

4. Observations

The thermal gradient (20° C cm^{-1}) available in the centre of the furnace from top to bottom of the sample allows one to observe, after water-quenching, the continuous transition from the monophased matrix (Fig. 2a) to the biphased material (Fig. 2b). We have thoroughly analysed this transition by transmission electron microscopy. The second phase appears both at the grain boundaries and within the grains (Fig. 3). We have analysed the composition of this phase by X-ray analysis with the electron probe using test-samples of YIG* and magnetite to obtain the best accuracy: the second phase corresponds to a magnetite with a slight substitution in aluminium and gadolinium (concentrations of 0.65 and 0.58 wt % respectively as compared with 1.57 and 13.4 wt % in the matrix).

The intragranular nucleation of magnetite from a gadolinium and aluminium substituted yttrium iron garnet is particularly interesting since the
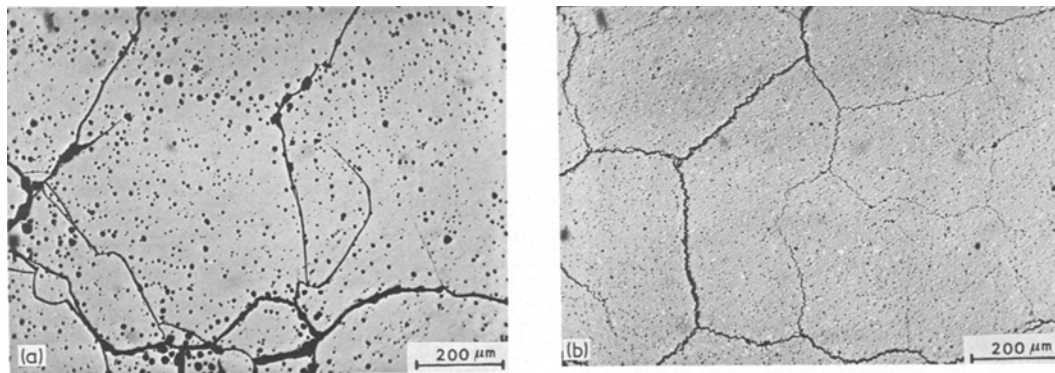

Figure 2 (a) Substituted garnet monophased matrix quenched from temperature θ ° $C > \theta_M$. (b) Substituted garnet + exsolved magnetite quenched from θ ° C < θ_M.
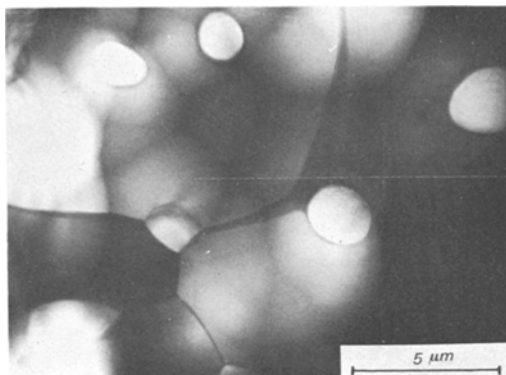
* YIG: yttrium iron garnet.

Figure 3 Magnetite exsolution in a substituted garnet matrix (magnetite appears as white globules).

nucleation occurs on a transitional phase. Fig. 4 shows the microstructure obtained in a sample quenched from a high temperature. The magnetite nucleates in the centre of zones having a mainly ellipsoidal section and about 1μm width along the small axis, which constitutes the transitional phase. By a selected area diffraction technique we cannot visualize any difference in the reciprocal lattice space between the matrix and the zones, though these zones show a structure contrast with the matrix and are bounded by fringes which should lead to extra-spots in the reciprocal space. The coherency between those zones and the matrix is clearly shown by the fact that the extinction fringes are not displaced at the boundary with the matrix. It is worth noticing that the nucleation of magnetite on these zones always occurs in their centres. Therefore this nucleation is coherent, since if it was incoherent, the nucleation would necessarily occur at the boundary with the matrix where the activation energy is lowered.
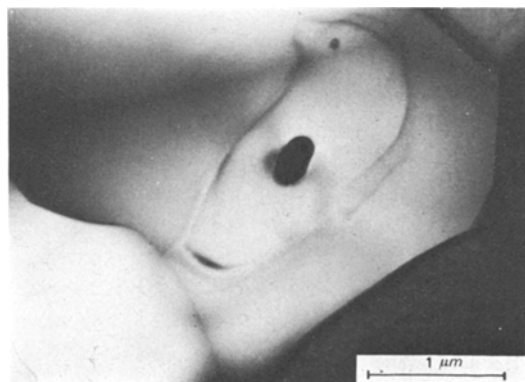

Figure 4 Nucleation of magnetite in the centre of a transitional zone in a substituted garnet matrix.

When the precipitate grows, it progressively becomes semi-coherent and incoherent as the misfit between the precipitate and the matrix (4%) is too high to be accommodated by elastic strains [7]. When the diameter of the precipitate becomes greater than $1000 \text{\AA}$, there is no more coherence between the planes of the precipitate and that of the transitional phase, whereas there was at least semi-coherence when the precipitate was small and full coherence between the planes of the transitional phase and of the matrix.

5. Garnet structure
To propose an ionic model for this transitional event, let us consider the garnet structure.

The ball-model of Fig. 5 shows the ionic structure of an yttrium iron garnet (YIG). The elementary cell contains four groups of $5 \text{Fe}_2\text{O}_3$, $3 \text{Y}_2\text{O}_3$ i.e. 160 ions, leading to the chemical formula $\text{Y}_3\text{Fe}_5\text{O}_{12}$. The lattice is body-centred and centro-symmetric. The 96 oxygen ions constitute the frame of the lattice. They are in general positions subordinated to 3 parameters. The 24 yttriums ions are located on dodecahedral sites (24c) with oxygen ion first neighbours. The 40Fe^{3+} ions are located partly in octahedral sites (16a) and partly in tetrahedral sites (24d).

One may substitute any rare earth ion for Y^{3+} ions as long as its ionic radius is smaller than the dodecahedral site size ($< 1.15 \text{\AA}$ [8]). That is the case for the Gd^{3+} ion that we shall consider later. Substitution by Gd will lead to an isomorphic structure. The other substituting ion we will consider is Al^{3+} ($r = 0.51 \text{\AA}$). Al^{3+} behaves like Fe^{3+} and occupies tetrahedral sites for small amounts of substitution and we again obtain an isomorphic structure of YIG. Therefore if we consider the ionic positions only, we may discuss the results as if there were no Gd or Al substitution. If we consider the strain on the different sites we will have then to take into account the ionic radius versus the site dimension.

6. Transitional ionic model in the vicinity of the (1 1 0) plane
The comparison of the garnet structure from the ball-model with the magnetite structure shows that (1 1 0) planes of garnet are very specific:

(1) they contain only Fe ions;
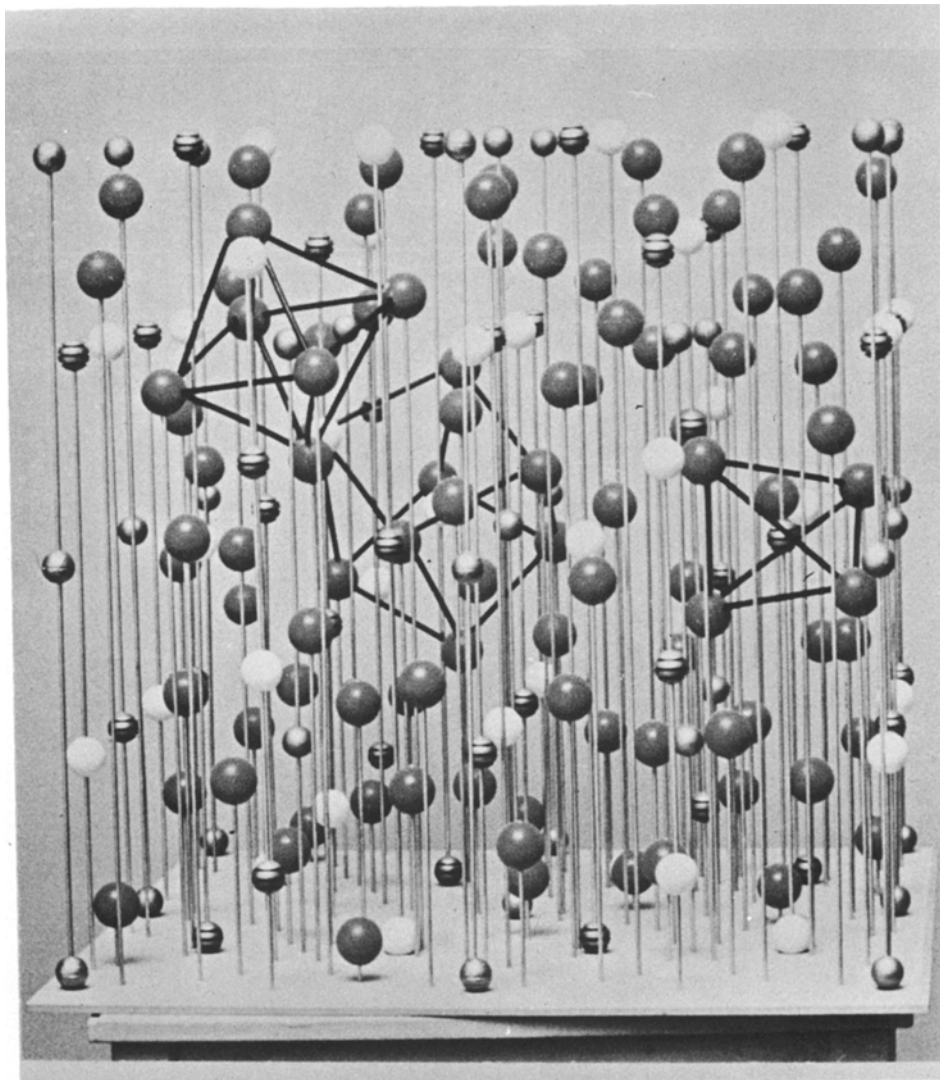(2) the configuration of Fe ions presents a close similarity with the (1 1 0) magnetite plane.

Figure 5 Yttrium iron garnet ball-model: ● grey balls ions O^{2-}; ○ white balls ions Y^{3+}; ◉ striped balls ions Fe^{3+} (tetrahedral site d); ○ smooth balls ions Fe^{3+} (octahedral site a);

If we superimpose the (1 1 0) planes of magnetite and garnet with the following epitaxial relationships:

$$[0\,0\,1]\ \text{garnet} \parallel [1\,\bar{1}\,0]\ \text{magnetite}$$

$$[1\,\bar{1}\,0]\ \text{garnet} \parallel [0\,0\,1]\ \text{magnetite}$$

we find that there is a partial rearrangement of Fe ions (Fig. 6) in the vicinity of the (1 1 0) plane, which can be decomposed into six vectors with easy direction and moduli which are simple fractions of planar spacings, and which allow the transition of the Fe ionic sublattice from garnet to magnetite structure. This rearrangement may be applied with a periodicity $\frac{1}{2}d_{1\,1\,0}$. This leads to the intermediate structure of Fig. 7.

The fine analysis of the reciprocal lattice of the pre-transformed zones in electron microdiffraction, by adapting the oscillating crystal method [9] agrees well with this intermediate structure. The reciprocal lattice of the zones is identical to the garnet but there is splitting of spots with h, k and l all even. This splitting can be explained by taking into account the oxygen environment for Fe ions. This environment will be different for each corner of the cubes with an edge $a/2$ corresponding to the rearranged ions in the intermediate structure. Therefore those cubes will
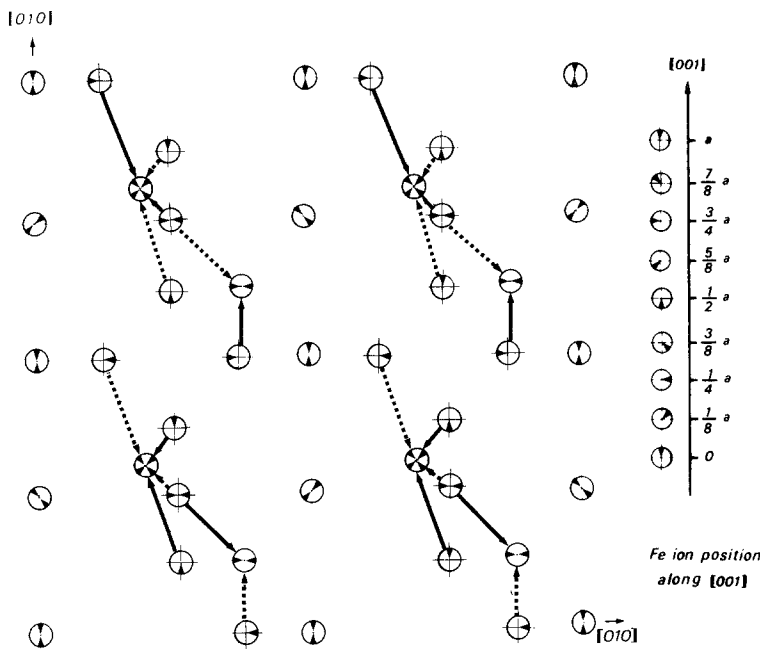
Fe ion position along [001]

7. Discussion

The exsolution of magnetite from a gadolinium and aluminium substituted yttrium iron garnet leads to a nucleation and growth phenomenon via a transitional phase. We have shown that this mechanism does not occur on unsubstituted YIG and have investigated the influence of gadolinium on this mechanism [10].

The ionic model we have proposed for this pre-transformation corresponds to small, partial ionic displacements. Such a rearrangement will require a small activation energy and will lead to a symmetry much closer to magnetite. Therefore the nucleation of magnetite from this transitional phase will require a lower activation energy than
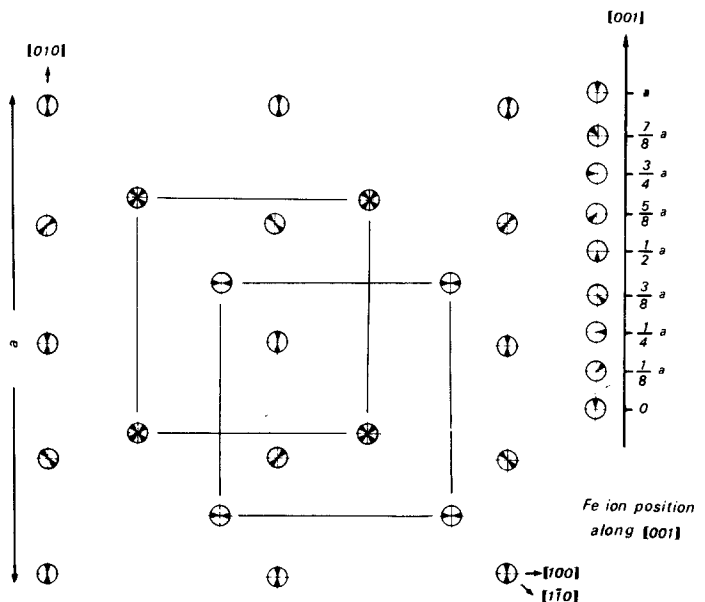
Figure 7 Intermediate structure; Fe ionic sublattice, projection on (0 0 1). (a = garnet parameter).

Fe ion position along [001]

1941

direct nucleation from the matrix, since the symmetry of magnetite and garnet are very different.

It is very likely then that the exsolution process of magnetite will be easier via a transitional phase. Such a process should apply to other oxides or similar complex structures.

8. Conclusion

Gadolinium and aluminium substitution in an yttrium iron garnet leads to a magnetite + garnet phase in the phase diagram, corresponding to an oxygen atmosphere. The exsolution of magnetite by homogenous nucleation would require significant undercooling. The easiest process is heterogeneous nucleation at grain boundaries. Nevertheless the nucleation can also occur with a small activation energy via a transitional phase coherent with the matrix and having a symmetry nearer to magnetite. Such a transitional phase can be obtained by a partial rearrangement of Fe^{3+} ions in the vicinity of the (1 1 0) plane.

References
1. P. E. CHAMPNESS and G. W. LORIMER, "Electron Microscopy in Mineralogy" (Springer–Verlag, Berlin, 1976) p.177.
2. H. J. VAN HOOK, *J. Amer. Ceram. Soc.* **45** (1962) 162.
3. *Idem, ibid.* **45** (1962) 369.
4. *Idem, ibid.* **46** (1963) 121.
5. A. HAMELIN, Thèse d'Etat, Orsay (1972).
6. M. PAULUS, "Microstructural Science", Vol. 3 (American Elsevier Co, Amsterdam, 1975) pp. 453–473.
7. R. B. NICHOLSON, "Phase Transformations" (American Society for Metals, Ohio, 1970) 269.
8. A. HERPIN, "Théorie du Magnétisme" Bibliothèque des Sciences et Techniques Nucléaires, Presses Universitaires de France, Paris, 1968).
9. J. Y. LAVAL, Proceedings of the 9th International Conference on Electron Microscopy, Toronto, 1978 (to be published).
10. *Idem, J. Amer. Ceram. Soc.* (to be published).