

An electron microscope study of thin ferrite films prepared by the oxidation of high purity vacuum-evaporated metal thin films

R. ENGIN, A. G. FITZGERALD

Carnegie Laboratory of Physics, University of Dundee, Dundee, Scotland

The oxidation of thin films of nickel, cobalt, iron, NiFe_2 and CoFe_2 has been investigated between 200 and 1200°C. The oxidation products for the elemental metals differ from the oxidation products observed in previous work upon bulk material. The oxidation mechanism proposed for bulk material is in general still valid in the thin film situation. Above oxidation temperatures of approximately 850°C both NiFe_2 and CoFe_2 form the respective ferrites, although in the case of nickel ferrite, traces of the $\gamma\text{-Fe}_2\text{O}_3$ tetragonal superstructure can still be detected at oxidation temperatures of 1200°C. Films of nickel ferrite and cobalt ferrite upon single-crystal magnesium oxide substrates, produced by oxidation of vacuum-deposited NiFe_2 and CoFe_2 thin films, have been investigated by transmission and scanning electron microscopy. It has been found that (100) nickel ferrite prepared by this technique grows epitaxially upon (100) magnesium oxide.

1. Introduction

In the past ten years a number of techniques for the preparation of thin films of ferrimagnetic oxides have been reported. The study of these films has been accelerated by possible applications in computer memories and in miniaturized microwave circuitry. Preparation techniques which have been studied include chemical deposition from mixed nitrate solutions with subsequent firing [1], sputtering [2, 3], chemical vapour-deposition from mixed halide vapours [4], vacuum-deposition of metals with subsequent oxidation [5], growth from molten solution (flux method) [6, 7], vacuum-deposition by arc-discharge [8] and pyrolytic hydrolysis of metal inorganic salts [9].

Although magnetic oxide films have been characterized by the study of magnetic properties such as ferrimagnetic resonance, magnetic domain patterns and Faraday effect hysteresis loops, and the crystal structures have in some cases been verified by X-ray diffraction, a detailed study has not been made of the microstructure of these films.

The present investigation of ferrite thin films prepared by oxidation of high purity metal thin

films stems from the original X-ray diffraction investigation of Banks *et al* [5]. Their investigation indicated that it may be possible to grow polycrystalline ferrite thin films by this technique. However, the quality of these films was not studied and no attempt was made to prepare single crystal films. The technique is attractive as a possible, relatively inexpensive and straightforward method for the preparation of high purity ferrite films.

The aims of the present study have been to prepare thin ferrite films by oxidation of vacuum-deposited high purity nickel-iron and cobalt-iron thin films, to determine the temperature range in which oxidation of composite metal thin films to ferrite occurs free from other oxide phases, and to examine the microstructure and growth of these ferrite thin films. The oxidation process has been investigated over a wide range of temperatures and oxide structures have been identified by electron diffraction. The oxidation processes in thin films of cobalt, nickel and iron have also been studied in order to follow the solid state reactions which occur on formation of ferrite thin films. The transmission electron microscope with the selected-area electron diffraction facility

and the scanning electron microscope have been used to study these problems.

2. Experimental

Thin films of iron, nickel, cobalt and films of composition NiFe_2 and CoFe_2 were prepared by vacuum-deposition in a 12 in. coating unit at a pressure of 10^{-6} torr. The iron, nickel and cobalt evaporation sources were of 99.999% purity and evaporation was effected by means of an electron-beam source. For NiFe_2 and CoFe_2 films evaporations were made sequentially without breaking vacuum. The thickness and stoichiometry of the vacuum-deposited films were controlled by means of a thickness monitor of the quartz crystal oscillator type. Thicknesses of films studied varied between 30 and 500 nm. The films were deposited upon freshly cleaved single crystals of rocksalt, magnesium oxide, and mica. The mica substrates were coated with a thin carbon film to enable subsequent detachment of the film from the substrate. Films deposited on rocksalt and carbon-coated mica were oxidized in air between 300 and 700°C. Higher temperature oxidations up to 1250°C were made with

films deposited on magnesium oxide and with films which had been detached, by immersion in distilled water, from the mica and rocksalt substrates and mounted upon platinum electron microscope grids.

The crystal structure and microstructure of films oxidized over the temperature range 200 to 1250°C for periods of time varying from 15 min to 48 h has been determined using an EM6G electron microscope operated at 100 kV. Oxide films grown upon magnesium oxide which were thicker than 200 nm were chemically thinned for transmission electron microscopy. In the early stages of thinning, a jet of hot orthophosphoric acid was used to etch away the MgO substrate from the ferrite film. For this purpose the MgO crystal with ferrite film uppermost was mounted in a Teflon holder above a jet of hot orthophosphoric acid (Fig. 1a). Compressible Teflon gaskets manufactured from Teflon tape enabled a seal to be made round the edges of the crystal. For the final and more gradual thinning stage, the Teflon holder with crystal still intact was transferred to a convection jet-thinning device (Fig. 1b) where only the lower, MgO, side was in

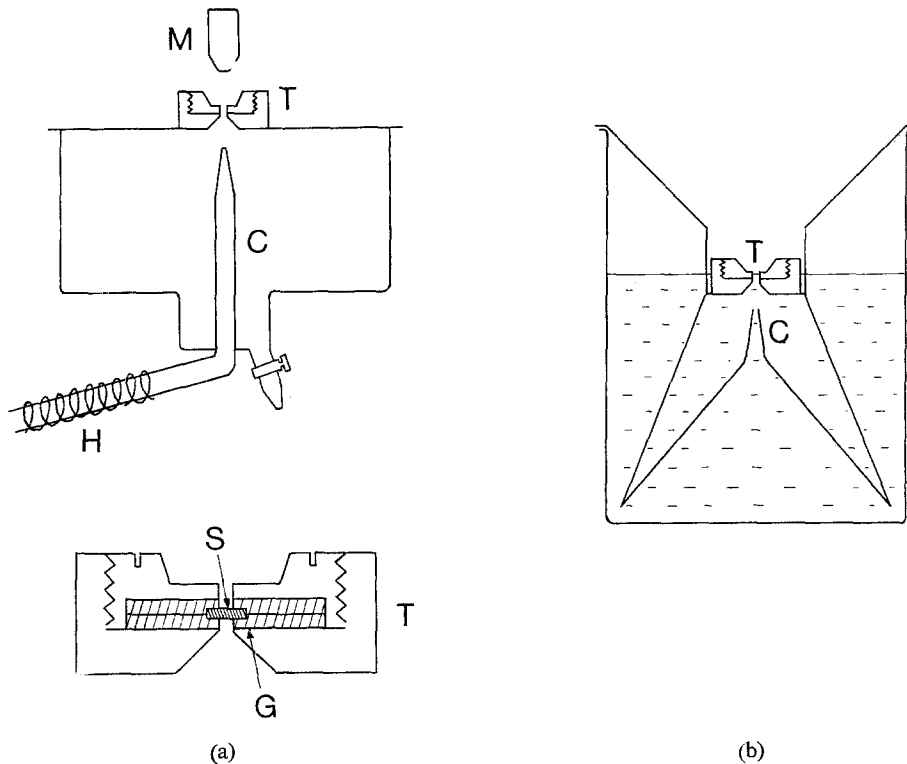


Figure 1 (a) Jet chemical thinning device; T - Teflon specimen holder, C - capillary tube, H - heater for orthophosphoric acid, S - specimen, G - Teflon gasket, M - microscope. (b) Convection jet thinning device: C - capillary tube, T - Teflon specimen holder.

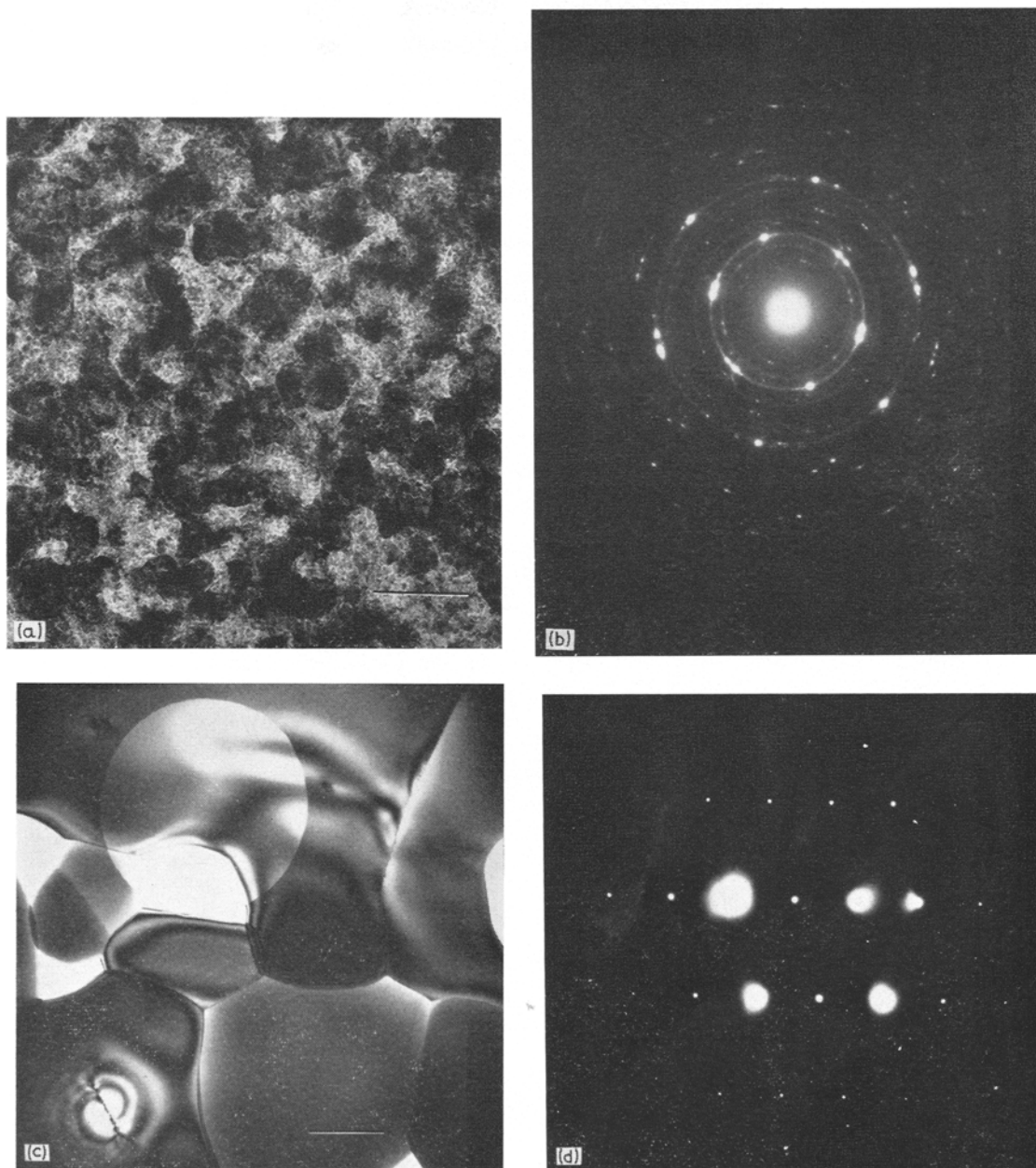


Figure 2 (a) Electron micrograph from an iron film oxidized at 300°C for 25 h containing oriented crystallites of $\alpha\text{Fe}_2\text{O}_3$ and the polycrystalline spinel phase. Bar mark = 0.2 μm . (b) Electron diffraction pattern from the area of crystals in Fig. 2a. The $\alpha\text{Fe}_2\text{O}_3$ crystallites are oriented with the (0001) axis parallel to the electron beam. The selected area contains two (0001) orientations slightly misaligned with respect to each other. (c) The grain structure of $\alpha\text{Fe}_2\text{O}_3$ produced by oxidizing an iron thin film at 1100°C for 20 min. Bar mark = 0.2 μm . (d) Selected area electron diffraction from the area outlined by the diffraction aperture in Fig. 2c. The electron beam is parallel to $[\bar{1}3\bar{2}2]$.

contact with a convection jet of hot orthophosphoric acid. Immediately a hole was formed in the crystal, the holder was quickly immersed in distilled water. Using this procedure, suffi-

ciently thin areas of ferrite film could be examined by transmission electron microscopy around the edges of the hole. The surface structure of the films was examined with a Cambridge Stereoscan

Mark 2A scanning electron microscope.

Oxidized films of the individual metals were studied initially in order to assist the analysis of the large amount of electron diffraction data from oxidized films of NiFe₂ and CoFe₂.

3. Oxidized iron, nickel, and cobalt thin films

3.1. Iron thin films

Oxidation of iron films between 300 and 700°C resulted in the formation of a mixture of oxides. From electron diffraction patterns α -Fe₂O₃ (haematite) and an oxide which could be indexed on a spinel lattice were identified. This spinel structure could be either γ -Fe₂O₃ or Fe₃O₄ (magnetite). Both structures have the same space group, and crystal lattice spacings corresponding to equivalent permitted reflections differ by less than 0.6%. The electron diffraction pattern from the spinel phase was of the Debye-Scherrer type. Because of the crystallite size, the rings were not sharp and were discontinuous (Fig. 2b). It was therefore difficult to decide which oxide spinel phase was present. The accuracy required to distinguish between these two phases, less than 0.6%, is also very close to the ultimate accuracy of electron diffraction measurements with an electron microscope. It is probable that both phases occur as their co-existence plays an important part in the oxidation process [10]. In general, the electron diffraction patterns from iron films oxidized in this temperature range consisted of polycrystalline ring patterns from the spinel phase together with single crystal patterns from oriented crystallites of α -Fe₂O₃ (Fig. 2a, b).

Above 900°C, α -Fe₂O₃ only is usually formed upon oxidation of thin iron films, although on very rare occasions single crystal spinel orientations have been identified. At this temperature, for periods of oxidation of greater than 6 h, the average grain diameter is of the order of 1 μ m and single crystal orientations of α -Fe₂O₃ are readily identified (Fig. 2c, d).

Between 700 and 900°C the oxidation products for all of the metal thin films are difficult to identify and crystallite sizes and randomness of orientations are such that selected area electron diffraction patterns are not easy to interpret.

The results of oxidation of iron, in thin film form, appear to contradict previous observations on the oxidation of this metal in bulk. Below 600°C the behaviour of iron both in bulk and in thin film form is similar, α -Fe₂O₃ with spinel

phases is formed. On bulk iron the oxides form a stratified scale upon the surface in the following sequence [10]:

$\text{Fe} + \text{Fe}_3\text{O}_4 + \gamma\text{-Fe}_2\text{O}_3 + \alpha\text{-Fe}_2\text{O}_3 + \text{oxidizing agent.}$

Above 900°C, a scale of FeO + Fe₃O₄ + Fe₂O₃ is formed upon bulk iron [10], whereas in oxidized iron thin films, α -Fe₂O₃ with occasional regions of magnetite or γ -Fe₂O₃, have been identified. These observations, however, are consistent since in a thin film there is not a large reservoir for formation of iron ions and therefore the oxides, FeO and Fe₃O₄, which depend for stability upon the diffusion of Fe²⁺ and Fe³⁺ ions [11] will be very rapidly replaced by α -Fe₂O₃ formed in contact with the oxidizing atmosphere at the surface of the film. This reaction proceeds by oxygen diffusion via anion vacancies in FeO and Fe₃O₄ until the film is completely oxidized to α -Fe₂O₃.

3.2. Nickel thin films

Thin films of nickel formed only one oxide, NiO, over the oxidation temperature range 200 to 1100°C. At 200 and 300°C oxidation is incomplete and nickel with NiO has been identified by electron diffraction for oxidation periods of as great as 24 h. This is consistent with bulk oxidation studies. Above 400°C nickel films oxidized completely to NiO. Increase in grain size in nickel oxide, with increased oxidation temperature, appeared to be less marked than in films of similar thickness of oxides of the other metals. The average NiO grain size was so small over the temperature range 400 to 1000°C that polycrystalline ring patterns only could be obtained by selected area electron diffraction (Fig. 3a, b). Although the grain size increase with increased oxidation or increased sintering temperatures is less marked in this material, it is still significant (Fig. 3c).

At an oxidation temperature of 1200°C a new nickel oxide phase is formed with a spinel structure. In thin films examined after short oxidation periods, inclusions of this new phase which are oriented within the NiO matrix can be observed (Fig. 4a), confirming the observations of Katada *et al* [12] for the oxidation of NiO films grown by chemical vapour deposition. After longer oxidation periods the reaction goes to completion and the film is totally spinel phase. This spinel phase has been identified previously as nickel deficient NiO [12]. Study of Fig. 4c

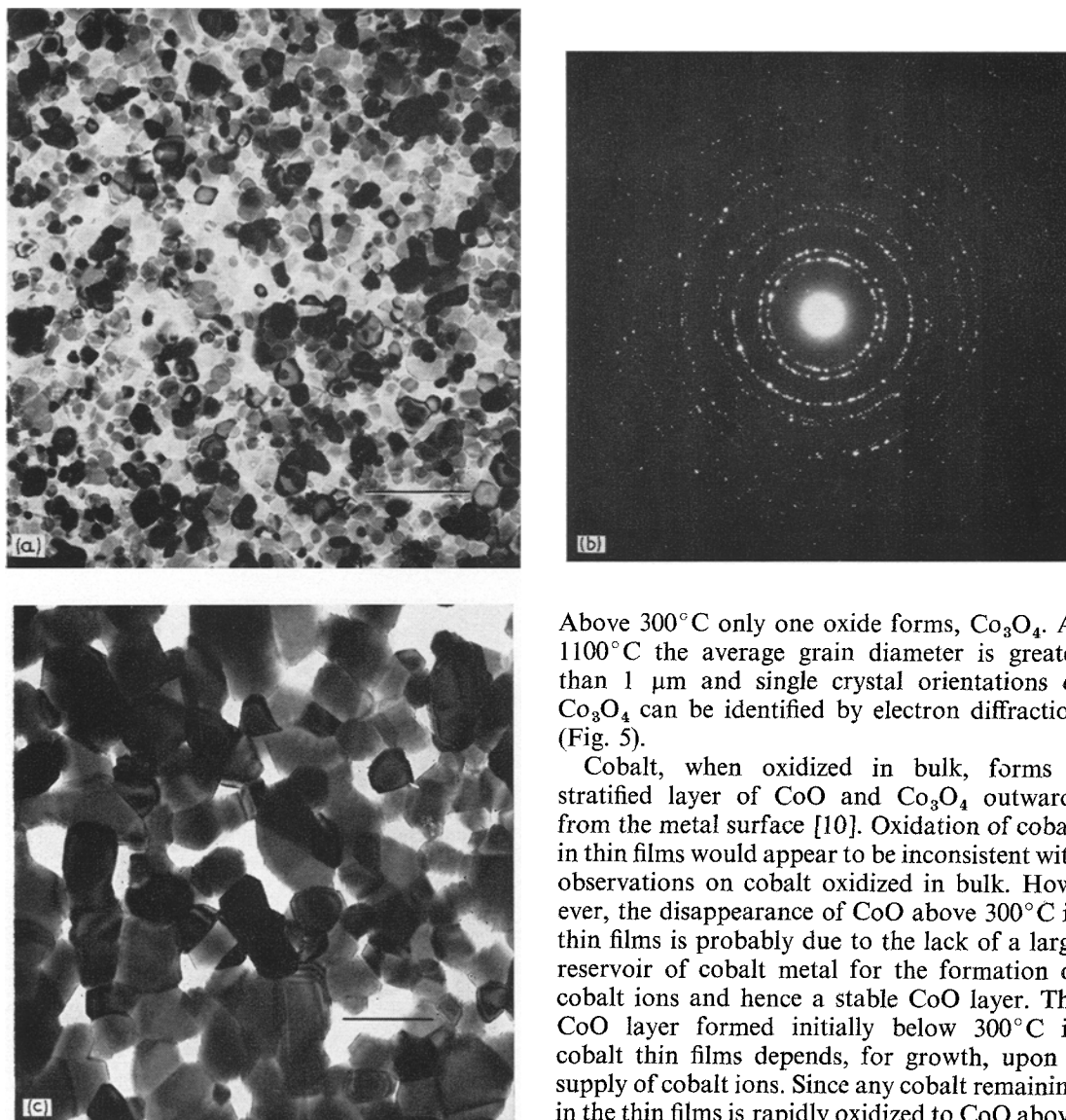


Figure 3 (a) The grain structure of a nickel oxide film produced by oxidizing a nickel thin film at 800°C for 12 h. Bar mark = 0.2 μm . (b) Selected area electron diffraction pattern from the area of NiO film shown in Fig. 3a. (c) The grain structure of a nickel oxide film produced by oxidation of a nickel thin film at 1100°C for $\frac{3}{4}$ h. Bar mark = 0.2 μm .

indicates that the new phase grows by addition of atoms at steps on the crystal surfaces.

3.3. Cobalt thin films

At 200°C the constituents of the oxidized cobalt film were identified as cobalt with CoO and Co₃O₄.

Above 300°C only one oxide forms, Co₃O₄. At 1100°C the average grain diameter is greater than 1 μm and single crystal orientations of Co₃O₄ can be identified by electron diffraction (Fig. 5).

Cobalt, when oxidized in bulk, forms a stratified layer of CoO and Co₃O₄ outwards from the metal surface [10]. Oxidation of cobalt in thin films would appear to be inconsistent with observations on cobalt oxidized in bulk. However, the disappearance of CoO above 300°C in thin films is probably due to the lack of a large reservoir of cobalt metal for the formation of cobalt ions and hence a stable CoO layer. The CoO layer formed initially below 300°C in cobalt thin films depends, for growth, upon a supply of cobalt ions. Since any cobalt remaining in the thin films is rapidly oxidized to CoO above 300°C, further oxidation can only proceed by diffusion of oxygen ions to form Co₃O₄.

Above 900°C in bulk cobalt, the Co₃O₄ layer eventually disappears and a scale of CoO only is left. The rate-determining step in cobalt oxidation is considered to be the rate of diffusion of cobalt ions via vacancies in the scaling layer of CoO. The disappearance of Co₃O₄ above 900°C in bulk is thought to be due to a complete predominance of this action, as the diffusion coefficient of oxygen ions in CoO, which is necessary for the formation of Co₃O₄, is appreciably smaller than the diffusion coefficient for cobalt ions. In an oxidized cobalt thin film, there is no longer a source for cobalt ions and

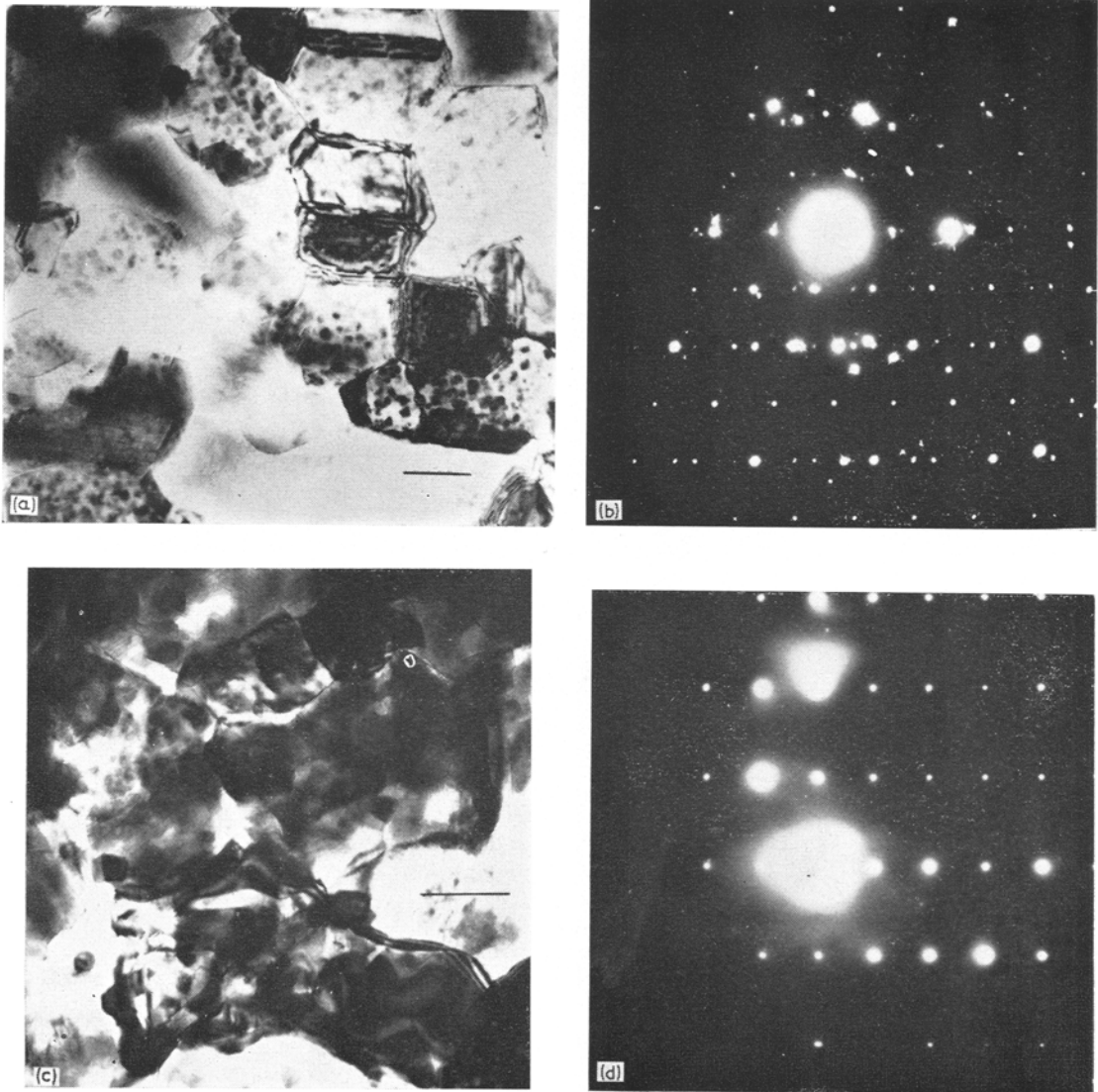


Figure 4 (a) Inclusions of a new oxide spinel phase in the NiO matrix produced by oxidation of a thin nickel film at 1200°C for 30 min. Bar mark = 0.1 μm . (b) Selected area electron diffraction pattern from the area of crystal in Fig. 4a. The inclusions are aligned with (110) atomic planes perpendicular to the electron beam. The extra spots in the pattern are produced by twinning about a $[1\bar{1}1]$ axis in the inclusion. (c) Area of the nickel-deficient NiO spinel phase produced by oxidizing a nickel thin film for 8 h at 1200°C. Bar mark = 0.2 μm . (d) Electron diffraction pattern from the area shown in Fig. 4c. The nickel oxide spinel has the (211) planes perpendicular to the electron beam.

further oxidation has to proceed by oxygen-ion diffusion, $6 \text{CoO} + \text{O}_2 \rightarrow 2 \text{Co}_3\text{O}_4$. The final products and the oxidation mechanism for cobalt in bulk and in thin film forms can therefore be reconciled, although it is claimed that the oxide Co_3O_4 in isolation, is unstable above 900°C and decomposes to form CoO [13].

4. Ferrite thin films

4.1. Oxidation of thin films of composition NiFe_2

Thin films of stoichiometric NiFe_2 formed by sequential evaporation in vacuum of nickel and iron were oxidized over the temperature range 200 to 1200°C and the oxidation products have

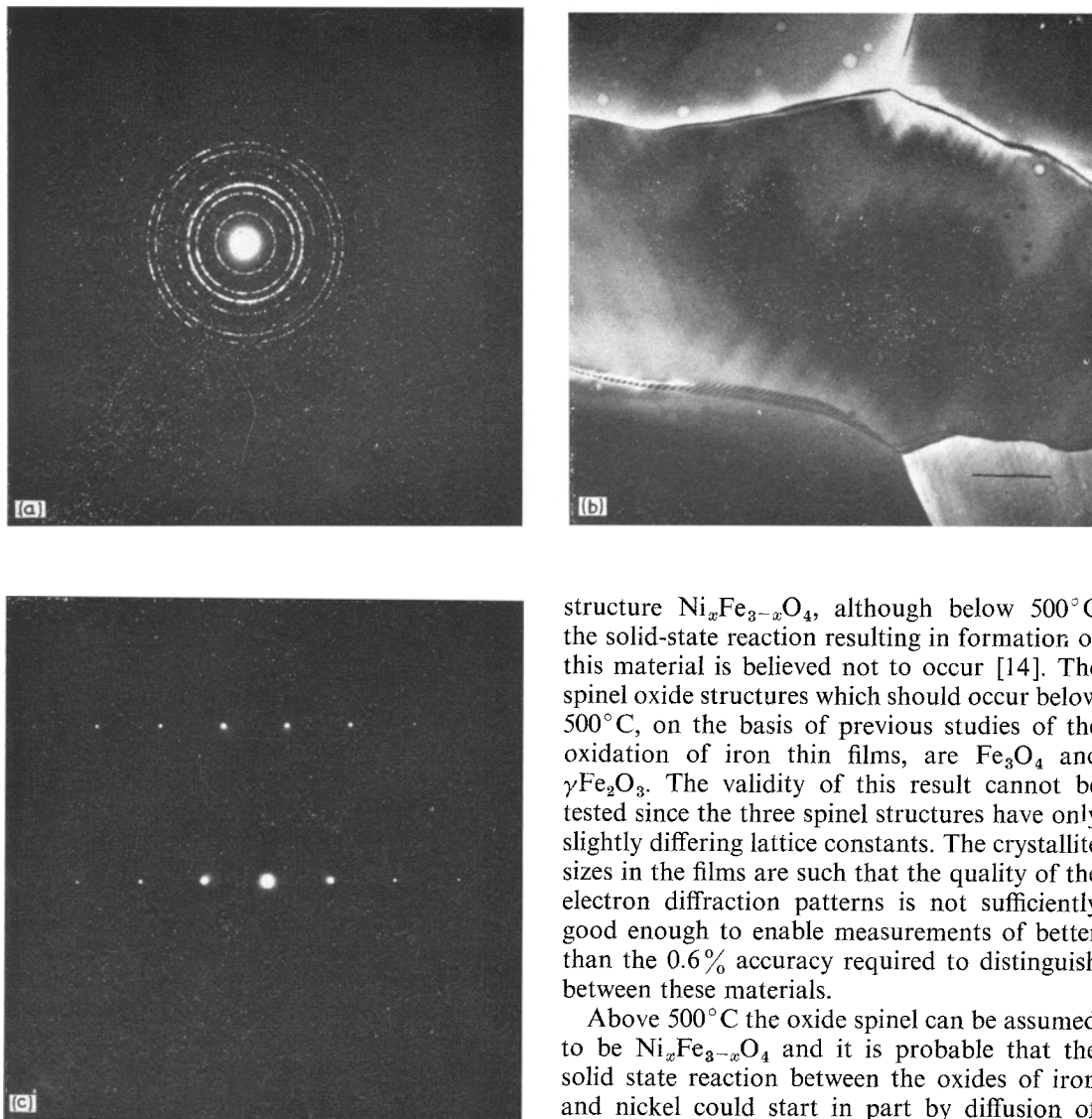


Figure 5 (a) Electron diffraction pattern from polycrystalline Co_3O_4 produced by oxidizing a cobalt thin film at 600°C for 6 h. (b) Grain structure of a Co_3O_4 thin film prepared by oxidation of a cobalt thin film at 1100°C for 8 h. Bar mark = $0.2\ \mu\text{m}$. (c) Electron diffraction pattern from the central grain in Fig. 5b. The (123) planes are perpendicular to the electron beam.

been identified by electron diffraction (Fig. 6).

In the temperature range 200 to 850°C the oxidation products are $\alpha\text{Fe}_2\text{O}_3$, NiO and a spinel structure. The oxide spinel and NiO occur in polycrystalline form whereas the $\alpha\text{Fe}_2\text{O}_3$ occurs as extensive regions of oriented crystallites. The oxide spinel is probably the defect ferrite

structure $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$, although below 500°C the solid-state reaction resulting in formation of this material is believed not to occur [14]. The spinel oxide structures which should occur below 500°C , on the basis of previous studies of the oxidation of iron thin films, are Fe_3O_4 and $\gamma\text{Fe}_2\text{O}_3$. The validity of this result cannot be tested since the three spinel structures have only slightly differing lattice constants. The crystallite sizes in the films are such that the quality of the electron diffraction patterns is not sufficiently good enough to enable measurements of better than the 0.6% accuracy required to distinguish between these materials.

Above 500°C the oxide spinel can be assumed to be $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ and it is probable that the solid state reaction between the oxides of iron and nickel could start in part by diffusion of nickel ions to fill the random vacant cation sites in the $\gamma\text{Fe}_2\text{O}_3$ lattice with the counter diffusion of Fe^{3+} ions.

Above 850°C the oxidized NiFe_2 films consists almost completely of nickel ferrite (Fig. 6b, c) apart from very rare crystallites which have the tetragonal superstructure of $\gamma\text{Fe}_2\text{O}_3$ [15]. A marked increase in grain size of the polycrystalline nickel ferrite films is observed with increase in oxidation temperature.

4.2. Oxidation studies of CoFe_2 films

Low temperature oxidations for CoFe_2 films are again consistent with the oxidation of individual metal thin films. Between oxidation temperatures of 300 and 650°C , polycrystalline Co_3O_4 , a

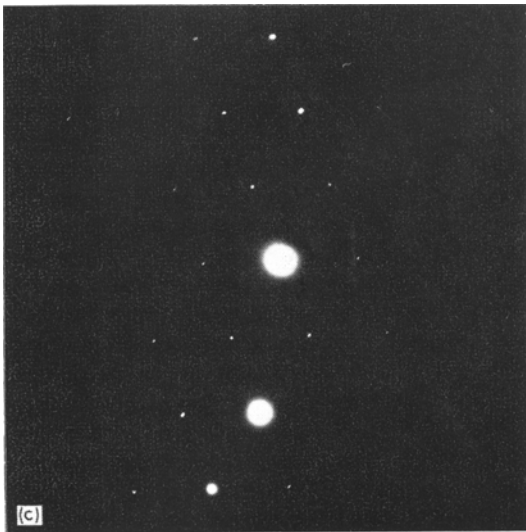
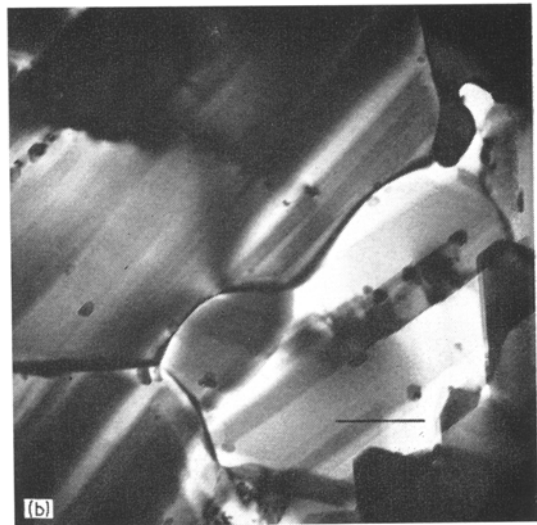
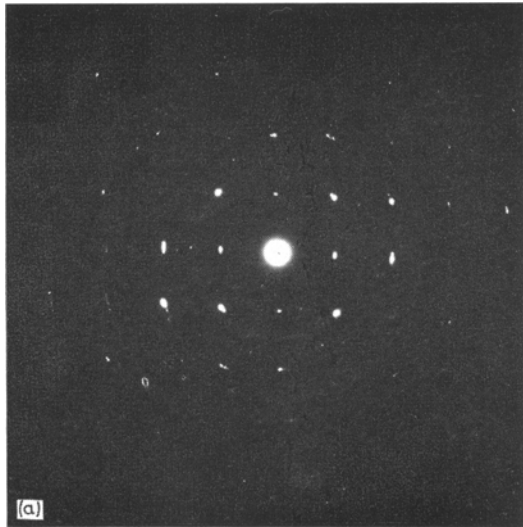


Figure 6 (a) Selected area electron diffraction pattern from a film of composition NiFe_2 oxidized at 400°C for 25 h. The electron diffraction pattern consists of weak polycrystalline patterns from NiO and spinel structures with a single-crystal electron diffraction pattern from $\alpha\text{Fe}_2\text{O}_3$ which is the $(\bar{2}201)$ reciprocal lattice section. (b) Area of a nickel ferrite film formed by oxidation of a film of composition NiFe_2 at 1100°C for 8 h. Bar mark = $0.2\ \mu\text{m}$. (c) Selected area electron diffraction pattern from the central grain in Fig. 6b, (110) planes perpendicular to the electron beam.

polycrystalline oxide spinel and extensive single crystal areas of $\alpha\text{Fe}_2\text{O}_3$ have been identified by electron diffraction (Fig. 7a). As in the case of oxidized films of composition NiFe_2 it is

difficult to determine whether the spinel structure is Fe_3O_4 , $\gamma\text{Fe}_2\text{O}_3$ or the defect spinel $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$.

Above 650°C cobalt ferrite is the sole oxidation product and single crystal orientations have been identified by electron diffraction (Fig. 7b, c).

5. Microstructure of polycrystalline oxide films

The oxide films produced by oxidation on rock-salt and mica substrates and on platinum grids are polycrystalline, and have been studied in two situations, after oxidation at temperatures in the range 200 to 1200°C and also after successive sinters at increasing temperatures within the same range. The observations in both cases are consistent: an increase in grain size is observed for an increase in oxidation or sintering temperature. An example of the increase in grain size with increased temperature is shown in Fig. 3 for nickel oxide.

A great deal of information on the crystal growth of the oxide films can be deduced from transmission electron micrographs. Growth steps and other surface features are clearly visible. The electron diffraction contrast at steps in a crystal surface has been discussed by Moodie and Warble [16] and the predominant contrast mechanism is due to the phase change of the electron beam at differing thicknesses of crystal. The electron diffraction evidence and image contrast observations suggest that above 850°C in most of the oxide thin films apart from NiO , the final oxidation product has formed and

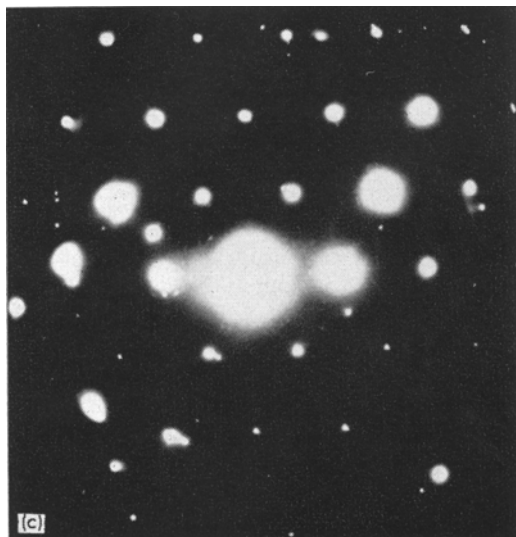
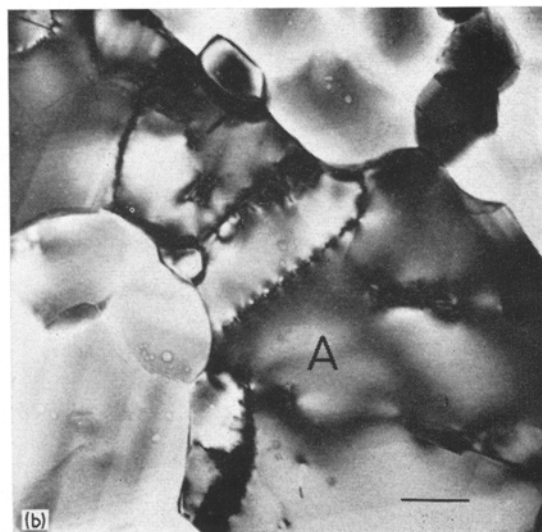
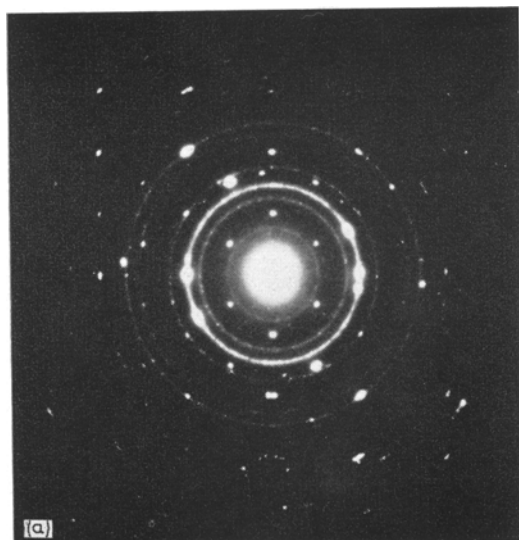


Figure 7 (a) Selected area electron diffraction pattern from a film of composition CoFe_2 oxidized at 500°C for 25 h. The electron diffraction pattern consists of polycrystalline ring patterns from Co_3O_4 and spinel structures with a single crystal pattern which is a $(01\bar{1}\bar{1})$ reciprocal lattice section of $\alpha\text{Fe}_2\text{O}_3$. (b) Area of cobalt ferrite thin film prepared by oxidizing a thin CoFe_2 film at 1100°C for 8 h. Bar mark = $0.1\ \mu\text{m}$. (c) Selected area electron diffraction pattern from grain A of Fig. 7b, electron beam along $[111]$.

crystallites then grow by sintering intergrowth with neighbouring crystallites. Evidence of the development of neck junctions between neighbouring crystallites can be seen in Fig. 3c and irregularly shaped grains are often formed by

coalescence from several smaller crystallites. Where two grains have coalesced with only a small misorientation, very often low-angle grain boundaries are observed. In the cobalt ferrite film, Fig. 8a, grains A and B are separated by a low-angle grain boundary. Both grains are in the (211) orientation. The neighbouring grain in the (111) orientation with respect to the electron beam, is separated from A and B by high-angle boundaries. The evidence from a large number of electron micrographs indicates that surface-diffusion is also a predominant transport mechanism for growth. Growth terraces of the type discussed by Frank [17] can be observed in grains of all the oxide thin films (Fig. 7b and 8).

The most interesting structural feature within grains of these oxide thin films were distributions of pores. Fig. 8b, which shows a nickel ferrite film formed by oxidation at 1000°C , illustrates clearly that the pores are concentrated close to the centre of each grain, suggesting that pores near grain boundaries shrink and disappear more rapidly than those within the grains during sintering. These observations agree with the experiments of Burke [18] and suggest that the most probable mechanism for pore shrinkage is the diffusion mechanism proposed by Nabarro [19] and Herring [20]. This model assumes that atoms diffuse from grain boundaries to neighbouring pores and fill the space left by the missing atoms.

With increase in oxidation temperature a gradual reduction in pore concentration is observed. The pores appear to form in the very

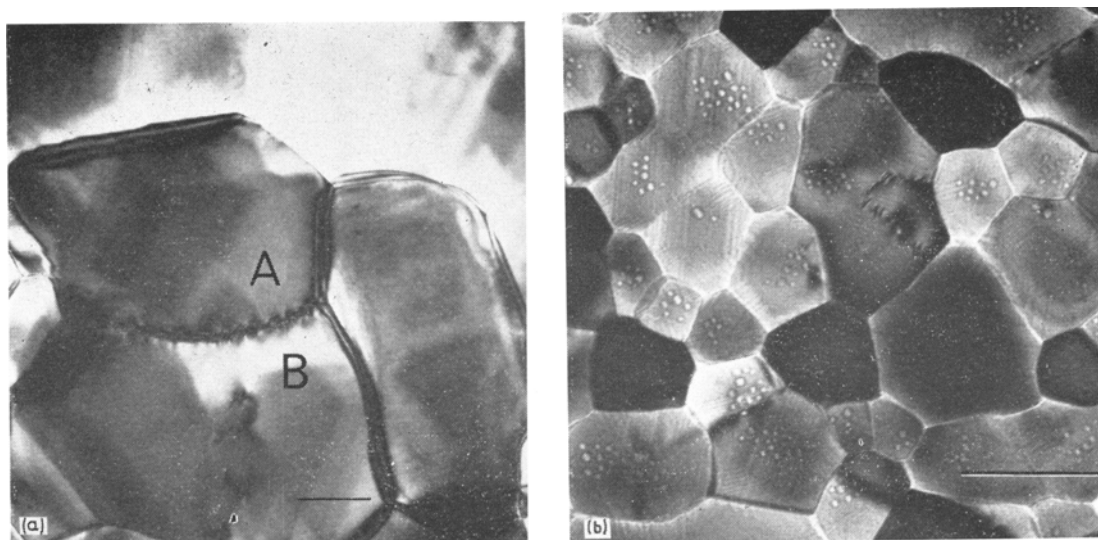


Figure 8 (a) An area of cobalt ferrite thin film showing low-angle and high-angle grain boundaries. Bar mark = 0.2 μm . (b) An area of nickel ferrite film produced by oxidation of an NiFe_2 film at 1000°C for 47 h. Pores can be seen concentrated at the centres of grains. Bar mark = 0.2 μm .

early stages of oxidation by overgrowth of small misoriented oxide crystallites.

6. Epitaxial growth of ferrite thin films on magnesium oxide substrates

The oxidation studies and the observations on microstructures discussed so far have been confined to the oxide thin films formed below 700°C on rocksalt and mica, and oxide films formed between 300 and 1250°C on platinum electron microscope grids. Rocksalt and mica are clearly unsuitable substrates, even for polycrystalline ferrite thin films, as both substrate materials degrade at 700°C, well below the temperature for formation of ferrite thin films by solid state reaction from the elemental oxides. Magnesium oxide is a suitable high temperature ceramic substrate and eight unit cells of magnesium oxide having a lattice constant of 0.421 nm fit perfectly into a unit cube of ferrite having a lattice constant of 0.842 nm. The oxygen ion positions are also identical in both materials, suggesting that magnesium oxide should be an ideal substrate for epitaxial growth of ferrite thin films.

Some preliminary results on the oxidation of NiFe_2 and CoFe_2 films on magnesium oxide substrates indicate that epitaxial growth of nickel ferrite and cobalt ferrite on the (100) faces of magnesium oxide can be attained at high

oxidation temperatures of the order of 1200°C. This is clearly demonstrated in Fig. 9 which shows scanning electron micrographs from nickel ferrite films on (100) faces of magnesium oxide single crystals produced by oxidation of NiFe_2 at 1000, 1100 and 1200°C. For 1000 and 1200°C oxidations, the magnesium oxide substrates were chemically polished with hot orthophosphoric acid prior to deposition of the metal thin films. The development of a smooth film at higher oxidation temperatures can be clearly seen. The films oxidized at 1000°C contain a large number of grains which have grown outwards from the surface with clearly developed crystallographic faces. This feature is less marked in films grown at 1100°C. Smoother areas which have aligned with the substrate are observed. At 1200°C large areas of smooth film are observed with only a few well developed crystallites growing outwards from the surface. In Fig. 9d spiralling growth steps can be observed on the epitaxially grown nickel ferrite thin films. This feature has not been observed on MgO substrates in the absence of a ferrite film. This evidence supports the observations by transmission electron microscopy which indicate that growth takes place by surface diffusion.

The beneficial effects of chemical polishing upon surface smoothness were slight at the maximum oxidation temperature; however, at

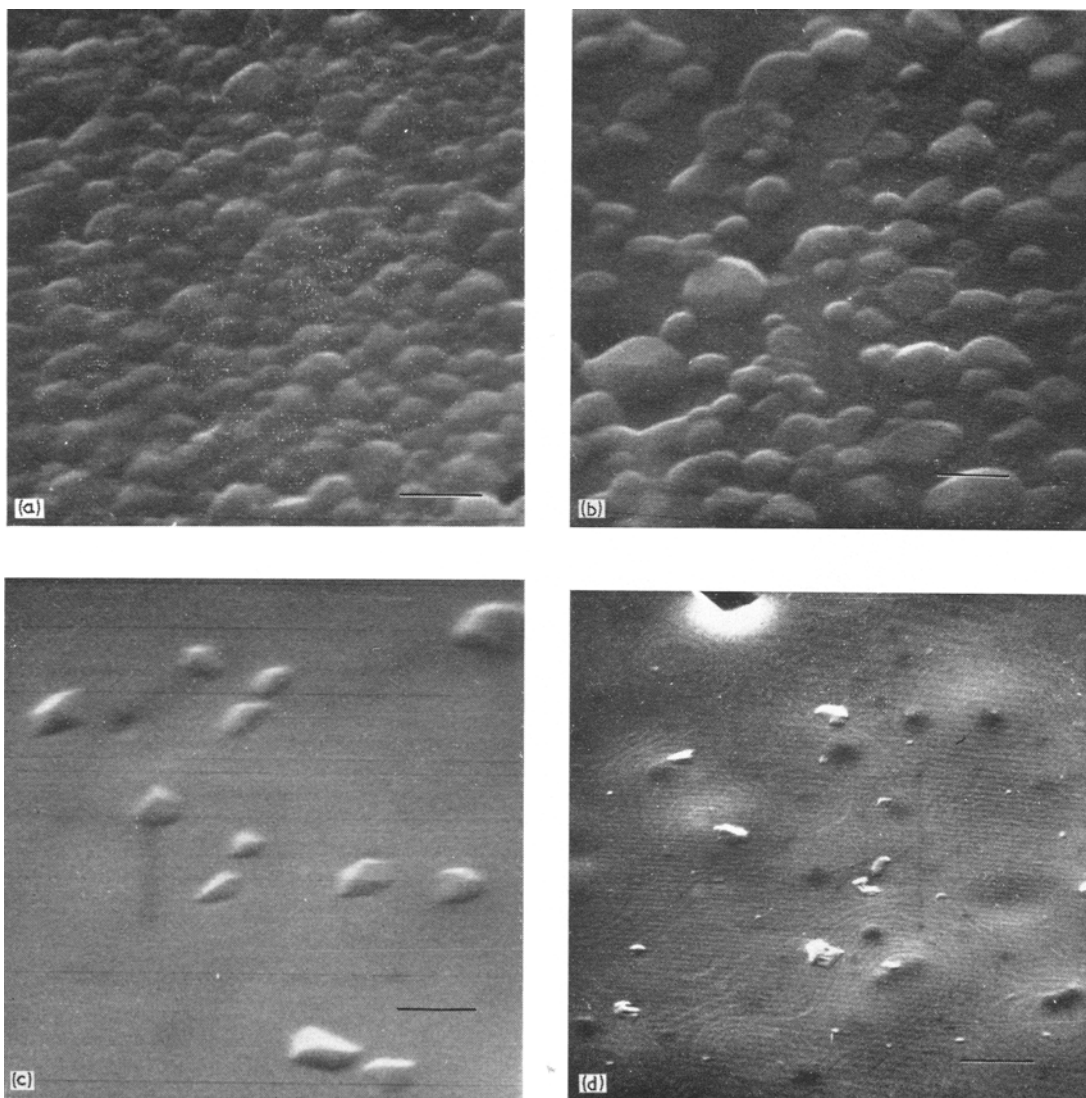


Figure 9 (a) Scanning electron micrograph from an oxidized NiFe_2 film upon a (100) face of a chemically polished magnesium oxide substrate, oxidation temperature 1000°C . Bar mark = $1\ \mu\text{m}$. (b) Scanning electron micrograph from similar film to 9a upon an unpolished MgO substrate, oxidation temperature 1100°C . Bar mark = $1\ \mu\text{m}$. (c) Scanning electron micrograph from a similar film to 9a, substrate preparation identical, oxidation temperature 1200°C . Bar mark = $2\ \mu\text{m}$. (d) Scanning electron micrograph from an oxidized NiFe_2 film on an unpolished (100) MgO substrate showing growth spirals. Oxidation temperature 1200°C . Bar mark = $2\ \mu\text{m}$.

lower oxidation temperatures, ferrite films upon chemically polished substrates have a smoother texture.

A preliminary examination of nickel ferrite films grown upon single crystal magnesium oxide supports observations by scanning electron microscopy. Extensive areas of single crystal

nickel ferrite have been identified by electron diffraction (Fig. 10) and it is clear that (100) nickel ferrite films grow epitaxially upon (100) faces of the MgO substrate crystals. Accompanying the single crystal nickel ferrite films, what is believed to be small crystallites are observed (A, Fig. 10a). Consistent with the investigation of polycrystalline nickel ferrite films, occasional

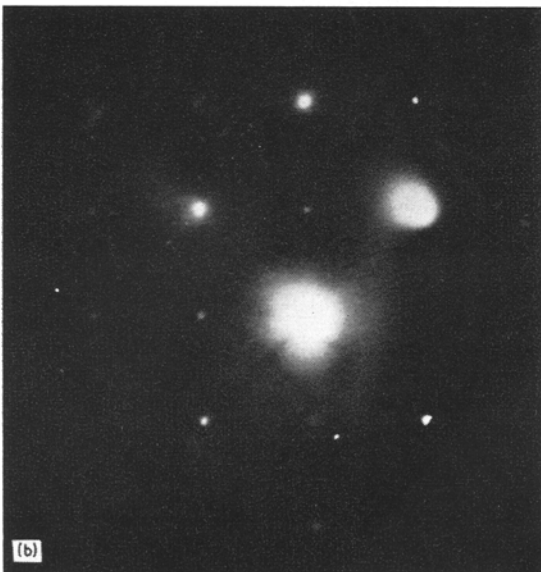
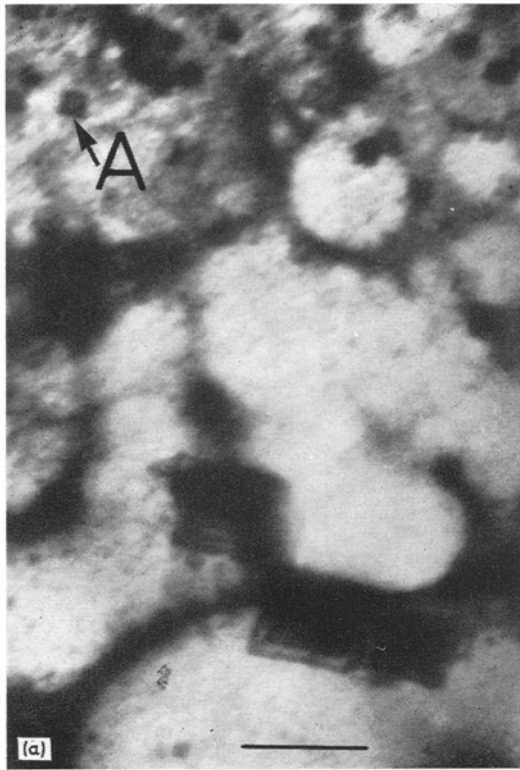


Figure 10 (a) Transmission electron micrograph of a (100) single crystal nickel ferrite film which has grown epitaxially upon (100) magnesium oxide. Bar mark = 0.2 μm . (b) Electron diffraction pattern from the above film. The electron beam is parallel to [100].

regions have been observed in the epitaxial films which have the $\gamma\text{Fe}_2\text{O}_3$ tetragonal superstructure. The observation of the single-crystal, highly insulating, ferrite thin films has proved to be extremely difficult owing to charging up in the electron beam. Coating the films with a carbon film has proved to be only partially successful so far and some image movement is still experienced. This problem is being studied at present and a more detailed discussion of the microstructure of the epitaxially grown ferrite thin films will be given elsewhere.

7. Conclusions

The oxidation of thin films of nickel, iron and cobalt has been found in general to be consistent with observations on oxidation of these materials in bulk. Although the final products differ, the accepted oxidation mechanisms appear to apply to both situations.

For thin films of NiFe_2 and CoFe_2 oxidation temperatures above 850 and 650°C respectively are required to form the respective ferrites, although in the case of nickel ferrite, small traces of the $\gamma\text{Fe}_2\text{O}_3$ tetragonal structure persist at oxidation temperatures of as high as 1200°C.

Preliminary observations suggest that the direct oxidation technique may be a conveniently quick and inexpensive technique for producing extensive areas of epitaxially grown ferrite thin films, provided that in the case of nickel ferrite traces of the $\gamma\text{Fe}_2\text{O}_3$ tetragonal phase can be tolerated.

Acknowledgements

We wish to thank Professor K. J. Standley for encouraging this research project and also the Science Research Council for the research grant B/SR/9281 for investigation of the growth and physical properties of ferrimagnetic thin films.

References

1. W. WADE, R. A. STERN, T. COLLINS, and W. D. SKUDERA, *Amer. Ceram. Soc. Bull.* **45** (1966) 571.
2. W. D. WESTWOOD, H. K. EASTWOOD, R. G. POULSEN, and A. G. SADLER, *J. Amer. Ceram. Soc.* **50** (1967) 119.
3. E. SAWATSKY and E. KAY, *J. Appl. Phys.* **42** (1971) 367.
4. J. E. MEE, G. R. PULLIAM, J. L. ARCHER, and P. J. BESSER, *IEEE Trans. Magnetics, Mag.* **5** (1969) 717.
5. E. BANKS, N. H. RIEDERMAN, H. W. SCHLEUNING, and L. M. SILBER, *J. Appl. Phys.* **32** (1961) 44S.
6. R. J. GAMBINO, *ibid* **38** (1967) 1129.

7. R. C. LINARES, "Crystal Growth", Eds. F. C. Frank, J. B. Mullin, and H. S. Peiser (North Holland, Amsterdam, 1969).
8. M. NAOE and S. YAMANAKA, *Japan J. Appl. Phys.* **9** (1970) 293.
9. F. R. GLEASON and L. R. WATSON, *J. Appl. Phys.* **34** (1963) 1217.
10. K. HAUFFE, "Oxidation of Metals" (Plenum Press, New York, 1965).
11. O. KUBASCHEWSKI and B. E. HOPKINS, "Oxidation of Metals and Alloys" (Butterworths, London, 1967).
12. K. KATADA, K. NAKAHIGASHI, and Y. SHIMOMURA, *Japan J. Appl. Phys.* **9** (1970) 1019.
13. M. HANSEN and K. ANDERKO, "Constitution of Binary Alloys" (McGraw-Hill, New York, 1958).
14. J. G. COHN, "Kinetics of Reaction in Ionic Systems", Eds. T. G. Gray and V. D. Freschette (Plenum Press, New York, 1969).
15. G. W. VAN OOSTERHOUT, *Acta Cryst.* **13** (1960) 932.
16. A. F. MOODIE and C. E. WARBLE, *Phil. Mag.* **16** (1967) 891.
17. F. C. FRANK, *Adv. Phys.* **1** (1952) 91.
18. J. E. BURKE, *J. Amer. Ceram. Soc.* **40** (1957) 80.
19. F. R. N. NABARRO, "Report of Conference on Strength of Solids" (The Physical Society, London, 1948).
20. C. HERRING, *J. Appl. Phys.* **21** (1950) 437.

Received 2 June and accepted 15 August 1972.