

Spinodal decomposition in a titanomagnetite

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Abstract

An optically homogeneous titanomagnetite from a dacite lava, containing 40 percent ulvöspinel, has been examined by transmission electron microscopy. A modulated structure is developed parallel to the {100} planes, with an average wavelength of 165 Å. Electron diffraction patterns correspond to a single lattice, with pairs of satellite reflections convoluted about each reciprocal lattice point, parallel to the cube axes. The microstructure is consistent with exsolution having taken place by the mechanism of spinodal decomposition. The coherent spinodal temperature for this composition is calculated to be 95°C below the solvus temperature, at about 505°C. Application of interdiffusion data indicates a timescale for the transformation of the order of 4 hours.

Two possible implications for palaeomagnetism are: spinodal decomposition may increase the time-stability of the thermoremanent magnetization (TRM) carried by a titanomagnetite, and it may also be responsible for the partial self-reversal of TRM that has previously been reported in titanomagnetites of similar composition.

Introduction

It has been recognized for some time that a miscibility gap in the solid solution series magnetite (Fe₃O₄)–ulvöspinel (Fe₂TiO₄) leads to the development of exsolution intergrowths in titanomagnetites of intermediate composition. The resulting textures have been well documented in the literature; useful reviews have been presented by Ramdohr (1953) and Haggerty (1976). Exsolution takes place on the spinel {100} planes, giving rise to a characteristic cloth texture, the exact appearance depending on the relative proportions of the coexisting phases.

Members of the titanomagnetite series are of great importance in palaeomagnetic studies as they provide the principal carrier of thermoremanent magnetization (TRM) in most igneous rocks. A problem that has attracted considerable attention recently is the high stability of the TRM of many rocks, which requires the titanomagnetite to possess single magnetic domain properties. This may be due either to the presence of sub-micron titanomagnetite grains, small enough to exist as single magnetic domains, or to the subdivision of larger grains by means of intergrowth structures. The potential of exsolution intergrowths for imparting high magnetic stability to titanomagnetites has been demonstrated by Evans and

Wayman (1974). An understanding of the relevance of this process to various rock types requires knowledge of the conditions under which the intergrowths may form. It is also important to determine the mechanism(s) by which the intergrowths form, as this controls their morphology. Knowledge of exsolution mechanisms in this system also has potential as an indicator of cooling rates (Price, 1979).

Mel'nikov and Khisina (1976) suggested from the morphology of an exsolved titanomagnetite that the intergrowths may form by spinodal decomposition. In this exsolution mechanism there is no nucleation event; phase separation proceeds by the gradual growth of sinusoidal fluctuations in composition (Cahn, 1968). These compositional waves may ultimately coarsen to give rise to distinct interfaces between two phases, but in the initial stages of decomposition no interfaces are created. The structure described by Mel'nikov and Khisina consisted of a periodic array of magnetite-rich cubes in an ulvöspinel-rich matrix, the spacing of the precipitates being about 425 Å. Although this texture is indeed very similar to that produced by coarsening of spinodally-decomposed metal alloys, it does not prove that spinodal decomposition has taken place, as a similar structure could form by homogeneous nucleation.

The present contribution describes an electron mi-

croscopic study of a titanomagnetite with a modulated texture that has not coarsened into a two-phase structure. The results provide a strong indication that spinodal decomposition does occur in this system.

Specimen description and experimental procedure

The material examined was titanomagnetite contained in a banded andesite–dacite lava from the SE flank of Mt. Hakone, Japan (sample 15383, Manchester University collection). The titanomagnetite occurs as phenocrysts up to 1 mm across, the typical size being about 200 μm , and appears homogeneous under the reflected light microscope. Analysis with the electron microscope microanalyzer EMMA-4 gave an ulvöspinel content of 40 ± 2 percent, assuming titanomagnetite stoichiometry. Coexisting ilmenite phenocrysts were found to have a hematite content of 9.2 ± 1 percent. Both phases contain a trace of manganese, amounting to less than 1 weight percent MnO. Application of the Buddington and Lindsley (1964) geothermometer–oxygen geobarometer gives equilibrium conditions of $T = 990^\circ\text{C}$ and $\log f_{\text{O}_2} = -11.0$ for this pair of compositions.

Samples were thinned by ion-beam bombardment, and examined in Philips EM301 and JEOL JEM 100B electron microscopes operating at 100 kV.

Observations

In the electron microscope the titanomagnetite displays a fine-scale modulated texture on the $\{100\}$ cube planes. This texture is best illustrated in micrographs taken with the electron beam axis parallel to a fourfold symmetry axis, say $[001]$, in which case modulations are seen parallel to the traces of the (100) and (010) planes (Fig. 1). This modulated texture was developed uniformly throughout 3 ion-thinned grains which were examined. The average wavelength of the modulations as estimated from the micrographs is $\sim 150\text{\AA}$.

Electron diffraction patterns in the $[001]$ orientation were recorded, initially using a relatively small diffraction constant ($\sim 20\text{\AA}$ mm) in order to include the whole of the zero-order Laue zone. Under these conditions the diffraction pattern corresponds to a single cubic phase with absences appropriate to spinel space-group symmetry ($Fd3m$), and slight streaking of reflections is observed parallel to the a^* and b^* reciprocal lattice directions (Fig. 2). When the same pattern is recorded using a somewhat greater camera length (diffraction constant $\sim 60\text{\AA}$ mm), two pairs of satellite reflections are resolved about each reflection, parallel to a^* and b^* (inset, Fig. 2). The

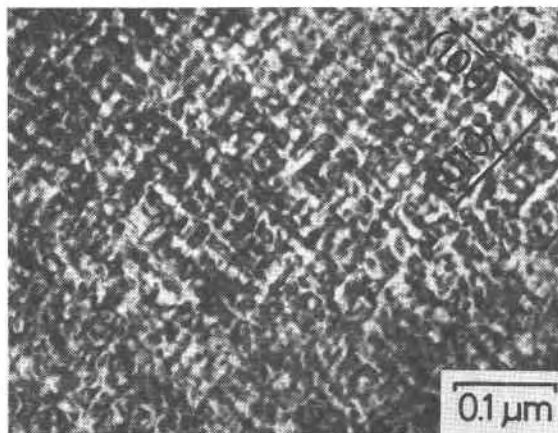


Fig. 1. Bright-field micrograph showing the modulated texture developed parallel to the $\{100\}$ planes of the titanomagnetite. Beam axis parallel to $[001]$.

presence of satellite reflections convoluted about a single reciprocal lattice point is a characteristic feature of spinodally-decomposed materials, the satellites resulting from the periodicity of the compositional waves. In the present case the spacing of the satellites indicates a modulation wavelength of $165 \pm 5\text{\AA}$, in agreement with that obtained from the images.

The nature of the $\{100\}$ modulations was further investigated by means of dark-field imaging. Cahn (1962) showed that spinodal decomposition in crystals with cubic symmetry should lead to the development of compositional modulations with wavefronts parallel to either $\{100\}$ or $\{111\}$, depending on the nature of the elastic anisotropy. No elastic constants are available for titanomagnetites, but the data given for magnetite by Birch (1966) indicate that the modulations will develop on $\{100\}$, as is the case for most cubic materials. The contrast seen in the electron microscope arises from the net strain in the lattice due to the periodic change in lattice spacing. Dark-field imaging with different diffracting vectors \mathbf{g} may be used to determine the orientation of the displacement associated with each compositional wave; a displacement \mathbf{R} will only lead to contrast in the image when $\mathbf{g} \cdot \mathbf{R} \neq 0$. Contrast arising from the change in structure factor can be shown to be negligible by means of a calculation similar to that described by Cadoret and Delavignette (1969) for spinodally-decomposed Cu–Ni–Fe alloys.

Figure 3 is a dark-field micrograph taken with the operating reflection 400, and the modulated contrast is only visible perpendicular to the diffraction vector. In dark-field micrographs where the diffraction vec-

tor is not parallel to one of the crystallographic axes, for example $g = 440$ (Fig. 4), cross-hatched contrast is seen, indicating that $g \cdot R \neq 0$ for both the (100) and (010) modulations. These results are similar to those obtained by Laughlin and Cahn (1975) for spinodally-decomposed Cu-Ti alloys, and are consistent with a model involving longitudinal displacement waves along the $\langle 100 \rangle$ directions.

Discussion

There has been much consideration in the literature for both metals (Hilliard, 1970) and minerals (Champness and Lorimer, 1976) of what constitutes proof that spinodal decomposition occurs in a given system. Conclusive proof requires either a detailed study of small-angle X-ray scattering, in order to follow the development of modulations during the early stages of the transformation, or application of the microstructural time sequence method of Laughlin and Cahn (1975). A more recent approach has been to reveal the variation in lattice spacing by means of high resolution electron microscopy (Wu *et al.*, 1978).

The presence of satellite reflections in X-ray or electron diffraction patterns has long been used as an indicator of spinodal decomposition. Some authors have objected to this, pointing out that Ardell and Nicholson (1966) described a periodic structure produced by the alignment of homogeneously nucleated precipitates. However, this periodicity only developed during the coarsening of an initially random distribution of precipitates, and micrographs demon-

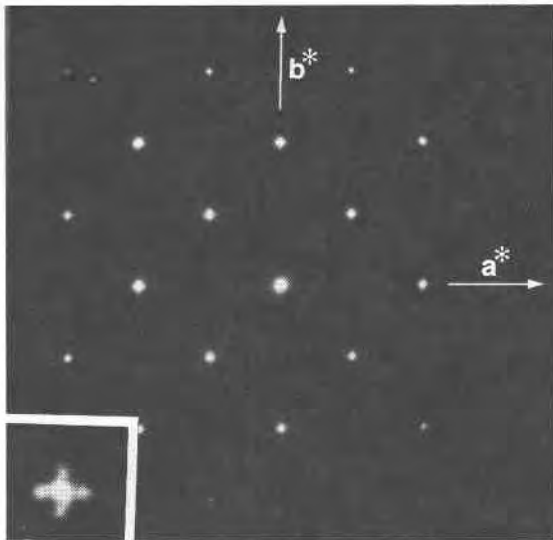


Fig. 2. A [001] electron diffraction pattern of the titanomagnetite. The inset, recorded at a higher instrumental magnification, shows the satellites about the 840 reflection.

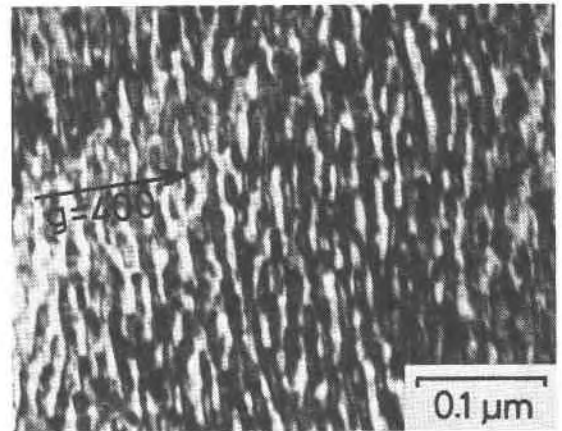


Fig. 3. Dark-field micrograph taken using the operating reflection 400. Only the modulations perpendicular to this diffracting vector are in contrast.

strated the presence of two distinct phases. Thus Laughlin and Cahn (1975) concluded that "periodicity and alignment from the start of a transformation is a strong indication of spinodal decomposition." The titanomagnetite described in the present paper fulfills this criterion, since the electron micrographs and diffraction pattern show that coarsening to a two-phase structure has not taken place.

A similar modulated microstructure resulting from spinodal decomposition has previously been recognized in the $\text{CoFe}_2\text{O}_4\text{-Co}_3\text{O}_4$ spinel ferrites (Takahashi *et al.*, 1971). Moore and Crawford (1978) described a periodic structure in some natural chrome-rich magnesioferrite spinels and ascribed this to spinodal decomposition, but the structures were considerably coarsened. Price (1979) considered that a mottled texture seen in a titanomagnetite with $x = 0.08$ ¹ resulted from spinodal decomposition. However, a similar texture has been reported in TEM studies of several ion-thinned spinels, including pure Fe_3O_4 (Smith, 1979 a,b; Putnis, 1979), and it seems likely that this texture is produced during ion-thinning (Smith, 1980). In the present example the random, mottled texture is observed immediately adjacent to the thin edge of the specimen, but the directional, periodic texture dominates in thicker areas. This is consistent with the view that a thin surface layer becomes damaged during ion-thinning.

Published optical micrographs of magnetite_{ss}-ulvöspinel_{ss} intergrowths all represent the hypabyssal or plutonic environments (Haggerty, 1976). A com-

¹ Throughout the present paper x denotes the mole fraction of ulvöspinel in the solid solution $(1-x)\text{Fe}_3\text{O}_4\text{-}x\text{Fe}_2\text{TiO}_4$.

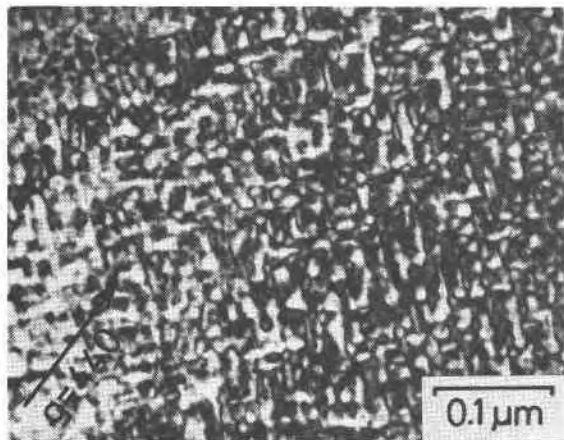


Fig. 4. Dark-field micrograph taken with the diffracting vector 440. Both sets of modulations are in contrast.

mon feature of these samples is the very uniform development of the cloth texture throughout the grain. This would be expected for spinodal decomposition, which occurs independently of any nucleation sites, and it may well be that such examples are coarsened spinodal textures. However, transformation mechanisms cannot be identified positively from coarsened microstructures, and it is also possible that homogeneous nucleation occurs at the slower cooling rates associated with these environments.

One attraction of spinodal decomposition is that a quantitative theory exists to describe it, and it thus holds considerable promise as an indicator of thermal history, at least in the initial stages of transformation. This is in contrast to exsolution mechanisms involving a nucleation step, for which the theory is less well defined. It is thus possible to estimate the temperature at which the microstructure in titanomagnetite 15383 developed, and the time taken for the transformation.

The most detailed study of the subsolidus phase diagram of the titanomagnetite system is that of Kawai (1956), giving the solvus depicted in Figure 5. The sometimes-quoted solvus of Vincent *et al.* (1957) was determined using an incorrect value for the cell parameter of ulvöspinel, leading to considerable errors in the positioning of the ulvöspinel-rich limb of the solvus. Use of the correct value for this cell parameter improves the agreement between the two studies. Kawai found difficulty in determining the low-temperature part of the diagram due to slow reaction rates, and based this part of the solvus on the compositions of natural examples. However, the crest of the solvus was determined experimentally to be at 600°C and $x = 0.42$.

The titanomagnetite from sample 15383 has a composition very close to the critical composition, and will therefore be assumed to have an equilibrium solvus temperature of 600°C. Since the equilibrium solvus and the chemical spinodal, defined by the locus of $(\partial^2 G/\partial x^2)_{T,P} = 0$, coincide at the critical composition, the chemical spinodal temperature may also be taken to be 600°C. Cahn (1968) showed that the coherent spinodal is depressed below the chemical spinodal by the amount $2\eta^2 Y/S''$, where η is the fractional misfit in cell parameter per unit change in composition, Y is a function of the elastic constants, and S'' is the second derivative with respect to composition of the entropy per unit volume. Values of η and Y may be determined using published cell parameters (Lindsley, 1965) and elastic constants (Birch, 1966). The factor S'' may be calculated using Rumble's (1977) model for the configurational entropy of titanomagnetites, and the generally accepted model of O'Reilly and Banerjee (1965) for the cation distribution in this series. For the composition $x = 0.40$ this gives a value of 95°C for the depression of the spinodal, leading to a coherent spinodal temperature of 505°C. No attempt is made here to calculate the rest of the coherent spinodal, as the low-temperature solvus data are considered insufficiently accurate to warrant this.

The time taken to form the observed microstructure may be estimated from the data of Freer

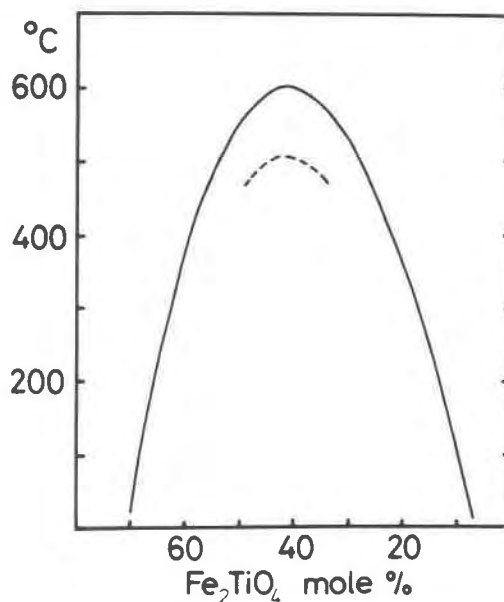


Fig. 5. Solvus for the system $\text{Fe}_3\text{O}_4\text{-Fe}_2\text{TiO}_4$, after Kawai (1956). The dotted line marks the crest of the coherent spinodal, as calculated in the present study.

and Hauptman (1978) for interdiffusion between pure Fe_3O_4 and titanomagnetite with $x = 0.20$. The exponential expression obtained by these authors leads to an interdiffusion constant of $1.1 \times 10^{-17} \text{ cm}^2/\text{sec}$ at 500°C . Freer and Hauptman showed how one may calculate the approximate time taken to create a lamellar intergrowth, given the interdiffusion constant and the scale of the microstructure. Taking the average interdiffusion distance in the spinodally-decomposed titanomagnetite to be half of the modulation wavelength, one obtains a transformation time of ~ 4 hours. This figure should only be treated as a rough guide, since the classical diffusion laws are not strictly applicable in the immediate vicinity of the spinodal, but it does indicate that this kind of microstructure may form in titanomagnetites on the time-scale of laboratory experiments.

Implications for palaeomagnetism

Exsolution in titanomagnetites was previously considered to be restricted to the hypabyssal and plutonic environments (Haggerty, 1976); the present results show that submicroscopic exsolution may occur in volcanic titanomagnetites of suitable composition. As mentioned in the introduction, such exsolution can lead to an increased coercivity, and therefore an increased time-stability, of the TRM carried by a rock. An analogous increase in coercivity was observed in spinodally-decomposed cobalt ferrite by Takahashi *et al.* (1971). The form of the titanomagnetite solvus indicates that the coherent spinodal will be at prohibitively low temperatures for spinodal decomposition to occur in titanomagnetites from submarine tholeiites, which typically have ulvöspinel contents of $\sim 0.6\text{--}0.7$; a TEM study of such a sample did not reveal any exsolution (Smith, 1979a). Spinodal decomposition is probably restricted to titanomagnetites from intermediate and acidic volcanic suites, which have lower ulvöspinel contents.

Fine-scale exsolution in titanomagnetite may also be relevant to the problem of self-reversal of the natural remanent magnetization of rocks. Although it is now well established that reversed magnetizations of rocks are almost exclusively the result of geomagnetic field reversals, there is still some interest in possible mechanisms for the complete or partial self-reversals recorded in a few rocks.

Shcherbakov *et al.* (1975) described a partial self-reversal that occurs in some synthetic mixed ferrites and in a natural $\text{Fe}_3\text{O}_4\text{--Mg}_2\text{TiO}_4$ spinel. The effect is manifested as a sharp peak in the thermal demagnetization curve of a thermoremanent magnetization

(TRM) near the final Curie point, implying that the partial TRM acquired by the sample over this temperature range is reversed. Bol'shakov *et al.* (1977) showed that this behavior is consistent with a model in which chemical inhomogeneities on a scale of $\sim 100\text{\AA}$ lead to a diffuse Curie temperature, the chemical composition being a continuous function of position. Spinodal decomposition clearly provides a possible mechanism to produce this kind of inhomogeneity. A similar partial self-reversal was observed by Petherbridge *et al.* (1974) in some partially unmixed synthetic titanomagnetites. The anomalous peak was present for samples cooled from 1350°C to room temperature over a 15-hour period, but was absent in a rapidly quenched sample. The timescale indicated for this exsolution process is thus similar to that calculated for spinodal decomposition in the present paper.

A natural example of a partially self-reversed rock is the lava from Mt. Etna, Sicily, described by Heller *et al.* (1979). The TRM of this rock is carried by optically homogeneous titanomagnetite that is zoned from $x = 0.34$ to 0.45 . The self-reversal was ascribed to magnetostatic interaction between exsolved Ti-rich and Ti-poor phases, with compositions $x \sim 0.12$ and ~ 0.55 . In view of the similar bulk composition and geological environment to the titanomagnetite from lava 15383, it is likely that the Etna material also exsolved by spinodal decomposition. Transmission electron microscopy of such thermomagnetically characterized samples would be of great value in understanding self-reversal mechanisms of the ferromagnetic spinels.

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