Subsolidus phase relations in the titanomagnetite solid solution series

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Abstract

The existence of exsolution textures in natural titanomagnetites indicates the presence of a miscibility gap in the titanomagnetite solid solution series. Previously the miscibility gap has been assumed to be a highly asymmetric solvus, with a consolute temperature near 600°C. It is shown, however, that the solvus is probably not strongly asymmetric, but more likely to be similar to that of a regular-solution model solvus. In addition, homogenization experiments indicate that the consolute temperature is less than 490°C, while annealing experiments on synthetic oxides indicate that the coherent spinodal crest temperature is less than 397°C. From calculations on the suppression of the coherent spinodal, it is inferred that the consolute temperature of the titanomagnetite solvus is less than 455°C.

Introduction

Iron-titanium oxides comprise a small, but significant part of all common igneous rocks, and are of great importance from the standpoint of yielding information on the geological past of their host rock. For example, a thorough knowledge of the behavior of the iron-titanium oxide minerals is necessary as a background to the study and interpretation of most phenomena associated with rock magnetism. In addition, iron-titanium oxides provide important paragenetic information on the rocks containing them, and can serve as useful geological thermometers and oxygen geobarometers. However, if these oxides are to be geologically useful, it is essential that their chemical and physical properties be fully understood. In particular, the possible effect of subsolidus exsolution upon the magnetic properties of both the titanomagnetites (*e.g.*, Price, 1980), and the ilmeno-hematites (*e.g.*, Hoffman, 1975), means that a detailed study of the subsolidus behavior of these oxides should be made. To this end, the subsolidus phase relations of the titanomagnetite solid solution series are investigated in this paper. Previous experimental results for the system are reviewed, and in some cases reinterpreted, and new results are presented.

Previous phase data

Mogensen (1946) first noted the existence of a two phase intergrowth of magnetite and ulvöspinel in titanomagnetites from Sodra Ulvön. This observation subsequently led to the suggestion that the solid solution between magnetite and ulvöspinel was not ideal, but contained a miscibility gap at low temperatures. In 1954, Kawai *et al.* proposed a schematic phase diagram for the titanomagnetite system, consisting of a hoop-like solvus, with a consolute point of about 750°C, at a composition of $Ulvö_{35}Mag_{65}$. Vincent and Phillips (1954), however, suggested that the ulvöspinel–magnetite intergrowths, observed in many titanomagnetites, were the result of a eutectoidal decomposition at 500°C, rather than the result of decomposition associated with the existence of a solvus.

Kawai (1956) reexamined the phase relationships in the titanomagnetite system, by studying synthetic materials. He found no evidence for the existence of a eutectoid, and produced a modified version of his earlier (1954) phase diagram, in which he placed the solvus crest at 600°C and 42 mole percent ulvöspinel. However, no experimental details, describing how these values were determined were given.

Vincent *et al.* (1957) performed homogenization experiments on some natural, exsolved titanomagnetites, in order to determine more accurately the subsolidus phase relations in the system. They found that the microstructures of samples held at 500°C for

15 hours showed little change, while complete mutual solution of the two components could be achieved on heating at 800°C for 12 hours. They also conclude that there was no evidence for the existence of a eutectoid in the titanomagnetite system. By studying the magnetic properties of these titanomagnetites after various heat treatments, they inferred that magnetite dissolved in ulvöspinel during heating, without itself taking much ulvöspinel into solution. On these grounds, they produced a schematic phase diagram (Fig. 1), showing an asymmetric, hoop-shaped solvus, with a crest at 600°C. This diagram was subsequently slightly modified by Basta (1960).

A theoretical study of the iron-titanium oxide phase relations, by Rumble (1970), using thermodynamic data, predicted an asymmetric solvus for the titanomagnetite system, with a crest at 650°C and $Ulvö_{65}Mag_{35}$. Subsequently, Rumble (1977) published a paper outlining errors in the model which he had used to calculate the titanomagnetite solvus in his 1970 paper; however, he did not repeat the calculation using the corrected model.
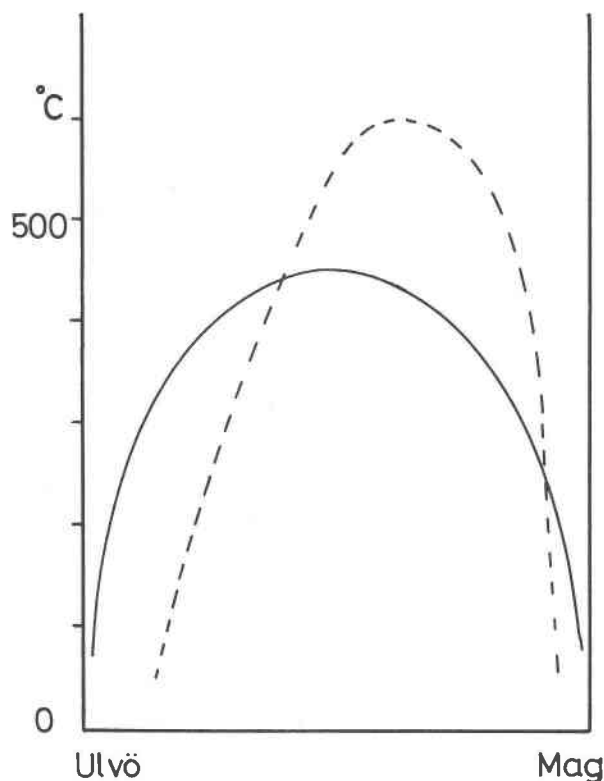

Fig. 1. A schematic diagram of the titanomagnetite solvus suggest by Vincent et al. (1957) (dashed line), and the solvus suggested as the result of the work presented in this paper (solid line).

In none of the above studies has the consolute temperature of the titanomagnetite solvus been strictly defined; 600°C has been adopted by consensus rather than having been experimentally proven. In addition, the results of the only study in which experimental data have been published (Vincent et al., 1957), are amenable to an interpretation other than that given by the original authors. Vincent et al. (1957) found that samples heat-treated at temperatures up to 500°C showed little change in Curie temperature. However, the specific saturation magnetization of these specimens fell rapidly in the early stages of the heating process. From this, they correctly inferred that in the early stages of homogenization there was a rapid reduction of the volume of ferrimagnetic material in the titanomagnetite, but because the measured Curie temperature remained constant, the composition of the magnetic phase was unchanged. Vincent et al. (1957) further inferred that these magnetic observations reflected the nature of the equilibrium phase diagram of the titanomagnetite system and interpreted the observed magnetic properties as being due to the ability of magnetite to dissolve readily into ulvöspinel, while ulvöspinel was unable to dissolve to such a great extent in magnetite.

It is doubtful, however, whether these experiments by Vincent et al. (1957) reflect equilibrium processes. Rather it is more likely that the magnetic observations reflect kinetically controlled events. The experiments of Vincent et al. (1957) were performed on titanomagnetites which carried ulvöspinel-rich lamellae with widths of between 2 and 0.25 μm. The samples were heated at 450°C for 504 hours, and at 500°C for 336 hours. From these conditions and from the known diffusion properties of the titanomagnetites (Price, 1981; Freer and Hauptman, 1978), it is clear that complete homogenization of these specimens was never achieved at these temperatures. Consequently, the Curie temperature and the specific saturation magnetization values reported for these oxides are those of partially homogenized titanomagnetites.

The likely nature of these partially homogenized titanomagnetites can be deduced by considering the changes which occur in exsolution microstructures during heating. Initially an exsolution microstructure can be envisaged as being comprised of magnetite-enriched cubes (or plates), surrounded on all sides by ulvöspinel-enriched lamellae (Price, 1980). On heating, at temperatures above the solvus, the ulvöspinel and magnetite begin to mix. The ulvöspinel-rich lamellae take up magnetite from the cube, and mag-

netite near the cube–lamellar interface takes ulvö-spinal up into solution. However, because mixing is diffusion controlled the magnetite near the ulvöspinel lamellae adsorbs considerable amounts of ulvöspinel, before any of the ulvöspinel component can diffuse into the magnetite at the center of the cube. Hence, if the magnetic properties of this partially homogenized titanomagnetite were studied, it would be found to have a final Curie temperature close to that of almost pure magnetite (from the magnetite at the center of the cube). However, it would also be found that the total amount of magnetic material had been reduced, because the magnetite near the ulvöspinel-rich la-mellae would have taken up the ulvöspinel into solu-tion. These magnetic properties would be purely the result of the mechanism and kinetics of homoge-nization, however, and could not be used to infer the possible shape of the titanomagnetite solvus. It is suggested that the observations made by Vincent *et al.* (1957) can be explained in this way, and that their observations do not, therefore, provide evidence for an asymmetric solvus.

Some evidence on the nature of the titanomagne-tite solvus can be obtained, however, by X-ray dif-fraction (*e.g.*, Basta, 1960) and from analytical elec-tron microscopy (*e.g.*, Price, 1981). Both of these techniques indicate that there is a slight asymmetry between the compositions of co-existing ulvöspinel-rich and magnetite-rich phases. The accuracy of the measurements of these compositions is, however, dif-ficult to assess since the X-ray diffraction measure-ments of cell parameters is complicated by the over-lap of the ulvöspinel and magnetite peaks. In addition, it is hazardous to estimate the composition of a titanomagnetite purely from its cell parameter because of the sensitivity of the cell parameter to the general composition of the spinel.

An estimate of the shape of the titanomagnetite solvus could also be obtained by studying the solvi of other spinel solid solutions. The best defined spinel solvus is that found in the magnetite–hercynite sys-tem (Turnock and Eugster, 1962). In this system, the solvus is slightly asymmetric, but does not deviate greatly from a regular-solution model solvus. The de-viation of the shape of a solvus from that of a regu-lar-solution model solvus, can, theoretically, be de-scribed as a function of the cell parameter and the bulk and shear moduli across the solid solution (Greenwood, 1979). The data on these moduli are not, however, available for ulvöspinel. From the data which are available for spinels (Birch, 1966), it seems that the moduli are relatively insensitive to composi-

tional changes. All these data are, however, for 2–3 spinels rather than 2–4 spinels, such as ulvöspinel; these latter may behave differently.

In conclusion, therefore, the data presently avail-able on the subsolidus phase relations in the titano-magnetite solid solution series indicate that a solvus exists in the system, but do not provide evidence for a highly asymmetric solvus. Rather, it is suggested that the solvus may be only slightly asymmetric (cf., mag-netite–hercynite) or even symmetric, with a crest temperature at or below 600°C. It was considered de-sirable, however, to perform further experiments in order to confirm or negate these findings, and to de-fine more precisely the consolute point of the titano-magnetite solvus.

Experimental details

Two categories of experiment were performed dur-ing this present study of the titanomagnetite solvus:

(i) Homogenization experiments were performed on natural, ulvöspinel–magnetite intergrowths;

(ii) annealing experiments were completed on ho-mogeneous, synthetic titanomagnetites, in an attempt to induce exsolution.

Homogenization experiments

Homogenization experiments were performed on titanomagnetites from the Taberg intrusion, Sweden (no. 54252 in the Harker collection, Cambridge) and from the Freetown Gabbro, Sierra Leone (no. 80397). These titanomagnetites had oxidation-ex-solution lamellae of ilmenite, lamellae of pleonaste and a cloth-texture intergrowth of ulvöspinel and magnetite, and have been described by Price (1981). The inhomogeneous oxide grains showed no sign of low temperature oxidation when studied by optical microscopy or by transmission electron microscopy (TEM). The average compositions of the titano-magnetites are given in Table 1 and are the mean of a number of analyses, obtained by electron micro-probe, of ilmenite-free areas of the oxides. Since the electron microprobe spot size was larger than, or equal to, the size of the various spinel exsolution tex-tures, the analyses are bulk analyses of all the spinel phases present. The mean analyses have been recast into idealized spinel end-members (Table 1), assum-ing stoichiometry. It is also assumed that the bulk compositions of the titanomagnetite-intergrowths are given by the proportion of ulvöspinel and magnetite in the recast analyses. For the Taberg specimen the mean analysis yields an ulvöspinel:magnetite ratio of

Table 1. Average analyses of ilmenite-free titanomagnetites from the Taberg (no. 54252) and Freetown Gabbro (no. 80397) intrusions

Sample	54252	80397
SiO_2	0.32	0.23
TiO_2	15.63	11.66
Al_2O_3	2.91	4.39
Fe_2O_3	34.81	40.30
Cr_2O_3	0.00	0.18
V_2O_3	0.82	1.07
FeO	44.02	38.65
MnO	0.34	0.20
MgO	1.43	2.47
TOTAL	100.33	99.15
End members (mole %)		
$MgAl_2O_4$	6.49	9.75
$MgCr_2O_4$	0.00	0.26
$MgFe_2O_4$	1.60	3.88
Fe_3O_4	47.62	53.02
Fe_2TiO_4	44.32	33.08

47:53, and for the Freetown Gabbro, a ratio of 38:62.

Fragments of the Taberg and Freetown specimens, of approximate size $1 \times 0.25 \times 0.25$ cm, were heated in small, sealed, evacuated silica-glass tubes. The duration of the homogenization experiments ranged from 30 minutes to 100 days. By sealing the rock fragments in evacuated tubes (total pressure $< 1 \times 10^{-4}$torr), the system was approximately self-buffering, since the number of moles of O_2 in the atmosphere was many orders of magnitude less than the number of moles of titanomagnetite. The titanomagnetite showed no sign of oxidation (or reduction) after these heating experiments.

After heating, the specimens were mounted in resin blocks, and polished to reveal the center of the rock fragments. The titanomagnetites were studied by reflected-light microscopy to determine the degree of homogenization which had been achieved. If the cloth-texture was not visible optically (Fig. 2), the specimen was prepared for study by TEM where it was inspected for any residual inhomogeneity. The TEM observations revealed no changes in the nature of the ilmenite lamellae, nor the development of any titanomaghemite. Furthermore, no changes in the

size or nature of the pleonaste lamellae were observed.

The exsolution microstructures in the titanomagnetites from both the Taberg intrusion and the Freetown Gabbro were successfully homogenized (on the electron optical scale) after heating for 100 days at 490°C (Table 2). This temperature is between
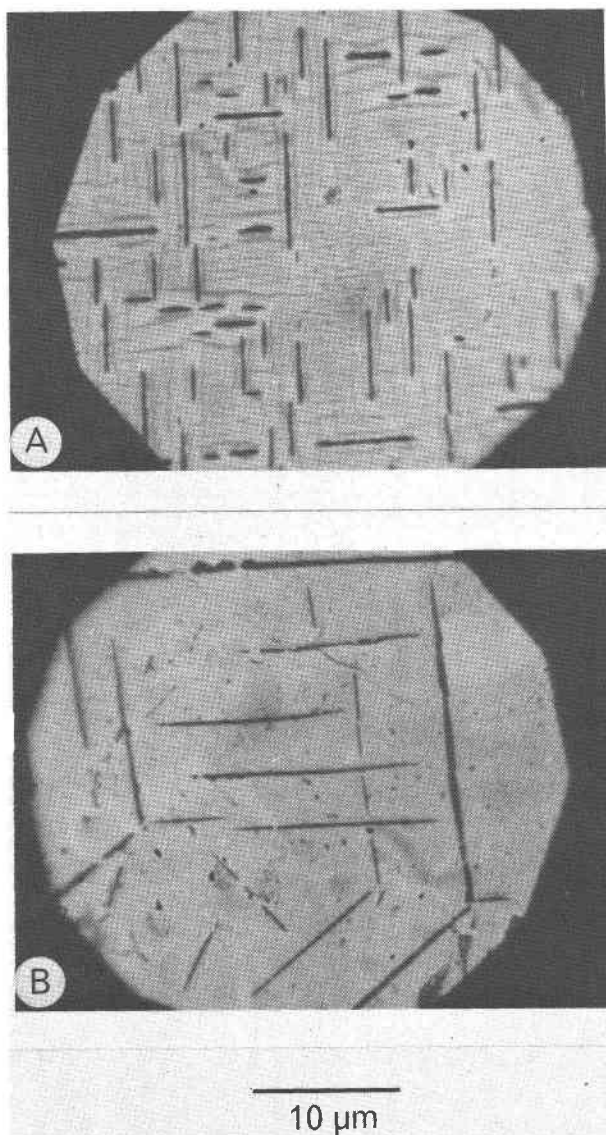

Fig. 2. (a) Optical micrograph of an unheated titanomagnetite from the Freetown Gabbro. Black pleonaste lamellae are set in the inhomogeneous titanomagnetite, in which ulvöspinel lamellae isolate cubes and plates of magnetite; (b) A similar titanomagnetite after annealing for 100 days and 490°C. The cloth-texture in the titanomagnetite has been completely homogenized, leaving the pleonaste lamellae uneffected. TEM study of the titanomagnetite revealed no heterogeneity within the titanomagnetite.

Table 2. Experimental data for titanomagnetite

Run Number	Starting Bulk	Material Phases	Temp °C	Time Days	
56	Ulvö$_{50}$	1	470	100	Homogeneous
57	Ulvö$_{50}$	1	450	100	Homogeneous
58	Ulvö$_{50}$	1	425	100	Homogeneous
59	Ulvö$_{50}$	1	400	100	Homogeneous
60	Ulvö$_{50}$	1	375	100	Homogeneous
107	Ulvö$_{47}$	2	520	5	Heterogeneous
108	Ulvö$_{47}$	2	520	20	TEM homogeneous
112	Ulvö$_{47}$	2	490	20	Heterogeneous
113	Ulvö$_{47}$	2	490	100	TEM homogeneous
120	Ulvö$_{47}$	2	480	100	Heterogeneous
140	Ulvö$_{38}$	2	520	20	TEM homogeneous
142	Ulvö$_{38}$	2	490	100	TEM homogeneous
145	Ulvö$_{38}$	2	480	100	Heterogeneous

80 and 110°C below the solvus temperature proposed by Vincent *et al.* (1957). It is inferred, therefore, that the solvus of the titanomagnetite solid solution series must lie below the points defined by the bulk compositions of the homogenized phases and the temperature at which homogenization was achieved. In addition, since it has already been suggested that the titanomagnetite solvus is not greatly asymmetric, and since the bulk compositions of the homogenized phases lie near the center of the solid solution series, it is inferred that the consolute temperature of the solvus is below 490°C.

Attempts to homogenize the titanomagnetite exsolution microstructures at temperatures lower than 490°C failed. This was either because insufficient time was available for full homogenization to occur (from the known diffusion data for interdiffusion in titanomagnetites (*e.g.*, Price, 1981), homogenization at 480°C will require at least 200 days annealing), or because the specimen lay within the two phase field.

Annealing experiments

The samples, which were annealed in an attempt to induce ulvöspinel–magnetite exsolution, were synthetic, polycrystalline aggregates of titanomagnetite of composition Ulvö$_{50}$Mag$_{50}$. The specimens were prepared by mixing in stoichiometric proportions spectroscopically pure TiO$_2$, Fe$_2$O$_3$ and Fe. The mixture was ground in an agate mortar and compressed into pellets. The pellets (0.5 cm tall and 0.25 cm in diameter) were placed in 60:40 Ag:Pd-tubes (to prevent Fe loss during heating). The Ag:Pd-tubes were placed within silica-glass tubes, which were then evacuated and sealed. They were heated at 1100°C for 24 hours, after which time the sintered oxide pellets were removed from the tubes, reground, and again pressed into pellets. The above process was repeated for another 24 hours heating cycle.

The resulting oxide was studied by X-ray diffraction and found to be a single phase of titanomagnetite, with a cell parameter of 8.455±0.003Å. Further study of the oxide by electron probe gave an analysis corresponding to a titanomagnetite of composition Ulvö$_{50}$Mag$_{50}$. No other chemical components were detected by the electron microprobe. When examined by TEM, the specimen appeared homogeneous and showed no signs of oxidation.

Portions of the synthetic titanomagnetite were heated (again in Ag:Pd-tubes, themselves in a sealed, evacuated silica-glass tube) at temperatures between 470 and 375°C for up to 100 days (see Table 2). After heating, the samples were again studied by X-ray diffraction, and no non-spinel lines or changes in cell parameter were found. Extensive TEM study of crushed grains of all the annealed titanomagnetite specimens revealed no inhomogeneity, even in specimens which had been heated for 100 days. From observations made on natural titanomagnetites (Price, 1980), it was inferred that if exsolution is to occur in titanomagnetites with compositions which lie near the center of the solid solution, it will occur most rapidly by spinodal decomposition (nucleation was found to occur only in titanomagnetites which had been cooled slowly). Decomposition, as a result of an annealing experiment would, therefore, only be expected to occur if the titanomagnetite were heated within its coherent spinodal. There are two possible explanations, therefore, why no exsolution was observed in the annealed samples: (i) the titanomagnetites were annealed outside the coherent spinodal; (ii) the titanomagnetites were annealed within the coherent spinodal, but insufficient time was available for the compositional separation to develop.

The latter possibility can be investigated by considering the early stages of spinodal decomposition. Spinodal decomposition is a diffusion-controlled process at temperatures well below the spinodal, but near the spinodal the change in the free energy produced by the decomposition is rate determining. The role of the free energy in determining the rate of decomposition has the effect of reducing the effective

diffusion coefficient to an extent given by (Hilliard, 1970):

$$D_{eff} = D(T_s - T)/T \qquad (1)$$

where T_s is the spinodal temperature.

As suggested by McConnell (1975), during the early stages of spinodal decomposition, the development of compositional inhomogeneity will approximately obey the diffusion relationship (Shewmon, 1969):

$$x^2 = 4tD_{eff} \qquad (2)$$

where x is the scale upon which the compositional inhomogeneity is developed.

During the course of the above annealing experiments, no inhomogeneities were observed, despite the fact that an inhomogeneity on a scale as small as 20Å could have been easily detected with the electron microscopes used (AEI G6 and JEM 100CX). The temperature of the coherent spinodal, compatible with the above observations, can be calculated from equations 1 and 2, using values of $T = 375°C$, t = 100 days and x < 20Å, and the diffusion parameters (D_o and ΔE, the pre-exponential factor and activation energy respectively) for Fe–Ti interdiffusion in titanomagnetite of $D_o = 2.38 \times 10^{-3} cm^2 s^{-1}$ and $\Delta E = 49.8$ kcal mole^{-1} (Price, 1981). This calculation indicates that the coherent spinodal temperature (T_s), for titanomagnetites of composition Ulvö$_{50}$Mag$_{50}$, has to be less than 397°C, if no inhomogeneity is to be detected, even after heating for 100 days at 375°C.

Although this estimate is only approximate, it is unlikely that this calculation is grossly in error, and it seems reasonable to suggest that the temperature of the coherent spinodal near the center of the solid solution is less than 397°C. In order to translate this inferred coherent spinodal crest temperature into a solvus consolute temperature, it is necessary to calculate the degree of suppression of the coherent spinodal with respect to the chemical spinodal. This can be done analytically only for a symmetric solvus, and requires much more complex calculatons for a highly asymmetric solvus. Since it has been inferred that the titanomagnetite solvus is not greatly asymmetric, the calculation will be performed using a regular-solution model solvus, and although the true solvus may differ slightly from this, it is not expected that the deviation would be so large as to significantly effect the calculations outlined below.

The coherent spinodal

The temperature dependence of the chemical spinodal (T_{chem}) upon the consolute temperature (T_{con})

and the composition of the unmixing phases (c and 1-c, in mole fractions), for a regular-solution model is:

$$T_{chem} = 4T_{con}c(1-c) \qquad (3)$$

The temperature dependence of the coherent spinodal (T_s), however, is related to that of the chemical spinodal by the equation (Hilliard, 1970):

$$T_s = T_{chem} + 2Yn^2V/S'' \qquad (4)$$

where n = 1/a(da/dc), a is the cell parameter of the oxide, da/dc is the rate of change of cell parameter with composition, Y is the Young's modulus of the 'soft direction' of the oxide ({100} in spinel), V is the molar volume, and S'' is the second derivative of the molar entropy (S) with respect to composition (c).

For a simple, binary regular-solution, the molar entropy is given by:

$$S = -R\{c\ln c + (1-c)\ln(1-c)\} \qquad (5)$$

and

$$S'' = -R/\{c(1-c)\} \qquad (6)$$

Previously, this function has been used in calculations of the temperature of the coherent spinodal for spinel solid solutions (Yund and MacCallister, 1970). However, this is not the correct entropy function for the structurally complex spinels. Spinel has both tetrahedral and octahedral cation coordination sites, and several models for cation distribution have been advanced (see Lindsley, 1976). Two of the most commonly discussed models are those of O'Reilly and Banerjee (1965), and of Neél (1955) and Chevallier et al. (1955). Bleil (1976) has indicated that the cation distribution in titanomagnetites is a function of temperature, and so it will not be fully described by either model; consequently both models need to be considered.

O'Reilly and Banerjee (1965) suggested that for titanomagnetites of composition 0.2 < c < 0.8 (where c is the mole fraction of ulvöspinel), the cation distribution is given by:

$$[Fe^{3+}_{1.2-c}Fe^{2+}_{c-0.2}]^{IV}[Fe^{2+}_{1.2}Fe^{3+}_{0.8-c}Ti_c]^{VI}$$

(where the Roman numerals refer to the two coordination sites). The corresponding entropy of mixing is given by:

$$S = k\ln(M^{IV}M^{VI}) \qquad (7)$$

where,

$$M^{IV} = N!/\{(1.2-c)N!(c-0.2)N!\} \qquad (8)$$

$$M^{VI} = 2N!/\{1.2N!(0.8-c)N!cN!\} \qquad (9)$$

Thus, by Stirling's formula:

$$S = R\{2\ln2 - 1.2\ln1.2 - (1.2-c)\ln(1.2-c) - (c-0.2)\ln(c-0.2) - (0.8-c)\ln(0.8-c) - c\ln c\} \quad (10)$$

and

$$\frac{d^2S}{dc^2} = R\frac{2(c-1)}{(1.2-c)(0.8-c)} - \frac{2c-0.2}{c(c-0.2)} \quad (11)$$

Evaluating equation 11 for c = 0.5, yields a value of $S'' = -10.1R$. This can be compared with a value of $S'' = -4R$, obtained from the simple regular-solution entropy function, equation (6).

Using values for n^2, Y and V of (Lindsley, 1976; Birch, 1966):

$$n^2 = 2.5 \times 10^{-4}\ m^{-2}$$
$$Y = 2.1 \times 10^{11}\ Nm^{-2}$$
$$V = 4.6 \times 10^{-5}\ m^3mole^{-1}$$

the temperature difference between the coherent spinodal and the chemical spinodal is calculated to be 58.5°C, for c = 0.5. This compares with a temperature difference, calculated from the simple entropy function, of 147.5°C.

Performing similar calculations to the ones above using the Neél–Chevallier–Bolfa–Mathieu model are more difficult because of the discontinuity, at c = 0.5, in the first derivative of the suggested cation distribution function. However, evaluating the equations which can be obtained near to c = 0.5, indicates that the value of S'' is close to $-21R$, and that the corresponding suppression of the coherent spinodal would only be approximately 28°C. The use of different spinel entropy function, therefore, has a significant effect on the calculated coherent spinodal temperature, and consequently previous calculations by Yund and MacCallister (1970), on the magnetite–hercynite system may be in error.

Discussion

From the annealing experiments described, a likely upper limit to the coherent spinodal was obtained. An upper limit to the solvus (assuming that the shape of the solvus is not greatly asymmetric) can similarly be obtained by adding the calculated coherent spinodal suppression temperature to the estimated spinodal temperature of 397°C. However, as seen above, the exact value calculated for the suppression of the coherent spinodal is dependent upon the cation distribution model chosen. Since an upper limit to the solvus is being sought, the larger value for the suppression of the coherent spinodal has been chosen to calculate the probable limits of the titanomagnetite solvus. Thus, it is inferred that, if the ti-

tanomagnetite solvus can be correctly described as being symmetric or nearly so, then the solvus crest lies at a temperature below 455°C. The validity of this estimate is not seriously effected if the solvus in this system is indeed slightly asymmetric (having a crest within approximately 50±5 mole percent), because (1) the curvature of the solvus near its crest is such as not to produce large changes in temperature with changes in composition, and (2) the equations used in the above calculations would not be significantly effected by small changes in the crest position.

It would be desirable to obtain more accurate results from annealing experiments on titanomagnetites; however from the kinetics of the processes involved in exsolution, it seems unlikely that the titanomagnetite solvus will be defined with the same accuracy as the solvi in some other systems (*e.g.*, magnetite–hercynite). It may indeed be necessary to use indirect methods (*e.g.*, thermodynamic calculations) to determine the nature of the titanomagnetite solvus more accurately.

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