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The magnetism and microstructure of pulverized titanomagnetite, $Fe_{2.4}Ti_{0.6}O_4$: the effect of annealing, maghemitization and inversion

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Abstract

Titanomagnetite, $Fe_{2.4}Ti_{0.6}O_4$, pulverized in a ball-mill to make the material readily maghemitize on the laboratory time scale, has been used as an analogue for the magnetic mineral of submarine basalts. The ball-milling, in addition to reducing particle size, produces an internal nanocrystalline structure. Annealing at high enough temperature ($600^{\circ}C-800^{\circ}C$) removes the nanocrystalline structure but the titanomagnetite crystals carry a relic of ball-milling induced non-stoichiometry which contributes to magnetic strain anisotropy. Despite this complication, the coercive force of the annealed material is close to the average coercive force of pillow basalts and should provide an improved synthetic analogue for laboratory studies inspired by the magnetism and mineralogy of the submarine crust. The nanocrystalline structure persists in maghemitized pulverized titanomagnetite, and the magnetization process parameters are consistent with an increasing importance of thermal fluctuations as maghemitization proceeds. In the transformations produced by annealing, maghemitization and inversion, the spinel component immediately post-transformation has composition and/or concentration inherited from the pre-transformation spinel, and does not correspond to equilibrium. Later re-equilibration of the coexisting phases, accelerated in the laboratory by elevated temperature, leads to diminution of the spinel component in favour of more stable phases. Unlike the inversion of maghemite to haematite, the inversion product of titanomaghemite is not a unique assemblage of phases. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Titanomagnetite; Maghemitization; Inversion

1. Introduction

The preparation of synthetic analogues of magnetic minerals has a long tradition in rock magnetism. The attempted synthesis of titanomaghemite by Akimoto et al. (1957) is a notable example. The synthetic analogues can provide highly specified systems in which to test models of the magnetization process. Of especial importance are the weak field remanence acquisition mechanisms, such as thermoremanence, which are the physical basis of the palaeomagnetic method. The chemical basis may also be studied when synthetic materials are used to

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simulate processes in which the palaeomagnetic carrier evolves, for example through the oxidation of silicates to produce magnetic particles (e.g., Brewster and O'Reilly, 1989) or maghemitization (Özdemir and Dunlop, 1988). A reference collection of the properties of well-specified minerals or synthetic analogues is essential to the magnetopetrological method by which the evolution of rocks is traced through the magnetic minerals (e.g., Housden et al., 1996).

The study of basalt samples recovered from the submarine crust (Marshall and Cox. 1972), and intensive exploration of the submarine crust in the following decades, led to an increased interest in the process of maghemitization and the properties of titanomaghemites. The production of the metastable titanomaghemite on the laboratory time scale requires fine grain starting titanomagnetite produced by prolonged ball-milling of solid state sintered material (e.g., Özdemir and O'Reilly, 1981). Whereas such material can plausibly account for the intensity of remanence of submarine basalt, the high stability of the remanence of the synthetics to alternating field demagnetization seems a poor analogue for the behaviour of the natural material (Özdemir and O'Reilly, 1982). The pulverized material acquires a large strain anisotropy. The origin of the strained state of the magnetic material has been found to lie in the heterogeneous internal microstructure of the pulverized particles (Brown and O'Reilly, 1996). The pulverized particles, of 0.1-1 µm in size, contain regions of relatively perfect crystal structure, the "nanocrystals" of size about 20 nm, separated by magnetically amorphous regions of the same composition. The magnetic properties of the pulverized material must now be looked at in a new light, thermal fluctuations playing a significant role.

The presence of the nanocrystals gives rise to a number of questions: can they be removed by annealing to produce relatively unstrained monodomain titanomagnetite crystals; while the amorphous region may act as a conduit for ionic diffusion and facilitate maghemitization, is the nanocrystalline structure inherited by titanomaghemites produced from the pulverized material; and finally, do the nanocrystals have any implications for the inversion of the nonstoichiometric titanomaghemites? This present study addresses these questions.

2. Preparation of pulverized titanomagnetite

Titanomagnetite, $Fe_{24}Ti_{06}O_4$, was synthesized by firing pressed pellets of stoichiometric mixtures of Fe, Fe_2O_3 and TiO_2 , sealed in evacuated quartz ampoules, at 1050°C for 20 h. The successful synthesis of $Fe_{24}Ti_{0.6}O_4$ is confirmed by Hagg–Guinier camera X-ray powder pictures (yielding a cell edge of 8.485 ± 0.002 Å), a measured Curie point temperature of $189 + 5^{\circ}C$ and a room temperature saturation magnetization of 31.4 + 0.6 A m² kg⁻¹. The material was milled in a methanol slurry for 15 h in a Syalon ball-mill. After milling, the saturation magnetization had fallen to 23.0 A m^2 kg⁻¹, the Curie point temperature, $T_{\rm c}$, had risen to 235°C. The cell edge after milling, 8.483 Å, had fallen slightly. The raised T_c indicates pulverization induced nonstoichiometry which corresponds to an oxidation parameter, z, of about 0.15. The magnetic hysteresis properties $(M_{rs}/M_s = 0.51 \text{ and } H_c = 143 \text{ kA m}^{-1})$ indicate the monodomain state. The constant in the law of approach to saturation and the work done to ascend the reversible branch of the hysteresis loop (Brown and O'Reilly, 1996) yield values of $0.49 \pm$ 0.2 T for K_{μ}/M_{s} and -0.20 ± 0.07 T for K_{1}/M_{s} .

An average crystallite size of 13 nm is derived from the coercive force value taken with a typical saturation magnetization value of 30 A m² kg⁻¹ and the inferred K_u/M_s . It is assumed that the crystallites are non-interacting and monodomain with randomly orientated axes of uniaxial anisotropy which dominates over the cubic symmetry, and that magnetization change takes place by coherent rotation. The validity of these assumptions is discussed in detail elsewhere (Brown and O'Reilly, 1996, 1999). The crystallite volume, v, is then calculated from the following equation (Néel, 1955):

$$v = \frac{kT}{K_{\rm u}} \left(1 - \frac{\mu_0 M_{\rm s} H_{\rm c}}{K_{\rm u}} \right)^{-2} \ln(f_0 t^*)$$

where f_0 , the frequency factor, is taken to be 10^9 s⁻¹, t^* is the measurement time (1 s), and k and μ_0 are the usual constants of nature. Optical examination indicates a particle size in the range $0.1-1 \ \mu$ m. The implied nanocrystalline structure within the par-

ticles is directly confirmed by transmission electron microscopy (a typical micrograph may be seen in Brown and O'Reilly, 1996) and is also consistent with the line broadening of the X-ray powder diffractograms. The X-ray diffraction lines are broadened by both the small crystallite volume and the effect of strain of the crystal structure. The residual strain maybe inferred from the inferred value of $K_{\rm m}$, the magnetostriction coefficient of Fe2.4Ti0.6O4 (Syono, 1965) and a typical Young's modulus for a ceramic material. For low angle diffraction lines such as (311) and (400), the estimated contribution of strain to line broadening is an order of magnitude smaller than that of the broadening expected due to crystallite size of the order of 10 nm. X-ray line broadening therefore supports the nanocrystalline description of the milled particles.

The mass-specific susceptibility, κ , of a random array of non-interacting monodomain particles with uniaxial anisotropy constant, K_u , and not subject to thermal fluctuation, is related to the mass-specific spontaneous magnetization, σ_s , by $\kappa = (\mu_0 \rho \sigma_s^2)/(3$

 $K_{\rm m}$). The ball-milled material is magnetically diluted by the intercrystal magnetically amorphous zones. If the magnetically contributing region is a fraction, α , of the whole, then the observed properties are κ (obs) $= \alpha \kappa$ and $\sigma_{\alpha}(\text{obs}) = \alpha \sigma_{\alpha}$. Taking $\alpha = \sigma_{\alpha}(\text{obs})/30$ where 30 A m^2 kg⁻¹ is a typical room temperature value of σ_s for Fe_{2.4}Ti_{0.6}O₄, we obtain κ (obs) = (10 $\mu_0 \rho \sigma(obs))/(K_u)$. Substituting values for the right hand side of this expression yields $\kappa(obs) = 20 \times$ 10^{-6} m³ kg⁻¹. The difference between this and the measured value of 35×10^{-6} m³ kg⁻¹ is readily accounted for by the distribution in crystallite sizes. At the lower end of the distribution, crystallites of dimension 9 nm and below are subject to thermal activation on a time scale of 10^{-3} s, the period of the driving alternating field in the susceptibility measurement. The susceptibility of such crystallites would be a factor 14 greater than the non-thermally agitated monodomain crystallites, and a fraction of 6% by volume of the total population lying in this size range would give the required enhancement to the susceptibility.



Fig. 1. The magnetic properties of pulverized $Fe_{2.4}Ti_{0.6}O_4$ after annealing for 17 h at a number of isotherms between 100°C and 800°C: (a) initial susceptibility, (b) coercive force, (c) ratio of saturation remanence to saturation magnetization, and (d) saturation magnetization.

3. Annealing of pulverized Fe_{2.4}Ti_{0.6}O₄

3.1. Observations

Samples of the pulverized material were sealed in evacuated quartz ampoules and heated for 17 h at 100°C, 200°C, 300°C, 400°C, 600°C and 800°C. The annealing period is typical of a laboratory maghemitization run. The magnetic properties of the annealed suite are shown as a function of annealing temperature in Fig. 1 together with the unannealed pulverized material. The initial susceptibility (Fig. 1a) remains more or less constant on annealing up to 600°C, increasing by a factor of about 4 after the 800°C annealing. The coercive force (Fig. 1b) falls steadily to about 50% of the initial value at the 600°C annealing followed by a fall to less than 10% after the 800°C annealing. $M_{\rm rs}/M_{\rm s}$ (Fig. 1c) lies between about 0.45 and 0.5 throughout, and $M_{\rm c}$ (Fig. 1d) seems to show some recovery of the loss due to pulverization. The Curie point temperatures were determined using a thermomagnetic balance in which the (10 mg) encapsulated sample is heated and cooled at about 10°C per minute to just above the Curie point. The Curie point temperature of the annealed material initially rises and then falls as annealing temperature increases (Fig. 2). The cell edge remains essentially unaltered throughout the annealing regime, but the line broadening is reduced after heating to 600°C and becomes comparable to instrumental broadening after heating to 800°C. No phase other than titanomagnetite was detected.



Fig. 2. Curie point temperature of pulverized $Fe_{2.4}Ti_{0.6}O_4$ after annealing for 17 h at a number of isotherms between 100°C and 800°C.

The presence of the nanocrystalline structure in the material annealed at 100°C, 200°C and 600°C was confirmed by observation of thin sections (60–90 nm thickness, sliced using a diamond knife) in the transmission electron microscope. The 100°C and 200°C material showed internal speckles of about 20 nm in dimension, and the selected area diffraction pattern consists of rings, indicating that many crystallites within the electron beam contribute to the pattern. In the 600°C material, the internal crystallites are now of the order of 50 nm in length and the diffraction pattern consists of spotty rings, suggesting fewer crystals lie within the beam. The 800°C material shows diffraction patterns attributable to single crystallites and no internal microstructure.

3.2. *The evolution of composition and microstructure during annealing*

The magnetic changes which result from annealing to 200°C can be explained by supposing that the cation-deficiency induced at room temperature by ball-milling is less stable than cation-deficiency produced during maghemitization in air at elevated temperature. The present observations are consistent with the inversion of the cation-deficient ball-milled material on heating to 200°C in vacuum. Cation-deficient material prepared by air-oxidation at elevated temperature is stable on the laboratory time scale up to temperatures of the order of 350°C. Complete inversion of the ball-milled material with composition parameters x = 0.6 and z = 0.15 can in principle produce an intergrowth consisting of 76% of iron-rich more magnetic stoichiometric titanomagnetite with composition x = 0.32, together with 24% of titanium-rich non-magnetic phase, ilmenite, FeTiO₃ (O'Reilly, 1983). This process would produce an increase in saturation magnetization of about 50% and a Curie point temperature of about 340°C. The observed rise in saturation magnetization of about 40% after the 200°C vacuum annealing and the rise in Curie point to 300°C are of the right order.

The crystallite size of the magnetic constituent of the inversion product can be worked out from the value of K_u/M_s inferred from parameters of the hysteresis loop, the coercive force and the observed rise of saturation magnetization, taking also a further

magnetic dilution by the 24% non-magnetic component of the inversion product. The result is a size of 11 nm compared with the 13 nm of the preannealed pulverized material, a plausible result if the segregation of the inversion products produces of a core of the major phase (titanomagnetite) surrounded by a mantle of the minor phase (ilmenite). This seems reasonable in view of the smallness of the particles. which could hardly contain (say) a trellis pattern lamellar intergrowth of phases as is found when large crystals of titanomagnetite undergo deuteric oxidation to produce a mixture of phases similar to an inversion product (Tucker and O'Reilly, 1980). The magnetic susceptibility after the 200°C annealing, together with the inferred saturation magnetization of the inversion product, suggests that the fraction which is thermally activated on the time scale of the measurement has risen to 15% compared to 6% before annealing. Again this is consistent with a reduction in crystallite size due to inversion.

The approximate constancy of the inferred value of $K_{\rm u}/M_{\rm s}$ throughout the range of annealing temperatures up to 400°C suggests that K_{u} must rise if $M_{\rm s}$ is also rising due to the iron enrichment of the spinel phase which results from inversion. The Fe²⁺ concentration of the spinel phase falls during inversion and, broadly speaking, the magnetostriction constant, λ , would be expected to fall (the question is slightly complicated by the fact that the room temperature observations are not made at a constant "magnetic temperature", T/T_c because T_c rises as Fe²⁺ concentration falls). If K_{μ} must rise while λ is falling, then the residual strain must rise on annealing. This apparent paradox can be resolved if it is remembered that inversion results in the addition of the third phase, ilmenite, producing an even more complex microstructural assemblage. This is reminiscent of the magnetic hardening of alloys by annealing-induced exsolution.

Changes in properties on annealing further up to 400°C are slight. At 600°C, both the transmission electron microscope and X-ray line broadening indicate crystallite growth. The parameters of the hysteresis loops lead to estimates of K_u/M_s (about 0.4 T) and K_1/M_s which are comparable, and it is therefore difficult to interpret the coercive force and susceptibility in terms of crystallite size. This is because the way the two sources of anisotropy com-

bine is unknown, and because the fall in H_c makes crystallite–crystallite interaction fields more effective. However, the reduction in K_u seems consistent with a reduction in strain as the crystallite regions grow at the expense of the amorphous zones.

After the annealing at 800°C, the particles may still be monodomain although the $M_{\rm ex}/M_{\rm a}$ value of 0.44 is the lowest of the suite. If the nanocrystalline microstructure has been largely removed, the residual strain should also be small and cubic magnetocrystalline anisotropy may dominate. Monodomain particles with only cubic anisotropy should have $M_{\rm m}/M_{\rm s} > 0.8$, higher than that observed here for the 800°C annealed particles. Also the coercive force of 15 kA m^{-1} if taken to be unaffected by thermal fluctuations corresponds to a K_1 of 4 kJ m⁻³ which is twice as big as that determined directly from single crystal torque magnetometry (Svono, 1965; Sahu and Moskowitz, 1995). Thus, it seems likely that strain still plays a role in controlling the magnetization process parameters. The susceptibility of the 800°C annealed particles, although dramatically increased compared to the rest of the suite, is only about one-third of the model non-thermally fluctuated value for an array of particles with cubic anisotropy constant 2 kJ m⁻³. A dominant strain anisotropy would produce a lowered susceptibility.

The Curie point temperature of the 800°C annealed material, at 190°C, is the same as the starting pre-milled titanomagnetite and therefore indicates a return to the starting composition, but the saturation magnetization is about 15% lower than the starting value indicating the presence of a non-magnetic diluent. At 800°C, it appears that ionic mobility is high enough that the mixture is self-equilibrating. The major phase near to the bulk composition of the mixture (x = 0.6, z = 0.15) with the same Fe/Ti ratio as the bulk composition is $Fe_{2.4}Ti_{0.6}O_4$ (x = 0.6, z = 0). The remainder of the mixture must then correspond to the point (x = 0.6, z = 1.0) on the right hand edge of the FeO-TiO₂-Fe₂O₃ ternary diagram (Fig. 8), and will consist of a mixture of Fe_2O_3 and TiO_2 or Fe_2TiO_5 . The molecular proportions will be 85% magnetic titanomagnetite and 15% of non-magnetic phases. The presence of the secondary phases could plausibly account for the persistence of strain anisotropy in the single crystal particles of the 800°C annealed material.

4. Maghemitization

4.1. The oxidation of the pulverized material

One-gram batches of ball-milled titanomagnetite were oxidized in air in a thermogravimetric balance at eight isotherms between 120°C and 300°C. After initial heating for 2 h at 100°C to drive off volatiles. the sample was held for between 12 and 20 h at the isotherm until the rate of weight increase had become undetectable, and the sample was allowed to cool slowly reaching room temperature in the order of an hour. The degree of oxidation, z, was determined from the weight increase data, the highest oxidation state achieved, z = 0.98 + 0.02, being essentially unity. The X-ray and magnetic properties of the nine-member suite (including the initial milled material with z = 0.15) were determined at room temperature. The data are in broad agreement with previous maghemitization studies (for example, Özdemir and O'Reilly, 1981) and will be only briefly reported here. The X-ray cell edge of the present suite falls from about 8.48 to 8.34 Å. Small quantities of haematite were detectable in the Hagg-Guinier diffractograms of the more highly oxidized material. An important result is the observation of an unchanged line-broadening throughout, showing that the nanocrystalline structure survives maghemitization. The main thrust of the present discussion will be the interpretation of magnetization process parameters, specifically the susceptibility and coercive force, with reference to this microstructure. The saturation magnetization falls with increasing z to about 10 A m² kg⁻¹ and the Curie point temperature rises to about 460°C.

4.2. The effect of the nanocrystalline structure

Determination of the constant in the law of approach to saturation and the work done to saturate yield values of K_1/M_s and K_n/M_s . K_1/M_s remains constant at about 0.2 T as maghemitization proceeds. $K_{\rm u}/M_{\rm s}$ falls from about 0.5 T at low z to about 0.4 T at z = 0.78, z = 0.98 having a $K_{\rm u}/M_{\rm s}$ value of about 0.3 T. The observed $M_{\rm c}$ is reduced by the dilution due to the intercrystalline magnetically amorphous material. The constancy of the X-ray line broadening, which indicates that the nanocrystalline structure is unaffected by maghemitization, suggests that the degree of dilution is constant throughout. and can be estimated from the initial ball-milled pre-oxidized material taken to have a crystallite $\sigma_{\rm s}$ of 30 A m² kg⁻¹ typical of Fe_{2.4}Ti_{0.6}O₄. M_s values may then be inferred for the whole suite and $K_{\rm m}$ values deduced (Table 1). H_c^* , the coercive force in the absence of thermal fluctuations, follows directly from the $K_{\rm u}/M_{\rm s}$ values, and may be taken with the observed coercive force (Fig. 3) to yield values of v^*/v , the ratio of the unblocking volume to the actual volume, using the expression:

$$\frac{v^*}{v} = \left(1 - \frac{H_{\rm c}}{H_{\rm c}^*}\right)^2.$$

Values of H_c^* and v^*/v are listed in Table 1. v^* can be calculated from $v^* = \ln(f_0 t^*) kT/K_u$, taking $f_0 = 10^9 \text{ s}^{-1}$ and t^* , the measurement time in the vibrating sample magnetometer, to be 1 s. The particle volume v can then be determined. Particle size, $(v)^{1/3}$, is listed in Table 1. The small systematic, and possibly significant, increase in v as maghemitiza-

Table 1

Inferences from the parameters of the hysteresis loops of maghemitized ball milled titanomagnetite. % SP is the postulated (but probably overestimated for the higher z values, see text) superparamagnetic fraction at an observation time of 10^{-3} s

z	K_u kJ m ⁻³	H_c^* kA m ⁻¹	$\frac{v^*/v}{(t^* = 1 \text{ s})}$	$(v)^{1/3}$ nm	%SP ($t^* = 10^{-3}$ s)	$(v^*)^{1/3}$ (t* = 10 ⁻³ s) nm
0.15	74	390	0.33	15	3	9
0.4	67	370	0.33	16	3	10
0.64	48	370	0.40	17	6	11
0.78	31	330	0.52	18	15	13
0.98	18	230	0.85	18	40	15



Fig. 3. The variation of coercive force and initial susceptibility of maghemitized $Fe_{2,4}Ti_{0,6}O_4$ as a function of degree of oxidation *z*.

tion proceeds is consistent with the fact that a particle of $Fe_{2.4}TiO_6$ increases in volume by about 15% when maghemitization takes place by addition of oxygen.

It can be seen that coercive force varies with degree of maghemitization due to both the effect of compositional change on the material properties K_u (via λ) and M_s , and hence H_c^* , and also the increasing effect of thermal fluctuations via the factor $\{1 - (v^*/v)^{1/2}\}$. Housden and O'Reilly (1990) modelled the $H_c - z$ variation of ball-milled titanomagnetite by a semi-empirical model based only on the effect of thermal fluctuations. The result was a faster fall of H_c with z than the analogous $H_c^* - z$ variation of the present model. This may be because the Fe²⁺-based model of Housden and O'Reilly (1990) postulated a faster fall of λ with z than is indeed the case, the contribution of Fe³⁺ to λ being neglected.

A non-thermally agitated susceptibility can be calculated as before from K_u and M_s . This falls steadily from about 20×10^{-6} m³ kg⁻¹ to about 14×10^{-6} m³ kg⁻¹ as *z* increases. The observed values (Fig. 3) are larger than those calculated values, and the difference may be ascribed to a fraction of the particles (Table 1) being affected by thermal fluctuations on the measurement time of 10^{-3} s. The corresponding particle sizes for unblocking at 10^{-3} s are listed in Table 1. The superparamagnetic fractions listed in Table 1 will be over-estimates because the combined cubic and uniaxial anisotropies produce terms like ($K_u \pm K_1$) on the denominator of the model susceptibility expression. When the anisotropies combine (the + sign), the susceptibility is reduced somewhat, when they compete (the -

sign), the susceptibility is dramatically enhanced. Thus, the coexisting anisotropies do not average out to more or less reproduce the effect of the dominant uniaxial symmetry but should invariably increase the susceptibility. The model coercive force expression contains $(K_u \pm K_1)$ on the numerator, averaging takes place, and the observed coercive force represents the dominant anisotropy alone.

5. Inversion

5.1. The observation of inversion

Inversion was induced in the maghemitized ballmilled $Fe_{2.4}Ti_{0.6}O_4$ in three ways: by heating vacuum-encapsulated samples in a thermomagnetic balance at heating and cooling rates of 20°C-30°C min⁻¹; by heating in an argon or nitrogen atmosphere in a differential scanning calorimeter (DSC) at 10°C min⁻¹ from 50°C to 700°C; and by heating vacuum-encapsulated samples for 5 min in a preheated furnace at 500°C and 700°C.

An example of a thermomagnetic curve is shown in Fig. 4. The rise in the heating curve shows the onset of inversion on the laboratory time scale. The use of magnetization as an analogue of concentration of inversion product, whilst adequate for isothermal experiments (e.g., Adnan and O'Reilly, 1999), is complicated when temperature is changing. The position of the peak will be dependent on heating rate, and if the rate is fast enough, may disappear into the magnetically invisible region above the Curie point of the inversion product (Housden et al., 1988).



Fig. 4. Variation of high field magnetization with temperature of vacuum-encapsulated titanomagnemite of composition x = 0.6, z = 0.5, heated and cooled at about 20°C per minute.

When a dynamic temperature-time regime is employed, a property related in a simpler manner to the phase concentration, such as the heat flow determined by differential thermal analysis, gives a more direct measure of the progress of inversion, and is not confined to the temperature zone below Curie points.

Two examples of the variation of heat flow with temperature determined in the DSC are shown in Fig. 5. Peaks in the curves indicate two exothermic reactions between about 150°C and 700°C. The position of the peak of the lower temperature reaction rises with z value from about 330°C to 460°C. The heat flow-temperature curve can be fitted to the rate equation:

$$\frac{\mathrm{d}\,\alpha}{\mathrm{d}\,t} = Z(1-\alpha)^n \exp\left(\frac{-E_{\mathrm{a}}}{kT}\right)$$

where α is the fraction of reaction, Z is the frequency factor, n is the thermodynamic order of the reaction, and E_a is the activation energy of the process, to yield values of Z, E_a and n. Because of



Fig. 5. Differential thermal analysis of maghemitized $Fe_{2.4}Ti_{0.6}O_4$ heated at a constant rate in inert atmosphere: (a) z = 0.28, (b) z = 0.98. The dash-dot curve is a base-line established by re-running the reacted sample.



Fig. 6. The Curie point temperature and cell edge of maghemitized $\text{Fe}_{2.4}\text{Ti}_{0.6}\text{O}_4$ as a function of *z* value after vacuum annealing for 5 min at 500°C and 700°C.

the uncertainty in the position of the base line, the fitted parameters are too scattered to indicate any systematic variation with z. The values lie in the ranges $Z \sim 10-10^8 \text{ s}^{-1}$, $E_a \sim 0.5-1.5 \text{ eV}$ and $n \sim 0.6-1.0$. The position of the upper peak is fairly constant at about 650°C and produces parameters $Z \sim 10^{14}-10^{21} \text{ s}^{-1}$, $E_a \sim 3-6 \text{ eV}$ and $n \sim 0.75-1.2$.

To elucidate the two exothermic reactions, batches of maghemitized material were annealed at about 500°C, at which the first exothermic reaction will have gone to completion, and at 700°C to induce the second reaction. The composition and microstructure of the annealed materials were studied using X-ray analysis and magnetic measurements. The composition and concentration of the spinel phase is the major interest because of its strong magnetism compared to the other phases. Within the fixed bulk composition of the closed system the compositions and concentrations of all of the phases are mutually interdependent. The composition of the spinel phase produced by annealing is indicated by the variation of Curie point and cell edge with z value (Fig. 6) and the concentration of the spinel phase reflected in the saturation magnetization (Fig. 7) provided no other phases, such as haemo-ilmenite, are significantly magnetic. The coexisting compositions determined by the X-ray analysis in which d-spacing values are used to estimate compositions within the solid solutions are shown in the ternary diagrams of Fig. 8. The phases have zero compositional moment about the bulk (x, z) composition. Phases remote in



Fig. 7. The saturation magnetization of maghemitized $Fe_{2,4}Ti_{0,6}O_4$ as a function of *z* value after vacuum annealing for 5 min at 500°C and 700°C.

compositional space (e.g., TiO_2) may be present in small concentration and difficult to detect. Some indication of the microstructure of the magnetic



Fig. 8. Coexisting phases in maghemitized $Fe_{2.4}Ti_{0.6}O_4$ annealed at 500°C and 700°C. The bulk compositions are shown by solid circles and the constituent phases by open circles.



Fig. 9. The initial susceptibility of maghemitized $\text{Fe}_{2.4}\text{Ti}_{0.6}\text{O}_4$ as a function of *z* value after vacuum annealing for 5 min at 500°C and 700°C.

product of inversion is given by the susceptibility and coercive force of the inverted material (Figs. 9 and 10). The ratio of $M_{\rm rs}/M_{\rm s}$ for the inversion product falls slightly with oxidation degree but lies in the range 0.4–0.5 suggesting the monodomain state.

5.2. The composition and concentration of phases in the inversion product

The composition of the components of the inverted phases after heating to 500°C are in qualitative agreement with the three-zone model of O'Reilly (1983), and the compositions remain the same



Fig. 10. The coercive force of maghemitized $Fe_{2.4}Ti_{0.6}O_4$ as a function of *z* value after vacuum annealing for 5 min at 500°C and 700°C.

after the 700°C treatment: the relative concentrations change, however. Ascent beyond the lower peak of the differential thermal analysis may correspond to the completion of inversion in the sense that the non-stoichiometric spinel phase has been completely removed. The higher temperature peak indicates a post-inversion re-equilibration of phases in which the spinel concentration is reduced and rhombohedral phase concentration increased. This is evident from both saturation magnetization data (Fig. 7) and the spinel (311) and rhombohedral (104) X-ray reflections for samples heated at the two temperatures. Because the pre-transformation crystal has the spinel structure, the immediate post-transformation assemblage is disproportionately rich in spinel material. The z = 0.64 composition, for example, lies very close to the haematite-ilmenite solid solution which. together with the titanomagnetites, the pseudobrookite solid solution and TiO₂ represent the only compositions which have ultimate stability in the FeO-Fe₂O₃-TiO₂ ternary system (if we were to consider also sub-solidus exsolution, we would be left with only the end members). Thus, the simplest inversion product of z = 0.64 would consist essentially of haemoilmenite with little or nothing of other phases, but this is achieved only at a high enough temperature where major structural reorganization is possible. This of course is the basis of synthesis of single phase, stable compounds by solid state reaction of constituent compounds, in the present case oxides. Thus, after inversion of cation-deficient (FeTiO) spinel, the nearest stoichiometric titanomagnetite (which is not the nearest stable composition) is present in as high concentration possible together with other remote phases such as TiO₂, but the nearby stable phase with different crystal structure is formed only in low concentrations. At a later stage, accelerated on the laboratory time scale by going to higher temperature, the spinel and TiO₂ decrease in concentration, the latter becoming undetectable by X-rays but remaining a required presence for compositional balance. The nearest stable composition increases in concentration. Inversion of titanomaghemite should therefore be thought of as the destruction of the non-stoichiometric phase rather than the creation of a specific product. This distinction is not necessary in the case of the inversion of γFe_2O_3 or $Fe_3O_4 - \gamma Fe_2O_3$ solid solution members.

5.3. The microstructure of the inversion product

The magnetization process parameters are governed by intrinsic composition-dependent parameters and microstructures; the susceptibility is also concentration dependent, the coercive force not so. After z = 0.5 the coercive force after annealing at 700°C remains more or less constant with bulk composition z. If the strain is constant, this implies that the crystallite size of the near Fe_2O_4 in the inversion product is more or less constant even though the Fe₃O₄ concentration is falling to a low value, and indeed is undetectable by X-ray analysis in the z =0.98 composition. The X-ray line broadening decreases somewhat after annealing at 700°C, and the increase in coercive force from the 500°C heating could be plausibly ascribed to crystal growth. By the same token the susceptibility of the z = 0.64 composition after the 700°C is only 35% of the 500°C value (Fig. 9a), whereas saturation magnetization has fallen to 45% (Figure). The extra fall in susceptibility could be accounted for by a smaller superparamagnetic fraction in the 700°C assemblage.

In the inversion product of the compositions with z < 0.5, several factors contribute to the variation in coercive force with composition. As z increases, the composition of the near stoichiometric spinel inversion product is more Fe³⁺ rich and has a lower magnetostriction constant, λ . M_s is also rising. If stress remains about the same in the intergrowth, H_c^* will fall. Because λ falls as z rises, v^* will increase. The fall in H_c^* and rise in v^* both contribute to the fall in H_c . Similarly, both contribute to the rise in susceptibility.

6. Conclusions

Ball-milling titanomagnetite brings about two changes apart from the reduction in particle size: the formation of nanocrystals within the particles, and the development of a small degree of non-stoichiometry. The non-stoichiometry is unstable and is removed by the process of inversion induced by heating in vacuum at 200°C. This does not reverse the oxidation that produces non-stoichiometry, the bulk composition remaining unchanged. The nanocrystalline structure persists after annealing at higher

temperatures, and the magnetization process is influenced by thermal fluctuations, until it is removed by heating to 800°C. However, the effects of ball-milling are not entirely reversed as the legacy of the milling-induced oxidation is the presence of a fraction of non-magnetic phases coexisting with titanomagnetite close to the original composition. The non-magnetic phases are not detected directly, but reduce the saturation magnetization, and the coexisting crystallites are the source of the strain anisotropy inferred from the magnetization process parameters. Despite the presence of the minor phase or phases. the $0.1-1 \mu m$ single crystals produced by annealing provide a much improved analogue for the titanomagnetites of submarine basalts, having a coercive force similar to the average of pillow basalts (Smith. 1987). Ball-milled synthetic titanomagnetite. annealed at high temperature, could be fruitfully used in laboratory experiments designed to elucidate the magnetism and mineralogy of the submarine crust. A first step would be to study the intensity and stability of thermoremanent magnetization (TRM) in annealed, pulverized material. This could be compared to the natural remanent of fresh unaltered submarine basalts (Zhou et al., 1997) which are responsible for the intense geomagnetic anomaly which may be observed at spreading centres. As the crystallite volume of the annealed material is 4 orders of magnitude bigger than pulverized nanocrystalline titanomagnetite, which itself has a specific TRM of about 25 (Özdemir and O'Reilly, 1982), the specific TRM of the annealed material may be exceptionally large. The data would allow the test of the theory for TRM in large monodomain crystals. It may be noted in passing that the physical interpretation of earlier work on pulverized titanomagnetite (e.g., Özdemir and O'Reilly, 1982), which did not invoke nanocrystalline structures, does not require drastic revision. This is because the crystallite size adopted in these earlier studies, on the basis of misinterpreted electron micrographs, was 20-60 nm, similar to the nanocrystals, but envisioned as discrete, probably flocculated particles.

The nanocrystalline structure survives the process of maghemitization of ball-milled titanomagnetite, and the magnetization process parameters can be plausibly interpreted with thermal fluctuations playing a progressively more important role as maghemitization proceeds and the blocking volume ascends. The nanocrystalline structure persists also through the process of inversion of maghemitized ball-milled titanomagnetite.

The present study and previous maghemitization studies have used ball-milled material as the starting point and, indeed, it may be presence of the amorphous internanocrystal regions which promotes rapid diffusion of cations and allows the production of highly cation deficient single phase spinels on the laboratory time scale. The availability of such material is essential to the determination of the intrinsic properties of titanomaghemite and the physics of the magnetization process in fine particles of titanomaghemite. It also provides the opportunity to study under what circumstances a pre-existing remanence may be preserved or lost in the subtle transformation from titanomagnetite to titanomagnemitite in the monodomain state (Özdemir and Dunlop, 1985). Whether the annealed pulverized material would maghemitize readily on the laboratory time scale, and whether a single phase product would result should be tested by experiment. The larger maghemitized particles in ocean basalts are heterogeneously maghemitized, containing a less oxidized core within a more oxidized shell (Pettersen and Vali, 1987). In particles larger than about 5 μ m, the outer shell develops cracks to accommodate the strain between the two spinel phases with different interatomic spacing. The present particles are probably not large enough to develop shrinkage cracks but may produce the heterogeneous maghemitization found in nature.

The product of the completion of inversion, inversion meaning the removal of non-stoichiometry in the pre-transformation spinel, is not unique in the case of titanomaghemite, which produces more than two phases in the inversion product. A common feature is observed in all three of the transformations studied in this present work: the low temperature annealing of ball-milled titanomagnetite, the maghemitization of the of the milled material, and the inversion of the maghemitized material. In each case, the pre-transformation spinel structure influences the products in the form of a spinel phase which is not ultimately stable in composition or concentration. The metastability of the cation-deficient product of maghemitization is clear. In the case of low temperature annealing of ball-milled material

and the inversion of maghemitized material, posttransformation re-equilibration, observed at higher temperature on the laboratory time scale, changes the phase assemblage. The spinel phase is over-represented immediately post-inversion, and reduces in favour of a stable phase closer in compositional space to the bulk composition coordinates of the mixture.

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