

THE FORMATION OF NICKEL FERRITE FROM HEMATITE, MAGNETITE AND SPINEL IRONSAND

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ABSTRACT

The reaction of titanium-containing magnetite ironsand with NiO in both air and inert atmospheres up to 1200 °C was compared with the analogous reactions of hematite (Fe_2O_3) and pure synthetic magnetite (Fe_3O_4). All three starting materials form NiFe_2O_4 in air, the reaction in magnetite proceeding via an oxidation step at 220 °C. Under inert conditions, the products have larger lattice parameters, indicating the presence of Fe^{2+} ; in hematite this is formed at about 1000 °C with evolution of oxygen. Mössbauer spectroscopy suggests that the Fe^{2+} in the ferrite spinels is located preferentially in the octahedral sites. Lattice parameter calculations suggest that the present NiFe_2O_4 formed in air is not fully inverse, as is usually assumed, but contains varying amounts of tetrahedral Ni^{2+} . The calculations confirm the location of Fe^{2+} in predominantly octahedral sites which, in the case of ironsand-derived spinels, also contain Ti^{4+} . The magnetic saturation moment of the ironsand-derived ferrites formed both in air and nitrogen is smaller than that of products derived from the pure iron oxides.

INTRODUCTION

For many purposes, the magnetic properties of ferrite ceramics have to be reproducible to closely specified tolerances, necessitating their preparation from high-purity reactants, which are often produced by specialized processes which give reactive spherical particles of specified grain size. However, for other applications, such as magnetic filtration materials, the specifications are less stringent, suggesting the possible application of solid-state synthesis using less-pure natural starting materials. One such material is a magnetite-like spinel ironsand found on the West coast of the North Island of New Zealand.

Since the preparation of ferrites by solid-state ceramic synthesis is normally carried out in air, with Fe_2O_3 as the starting material, little is known

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of the reaction or the properties of the products obtained using magnetite, Fe_3O_4 , or related spinel ironsands. Such work as has been published on binary oxide mixtures suggests that, in air, magnetite is first oxidized to hematite, Fe_2O_3 , which then reacts with the second oxide to form a ferrite [1]. If oxygen is excluded, ferrites containing both Fe^{2+} and Fe^{3+} may be formed [1], provided no other species is present which can bring about internal oxidation of the Fe^{2+} to Fe^{3+} . Such redox phenomena have been reported in the reaction of magnetite with CaO [2] and with CaCO_3 [3].

A preliminary study of the formation of NiFe_2O_4 from both magnetite and New Zealand spinel ironsand [4] suggests that, in air, ferrite formation is preceded by oxidation to hematite, but in nitrogen atmospheres, oxidation is suppressed, the product containing a significant proportion of Fe^{2+} in the octahedral sites. This paper reports a more complete study of the formation of nickel ferrite, NiFe_2O_4 , both from chemically pure Fe_3O_4 and from New Zealand spinel ironsands, with particular reference to the cation distributions and magnetic properties of the reaction products formed under both oxidizing and non-oxidizing conditions. For comparison, the reaction with chemically pure hematite was also studied.

EXPERIMENTAL

The ironsand is titaniferous magnetite from Waipipi, New Zealand. After magnetic separation from the non-ferrous beach sand and grinding for 60 s in a vibrating ring mill, its composition is as shown in Table 1.

The alkali, alumina and silica contents arise from alkali aluminosilicate impurities, shown by X-ray diffraction to be of the mellilite group. The other significant impurity, Ti, is incorporated in the spinel, which has a cell parameter of 8.410 Å (cf. synthetic magnetite, 8.396 Å, JCPDS Card No. 19-629).

TABLE 1

Chemical analysis of magnetically concentrated ironsand from Waipipi, New Zealand, by X-ray fluorescence spectroscopy

Component	%	Component	%
Fe_2O_3	75.66	CaO	2.01
TiO_2	7.40	P_2O_5	0.58
MgO	4.57	MnO	0.51
Al_2O_3	4.53	K_2O	< 0.01
SiO_2	4.04	Loss on ignition	-2.40
Na_2O	3.02	Sum	99.92

Analyst: J.L. Hunt.

The comparative experiments were carried out using reagent-grade Fe_2O_3 (Hopkin and Williams) and precipitated Fe_3O_4 (Alfa Chemicals, lot J21G). The NiO was prepared by thermal decomposition of analytical-grade $\text{Ni}(\text{NO}_3)_2$ in a nickel crucible. Mixtures of the reactant oxides (2 mol magnetite to 3 mol NiO, and equimolar mixtures of Fe_2O_3 and NiO) were blended and thermally reacted both in air and flowing instrument-grade nitrogen as described elsewhere [4]. Experiments were made with both powder samples and 10 mm diameter pellets. After reaction, the samples were examined by X-ray diffraction and Mössbauer spectroscopy as described elsewhere [4]. Evolved gas analysis (EGA) was carried out on the reactants and their mixtures both in non-oxidizing (Ar) and oxidizing (Ar + 1% O_2) atmospheres at a heating rate of $10^\circ\text{C min}^{-1}$, using a quadrupole mass spectrometer (Extranuclear Corp.). Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out at a heating rate of $10^\circ\text{C min}^{-1}$ under both dynamic air and oxygen-free nitrogen atmospheres (120 ml min^{-1}) using a Stanton TG770 thermobalance and a Stone model 202 thermal analyser, respectively. Measurements of the magnetic saturation moment were made on the pellet samples by a method described elsewhere [5] using a 1.5 kG permanent magnet and a Hall effect gaussmeter (model 505, RFL Industries, New Jersey). The calibration material was pure nickel metal, for which a room-temperature saturation moment of $55.3\text{ Am}^2\text{ kg}^{-1}$ was assumed.

RESULTS AND DISCUSSION

Thermal analysis of the reactants and reaction mixtures

The DTA curves of most of the samples were rather featureless, but more useful information was gained from the EGA curves, augmented by weight-change measurements. Figure 1 shows EGA plots of changes in the oxygen concentration in the reaction atmospheres of the various materials during heating. The concentrations of the other gas species monitored in these experiments were largely unchanged during heating.

Figure 1 shows that, under oxidizing conditions, hematite alone neither evolves nor absorbs oxygen (Fig. 1C) whereas under inert (non-oxidizing) conditions, oxygen begins to evolve strongly at ca. 1100°C , suggesting the progressive formation of magnetite (Fig. 1A). When heated by itself, NiO shows no absorption or evolution of oxygen in either oxidizing or inert conditions, and when it is mixed with hematite in the correct proportions to form NiFe_2O_4 and heated in oxidizing conditions, the reaction proceeds without gain or loss of oxygen (Fig. 1D). However, when the same mixture is heated under inert conditions, oxygen loss occurs at about 1000°C (Fig. 1B), again indicating the formation of an Fe^{2+} -containing spinel within the

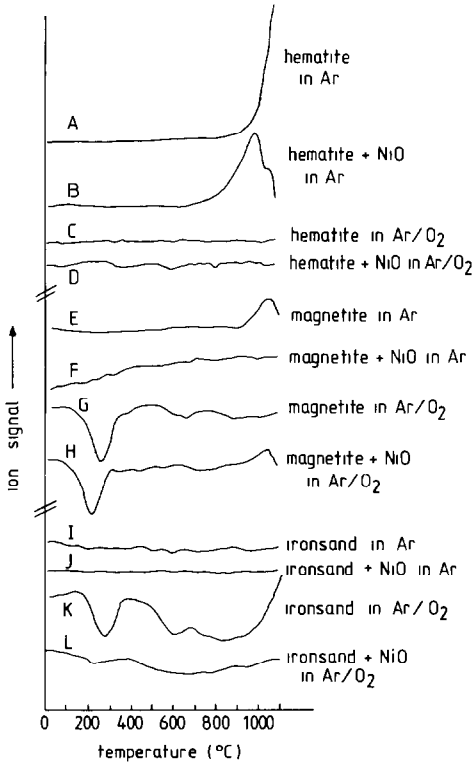


Fig. 1. Oxygen concentration changes in the reaction atmosphere above various iron oxides and their mixtures with nickel oxide, as a function of heating temperature. Heating rate $10^{\circ}\text{C min}^{-1}$.

temperature range of the present heating. Thermobalance experiments indicate an increased degree of hematite reduction when NiO is present. X-ray diffraction indicates the formation of an increasing proportion of spinel throughout the temperature range $800\text{--}1200^{\circ}\text{C}$ (Fig. 2); by 1100°C the formation of spinel from hematite is complete after firing for 2 h in nitrogen. The lattice parameter of the spinel formed in nitrogen progressively approaches that reported for a ferroan trevorite (NiFe_2O_4 containing 13% of FeO), in which $a = 8.367 \text{ \AA}$ (JCPDS Card No. 23-1119). This result is consistent with the EGA finding that an Fe^{2+} -containing phase is formed under inert conditions. The lattice parameter of the spinel formed from hematite under oxidizing conditions progressively approaches that of pure trevorite (NiFe_2O_4) during firing (Fig. 3), but does not achieve the published value for this phase ($a = 8.339 \text{ \AA}$, JCPDS Card No. 10-325) under the heating conditions of this study.

The EGA results indicate that, when heated alone under oxidizing conditions, the present pure magnetite sample takes up oxygen at ca. 300°C , being partially oxidized to hematite (Fig. 1G). Very small amounts of CO_2

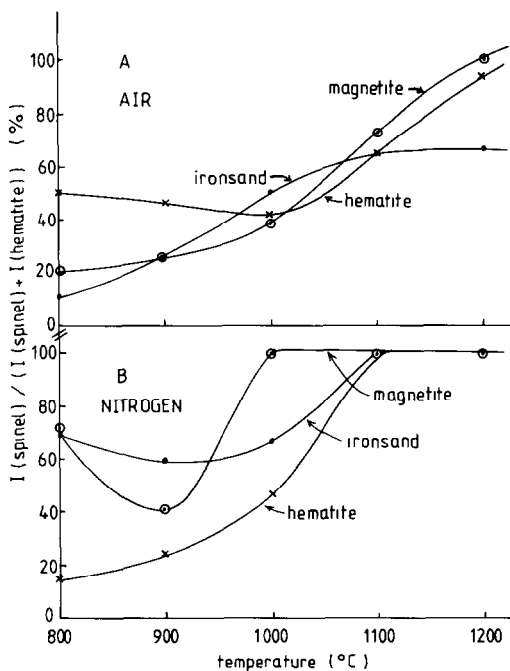


Fig. 2. Degree of trevorite formation from various iron oxides under air and nitrogen as a function of heating temperature. Heating time at each temperature 2 h.

were also evolved from this material at ca. 250, 480 and 650 °C, probably resulting from the thermal decomposition of organic precursors. Under inert conditions, a small amount of oxygen is evolved at 1080 °C (Fig. 1E), resulting from the trace of hematite detectable in the X-ray pattern for the unheated material. CO₂ evolution from trace organic contaminants also occurred in this experiment.

When mixed with NiO in the ratio 2 mol magnetite to 3 mol NiO and heated under oxidizing conditions, oxygen absorption occurs at ca. 220 °C (Fig. 1H) indicating oxidation to hematite, as was found in magnetite alone. At ca. 990 °C, some of this oxygen is evolved, suggesting the formation of some Fe²⁺ in the product ferrite (although this is not reflected in its lattice parameter, which tends towards that of trevorite; see Fig. 3). This gas evolution behaviour is unlike that of hematite reacted with NiO under oxidizing conditions; the hematite formed by in situ oxidation of magnetite may be more reactive because of its small particle size. The theoretical composition of the product formed from magnetite in the presence of oxygen is Fe_{0.66}²⁺Fe_{1.33}³⁺NiO₄, but, because the reaction is preceded by the oxidation of the magnetite and accompanied by the formation of some Fe²⁺, the actual composition of the product may differ considerably from the theoretical.

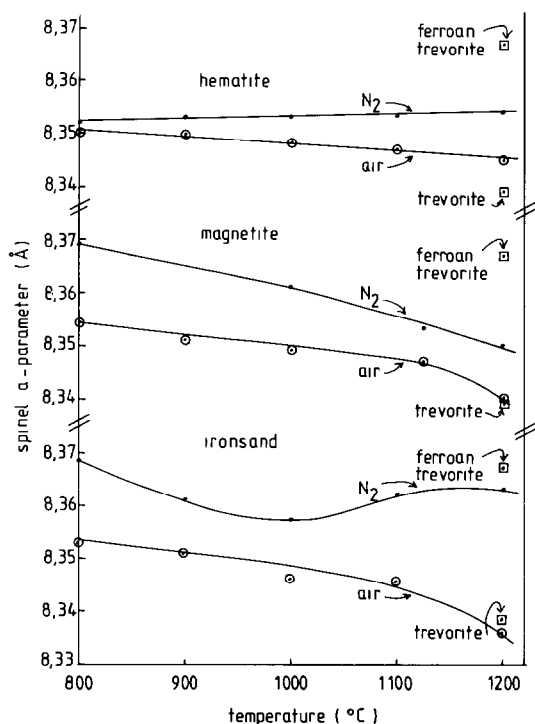


Fig. 3. Effect of reaction temperature on the a parameter of the spinel formed from various iron oxides with nickel oxide. Heating time at each temperature 2 h.

No gross change in the oxygen level is observed when this mixture is heated under inert conditions (Fig. 1F), suggesting that the oxygen stoichiometry of the product formed under these conditions is similar to that of the starting mixture. On this basis, the product should be $\text{Fe}_{0.73}^{2+}\text{Fe}_{1.45}^{3+}\text{Ni}_{1.09}\text{O}_4$; its cell parameter indicates the presence of some Fe^{2+} even at 1200°C (Fig. 3).

When heated alone under oxidizing conditions (Fig. 1K), Waipipi ironsand behaves similarly to synthetic magnetite, absorbing oxygen by oxidation at 300°C and again at ca. 600°C (the latter event in synthetic magnetite is very weak by comparison with the ironsand). The two stages of oxidation in ironsand are accompanied by weak, diffuse endotherms in the DTA curve which are absent from the DTA curve run in nitrogen. Oxygen evolution (reduction) occurs at ca. 1100°C in ironsand heated under oxidizing conditions (Fig. 1K); this reaction is not accompanied by any event in the corresponding DTA curve, neither was any comparable oxygen loss observed from synthetic magnetite under the same conditions. These differences in behaviour between the two magnetites probably arise from the presence of titanium in the ironsand, but a contributing factor may also be the larger particle size of the ironsand.

Heating ironsand alone under inert conditions produces no marked

oxygen change (Fig. 1L). A small amount of CO_2 evolution observed at ca. 900°C under both oxidizing and inert conditions probably arises from the decomposition of an impurity carbonate mineral.

Little change is found in the oxygen content of the atmosphere surrounding ironsand–NiO mixtures heated under oxidizing and inert conditions, although there is slight evidence of low-temperature oxidation in the former (Fig. 1L). The comparatively smaller tendency for ironsand to form trevorite (Fig. 2) is most probably due to its larger particle size. The lattice parameter of the ferrite formed from ironsand under oxidizing conditions at 1200°C is slightly smaller than that of pure trevorite (Fig. 3), whereas the parameter of the phase formed under inert conditions suggests a higher Fe^{2+} content than in the spinels formed from the pure iron oxides (Fig. 3).

Magnetic properties of the ferrite products

The bulk magnetic properties of the ferrite phases formed from the various reactants under both oxidizing and reducing conditions are shown as a function of the reaction temperature in Fig. 4.

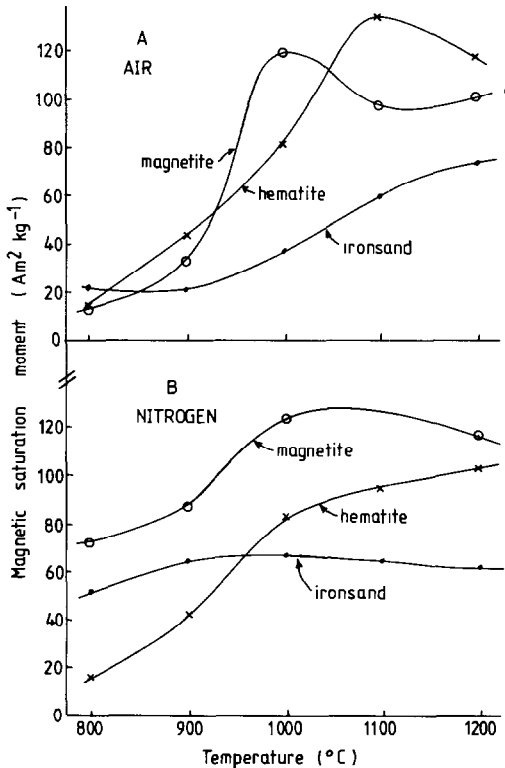


Fig. 4. Effect of reaction temperature on the magnetic saturation moment of pelletized reaction products from various iron oxides and nickel oxide. Heating time at each temperature 2 h.

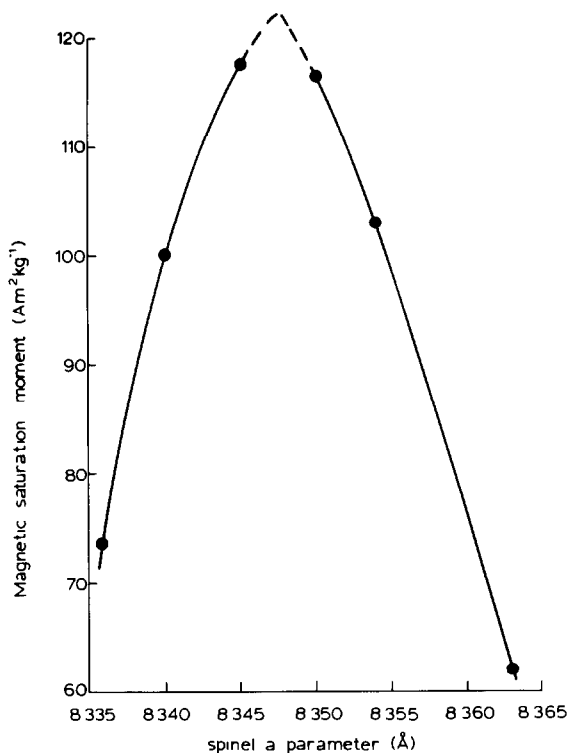


Fig. 5. Relationship between the magnetic saturation moment and the crystallographic a parameter of spinel pellets formed from various iron oxides with nickel oxide fully reacted at 1200°C for 2 h.

These bulk property measurements were all made on pellet samples, which differ from the powder samples referred to in Figs. 1–3 only in that ferrite formation is comparatively more advanced at all temperatures due to enhanced interparticle contact. The effect of restricted access of the atmosphere within the pellets does not appear to exert a major effect on the progress of the reaction.

At temperatures where ferrite formation is still incomplete, the bulk magnetic property reflects the proportion of magnetic phases present in the reaction mixture, and increases with increasing temperature (Fig. 4). On the other hand, differences in the magnetic saturation moment in fully reacted samples reflect the magnetism of the ferrite phase itself. A plot of the magnetic moment for fully reacted samples fired at 1200°C for 2 h is shown in Fig. 5 as a function of the lattice parameter, which is itself a function of the cation composition of the ferrite.

Figure 5 indicates that the highest magnetic moments are found in samples with lattice parameters of $8.345\text{--}8.350\text{ \AA}$. Such parameters correspond to trevorite with a small amount of Fe^{2+} substitution, estimated to be about 2.8–5.1% of FeO , by interpolation of the published cell parameters of

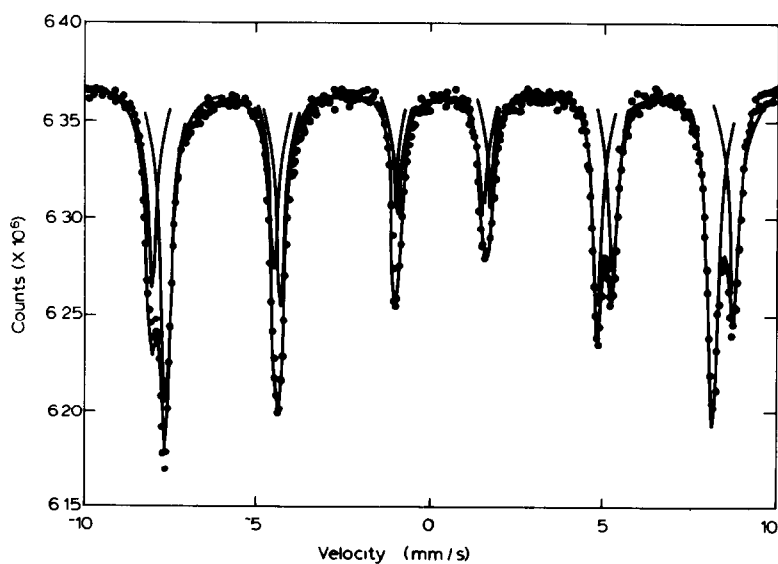


Fig. 6. Typical room-temperature Mössbauer spectrum of NiFe_2O_4 formed in the present experiments.

pure trevorite and a highly ferrous trevorite (JCPDS cards 10-325 and 23-1119 respectively). Samples with lattice parameters most nearly corresponding to this composition range were generated in the present work from hematite heated in air, and from synthetic magnetite heated under an inert atmosphere. The lattice parameters of ironsand samples heated under both oxidizing and inert conditions fall outside the optimum range, but this may also reflect the presence of other ions such as titanium.

Further information about the cation distribution in these spinels is provided by Mössbauer spectroscopy. The room-temperature Mössbauer spectra of all the fully reacted ferrites are composed of at least two partially overlapping magnetically split 6-line spectra (Fig. 6) similar to the spectra reported for NiFe_2O_4 by Linnett and Rahman [6].

One magnetic sextet has an isomer shift (IS) of $0.36\text{--}0.38\text{ mm s}^{-1}$ relative to natural iron, and a magnetic hyperfine field B_f of $50.9\text{--}52.4\text{ T}$; by analogy with the previous assignment of the Mössbauer spectrum of NiFe_2O_4 [6] and magnetite [7], this sextet is assigned to cations in the octahedral sublattice. By similar reasoning, the other sextet (IS = $0.26\text{--}0.29\text{ mm s}^{-1}$, $B_f = 47.3\text{--}49.3\text{ T}$) is assigned to cations in the tetrahedral sublattice. In ideal NiFe_2O_4 , the intensities of the tetrahedral and octahedral 6-line spectra should be equal if the recoilless fractions for the two sublattices are assumed to be similar [6], but in all of the present spectra the intensity of the tetrahedral component is $> 50\%$, which has previously been taken to suggest the contribution of a proportion of octahedral Fe^{3+} to this resonance [6].

Of all the ferrites formed in nitrogen, only the sample prepared from hematite shows a third 6-line magnetic spectrum with parameters similar to

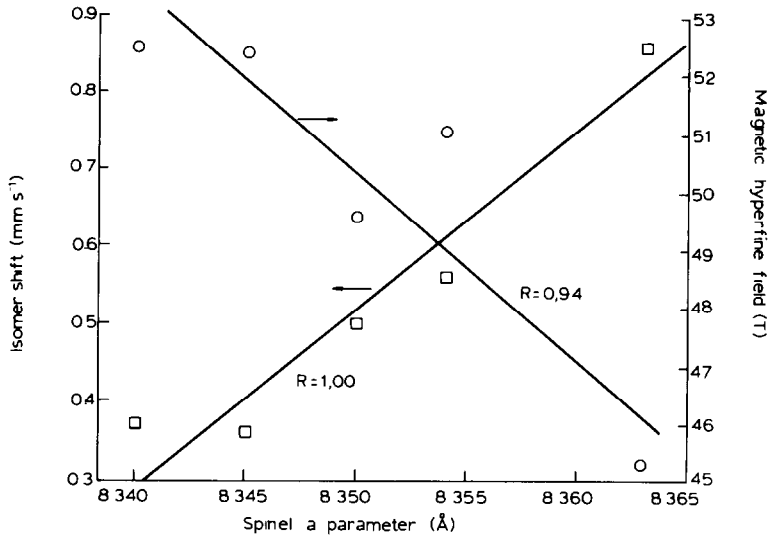


Fig. 7. Relation between the Mössbauer parameters and the crystallographic a parameter of spinels formed from various iron oxides with nickel oxide, fully reacted at 1200°C for 2 h.

those of a spectrum reported by Linnett and Rahman [6] and attributed by them to Fe^{3+} and Fe^{2+} rendered indistinguishable by electron exchange. The spectra do not differentiate between Fe^{3+} and Fe^{2+} ions in the tetrahedral and octahedral sublattices; these would be resolved only in spectra of samples cooled below the temperature of the Verwey transition. Spectra obtained at liquid nitrogen temperatures (77 K) are similar to the room-temperature spectra, suggesting that cooling to liquid helium temperatures would be necessary to resolve the Fe^{3+} and Fe^{2+} components.

The Mössbauer parameters of the tetrahedral sublattice of all the fully reacted ferrites are similar, but the octahedral sublattice parameters vary linearly with the cell dimension (i.e., the degree of Fe^{2+} substitution), as shown in Fig. 7. Figure 7 shows that the decrease in the cell dimension is accompanied by an increase in the IS value and a corresponding decrease in the hyperfine field of the octahedral sublattice, both changes being consistent with an increase in the Fe^{2+} substitution of the octahedral sites. Thus, these results indicate that any Fe^{2+} ions formed during the reaction are accommodated preferentially in octahedral sites, as would also be expected from the octahedral site preference energy of Fe^{2+} in spinels [8].

Cation composition of these ferrite spinels

Some inferences may be drawn about the cation distributions in the various spinels formed in these experiments by calculations of the spinel a parameters as follows.

(a) The gross composition of the spinel is first determined from the composition of the starting materials, taking into account any changes in the oxidation state of the iron, as reflected, for example, in the EGA results. The unfortunate inability of 77 K Mössbauer spectroscopy to provide a direct measurement of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios of these spinels introduces a degree of uncertainty in the compositions by placing a heavier reliance on evidence such as weight loss and cell parameter measurements.

(b) The probable cation distribution for each composition is then deduced from considerations of site preference energies of the various cations, and is tested by calculations of the two structural parameters u (the oxygen positional parameter) and a (the unit cell edge). Calculations are made for a range of assumed cation distributions, and the most probable configuration is identified by comparison of the calculated and measured cell parameters for each of the spinels.

The calculation was made by the method of O'Neill and Navrotsky [9], in which the tetrahedral and octahedral metal–oxygen distances R_{tet} and R_{oct} are related to the crystallographic parameters u and a by

$$R_{\text{tet}} = 1.732 a(u - 0.125) \quad (1)$$

and

$$R_{\text{oct}} = a(3u^2 - 2u + 0.0375)^{1/2} \quad (2)$$

The appropriate cation–oxygen distances were calculated from the ionic radii as tabulated by O'Neill and Navrotsky [9], the value for O^{2-} being taken as 1.380 Å. For a given distribution of cations over the available tetrahedral and octahedral sites, the values for R_{tet} and R_{oct} are obtained by linearly combining the contributions of each cation.

Hematite and magnetite reacted in air

The thermal analysis results and the measured a parameters suggest that the spinels formed under oxidizing conditions are essentially ferric; although the very small oxygen evolution from oxidized magnetite at the reaction temperature may suggest the formation of a trace of Fe^{2+} , this is not reflected in the measured cell parameter. The fully ferric spinel NiFe_2O_4 is usually stated to be fully inverse (i.e. the degree of inversion $x = 1$), with the Ni statistically distributed over the octahedral sites and the Fe^{3+} occupying both tetrahedral and octahedral sites [10]. The calculated a parameter for such a structure (8.3297 Å) is in poor agreement both with published values and with the present measured values (Table 2). If, however, the spinel is assumed not to be fully inverse, as suggested by Robertson and Pointon on the basis of magnetic measurements [11], excellent agreement is obtained between the calculated and observed a values where $x = 0.74$ and 0.83 for spinels derived from hematite and magnetite respectively (Table 2).

TABLE 2

Possible cation configurations of spinel ferrites derived from hematite, magnetite and ironsand, and their calculated and observed crystallographic parameters

Reactant	Atmosphere	Cation configuration ^a	<i>a</i> parameter (Å)		Calculated <i>u</i> parameter
			Measured	Calculated	
Hematite	air	(Fe _{0.74} ³⁺ Ni _{0.26} ²⁺)(Fe _{1.26} ³⁺ Ni _{0.74} ²⁺)O ₄	8.345	8.3451	0.2551
Hematite	inert	(Fe _{0.48} ³⁺ Ni _{0.52} ²⁺)(Fe _{1.36} ³⁺ Fe _{0.18} ²⁺ Ni _{0.45} ²⁺)O ₄	8.354	8.3540	0.2568
Magnetite	air	(Fe _{0.83} ³⁺ Ni _{0.17} ²⁺)(Fe _{1.18} ³⁺ Ni _{0.82} ²⁺)O ₄	8.340	8.3401	0.2551
Magnetite	inert	(Fe _{0.47} ³⁺ Ni _{0.53} ²⁺)(Fe _{1.39} ³⁺ Fe _{0.16} ²⁺ Ni _{0.44} ²⁺)O ₄	8.350	8.3520	0.2568
Ironsand	air	(Fe _{0.4} ³⁺ Ni _{0.6} ²⁺)(Fe _{1.28} ³⁺ Ni _{0.55} ²⁺ Ti _{0.16} ⁴⁺)O ₄	8.336	8.3365	0.2575
Ironsand	inert	(Fe _{0.31} ³⁺ Ni _{0.69} ²⁺)(Fe _{1.17} ³⁺ Fe _{0.17} ²⁺ Ni _{0.49} ²⁺ Ti _{0.16} ⁴⁺)O ₄	8.363	8.3653	0.2575

^a Tetrahedral ions shown in parentheses, octahedral ions in square brackets.

The calculated u value for both spinels in 0.255, in reasonable agreement with previously published values of 0.2573 [9] and 0.256 [12]. The apparent discrepancy between these values and the u value quoted by Derbyshire and Yearian [13] arises from their use of an alternative cell origin; when referred to the present cell origin, their u value becomes 0.254, in reasonable agreement with the other values.

Hematite and magnetite reacted in inert atmosphere

The larger a parameters of these ferrite products are consistent with the presence of Fe^{2+} [14], a conclusion supported by the thermal analysis results, which indicate a degree of oxygen loss from hematite–NiO mixtures. Under inert conditions, the oxygen stoichiometry of magnetite–NiO mixtures is unchanged from the original stoichiometry. If oxidation is completely suppressed in mixtures containing magnetite, the resulting spinel should have the composition $\text{Ni}_{1.09}\text{Fe}_{1.45}^{3+}\text{Fe}_{0.73}^{2+}\text{O}_4$. However, the measured a parameters of the spinels formed from magnetite and hematite in nitrogen (Table 2) are consistent with a considerably smaller proportion of Fe^{2+} in those phases. Although the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios could not be estimated by Mössbauer spectroscopy, an approximate estimate of the Fe^{2+} content was made by comparison of the lattice parameters with those of a ferroan trevorite of stated composition (JCPDS Card No. 23-1119). On this basis, the composition of the ferrite formed from magnetite in nitrogen is calculated as: $\text{Ni}_{0.97}^{2+}\text{Fe}_{1.86}^{3+}\text{Fe}_{0.16}^{2+}\text{O}_4$, and from hematite in nitrogen: $\text{Ni}_{0.97}\text{Fe}_{1.84}^{3+}\text{Fe}_{0.18}^{2+}\text{O}_4$. Calculations of the a parameters for a large number of different cation distributions of these spinels suggest that the tetrahedral sites contain Fe^{3+} and a significant amount of Ni, as in the case of the spinels formed in air, whereas the Fe^{2+} is located solely in the octahedral sites (Table 2), as would be expected from the octahedral site preference energy of Fe^{2+} [8]. The a parameters calculated on this basis are in good agreement with the measured parameters, and the calculated u values are also within the range of values reported for trevorite (Table 2).

Ironsand reacted in oxidizing and inert conditions

In calculating the composition of the ironsand-derived spinels from the analysis of the starting material, it is assumed that only the iron and titanium components participate in spinel formation. The further simplifying assumption is made that the air-fired spinels are fully oxidized. This is consistent with the virtually identical Mössbauer spectra of the spinels derived from ironsand, hematite and magnetite in air, and is also supported by thermal analysis evidence of some oxygen uptake in these mixtures. A previously reported study of the substitution of Ti^{4+} in nickel ferrite indicates that, in samples fired in air, charge balance is maintained by the formation of cation vacancies rather than Fe^{2+} , except at higher Ti concentrations [15]. On the basis that no Fe^{2+} occurs in the present air-fired

samples, the composition of the fully oxidized spinel from Waipipi ironsand is calculated as $\text{Ni}_{1.15}\text{Fe}_{1.68}^{3+}\text{Ti}_{0.16}^{4+}\text{O}_4$. In setting up models for the various possible distributions of these cations over the tetrahedral and octahedral sites of this spinel, for use in calculation of the a parameters, account was taken of the strong octahedral site preference of Ti^{4+} [16]. Of all the cation distributions tested by calculation of the a parameter, the configuration which yielded a value closest to the measured value contained Ti^{4+} in octahedral sites only, with Fe^{3+} and Ni^{2+} occupying both tetrahedral and octahedral sites (Table 2). As with the spinels derived from hematite and magnetite in both oxidizing and inert atmospheres, a sensible a value could be obtained only with a appreciable proportion of Ni in the tetrahedral sites.

In determining the composition of the spinel derived from ironsand under inert conditions, the lack of knowledge of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio again presents a difficulty. If the 2.4% weight gain on ignition (Table 1) is assumed to be due solely to the complete oxidation of Fe^{2+} , the totally unoxidized ferrite has the calculated composition $\text{Ni}_{1.18}^{2+}\text{Fe}_{1.48}^{3+}\text{Fe}_{0.27}^{2+}\text{Ti}_{0.17}^{4+}\text{O}_4$. However, as in the case of pure magnetite reacted under inert conditions, some internal oxidation is probably inevitable. By analogy with pure magnetite, the true Fe^{2+} content is probably nearer 0.17 atoms per mole of spinel, giving an adjusted formula of $\text{Ni}_{1.18}^{2+}\text{Fe}_{1.48}^{3+}\text{Fe}_{0.17}^{2+}\text{Ti}_{0.16}^{4+}\text{O}_4$. In calculating the a values for various models of cation distribution in this ferrite, Ti^{4+} was again assumed to be located solely in the octahedral sites [16], with the Fe^{2+} and some Ni^{2+} being localized in the vicinity of the Ti, as suggested by Müll et al. [17] as a result of their study of the magnetic anisotropy of Ti–Ni–Fe spinel ferrites. Table 2 shows the cation distribution which yields a calculated a value in best agreement with the measured parameter. The calculated u parameter for the ironsand-derived spinels lies in the range of values reported for pure trevorite.

Although the cation distributions shown in Table 2 for the various spinel ferrites led to realistic calculated values of a and u , they may not necessarily be the only distributions giving rise to reasonable parameters. However, these models have the advantage of being consistent with the known experimental facts, including chemical and thermal analysis data, Mössbauer spectroscopy and site preference energies of the various ions.

CONCLUSIONS

(1) When heated with NiO in air, hematite, synthetic magnetite and titaniferous magnetite ironsand all eventually form trevorite, NiFe_2O_4 , with lattice parameters very similar to those of the pure ferric phase. The reaction with magnetite involves pre-oxidation at 220°C ; although a similar pre-oxidation probably occurs in ironsand, the EGA evidence for this is less marked. Differences in the reactivity of the materials arise from differences

in the particle size of the reactant oxides, or from improved interparticle contact achieved by pelletizing the samples. The magnetic saturation moment of the ironsand-derived ferrite is less than those of materials derived from the pure oxides.

(2) The spinels formed with NiO in an inert atmosphere from hematite, magnetite and ironsand have larger lattice parameters than the corresponding air-reacted samples, indicating a degree of Fe^{2+} substitution. This is especially marked in the ironsand-derived ferrite, in which the magnetic saturation moment is again less than in the ferrites derived from pure iron oxides. The formation of Fe^{2+} in hematite-derived ferrite occurs at ca. 1000°C and is accompanied by oxygen evolution, whereas, in magnetite and ironsand, the oxygen stoichiometry is largely unchanged from that of the starting material.

(3) Although Mössbauer spectroscopy down to 77 K is incapable of differentiating between Fe^{2+} and Fe^{3+} in these spinels, changes in the hyperfine field and isomer shift of the octahedral sublattice accompanying increased Fe^{2+} substitution (as judged from the measured lattice parameters) are consistent with the location of the Fe^{2+} formed during the reaction in *octahedral* sites preferentially.

(4) Calculations of the lattice parameters, based on various assumed distributions of the available cations over the tetrahedral and octahedral sites, suggest that none of the ferric trevorites formed here is fully inverse, as is usually assumed, but that varying degrees of Ni substitution occur in the tetrahedral sites. Best agreement with the observed lattice parameters is given by models in which the Fe^{2+} is largely in the octahedral sites, where the Ti^{4+} is also located in ferrites derived from titanomagnetite.

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