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Reduction–Reoxidation Behavior of Manganese Cation-Deficient Spinels

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Thermogravimetry and electrical conductivity were used to study the reduction–reoxidation behavior of submicronic manganese-cation-deficient spinels. The aim is to control the hydrogen reduction of a number of Fe^{3+} ions in partially oxidized spinels at room temperature so that an "original state" can be obtained. In more oxidized spinels at 400°C, the availability for reduction of Fe^{3+} ions is much less than that of Mn^{3+} ions in octahedral sites. The reduced phase could be reoxidized to the original oxygen level and further oxidation–reduction cycles resulted in no change in cation distribution but were accompanied by sintering. © 1987 Academic Press, Inc.

Introduction

During a detailed study on the reactivity of several ferrous spinels corresponding to the formula $(Fe_{3-x}M_x)^{3+}O_4$, it was found that these mixed oxides can be oxidized at low temperatures (<300°C) to cation-deficient spinels for crystallite sizes less than about 200 nm. This is the case for several fine-grained magnetites substituted by divalent, trivalent, or tetravalent ions for which the formation of metastable defect spinels has been observed (*1–6*). Finely divided material may, indeed, partially oxidize in air at room temperature and one of the major problems encountered has been the ability to reproduce the same initial state in a freshly synthesized specimen for the purpose of correlating different types of experimental measurements.

This tendency for oxidation of Fe^{2+} ions with time is called "maghemitization" and titanomagnetites, metastable cation-deficient spinels, resulting from low-temperature oxidation, have been the subject of numerous investigations because of their geophysical importance in paleomagnetic and paleointensity studies (*7–9*). A systematic study has been made in which it was estimated that an appreciable degree of nonstoichiometry would be obtained in a time of the order of 10^6 years at 20°C for ground materials. In a recent paper we pointed out that the oxidation rate of octahedral site (B-site) Fe^{2+} ions is greater than that of tetrahedral site (A-site) Fe^{2+} ions

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because of the weaker ionic bonding of the B-site as compared with the stronger A-site covalent bond. From very precise thermogravimetric (TG) measurements, this discrepancy of reactivity has been used to determine the iron cation distribution between the sublattices (*6*) but the measurements must be made on "fresh samples" since the previous observation indicate that Fe^{2+} ions on B-sites in divided titanomagnetites are partially oxidized in air at room temperature. For manganese-substituted magnetites in which two cations are oxidized (Fe^{2+} on B-sites and Mn^{2+} on A-sites) it was also found that the availability for oxidation of Fe^{2+} ions in normal static air is greater than that of an A-site Mn^{2+} ion (*10*). As the oxidation reaction at room temperature is essentially due to the absorbed oxygen ionized by the extra electron of the M^{2+} ions which diffuse through the solid at higher temperatures, it may be seen that for cubic crystals of about 100 nm approximately 3% of all the unit cells in each crystallite will be exposed on the exterior faces; the rates of the earliest stages in the oxidation will be large and play an important role for the degree of nonstoichiometry in ambient air.

The question is then whether it is possible by heating these compounds in a reducing gas atmosphere to reach an "original state." Careful reduction studies in the cation-deficient spinels $(Fe^{3+}_{(24-8x)/9}M^{3+}_{8x/9}\square_{1/3})O_4^{2-}$ with $M^{3+} = Al^{3+}$ or Cr^{3+} showed that up to grain sizes 100 nm, powders react easily with hydrogen between 200 and 400°C and form the stoichiometric spinel $(Fe^{2+}Fe^{3+}_{2-x}M^{3+}_x)O_4^{2-}$ (*11*). Recently, for γ-Fe_2O_3 with $x = 0$ a remarkable gas-sensitive phenomenon based on the reversible oxidation–reduction process has been observed (*12*).

The present work investigates the hydrogen reduction of deficient manganese-substituted magnetites without destroying the spinel structure for the purpose of obtaining a well-defined reference state whatever the degree of oxidation. Reduction–reoxidation cycles are also envisaged in order to check the original cation distribution.

The preparation of samples and the experimental procedure for oxidation in cation-deficient spinels have already been reported (*5*, *10*). The formula of these freshly prepared spinels can be structurally represented as follows $(Mn^{2+}_{0.8x}Fe^{3+}_{1-0.8x})_A(Fe^{3+}_{1+0.6x}Fe^{2+}_{1-0.8x}Mn^{3+}_{0.2x})_BO_4^{2-}$ $(0 < x < 1)$ with Mn^{2+} on A-sites and a small amount of Mn^{3+} ions on B-sites. The samples consist of almost spherical grains of average diameter 35 nm.

Thermogravimetry and electrical conductivity were used to study oxygen stoichiometry in an oxidizing or a reducing atmosphere. Phase was analyzed by X-ray diffraction and composition by chemical analysis of samples cooled from various temperatures in the TG apparatus or conductivity cell.

Behavior in Air of Mn-Substituted Magnetites and Reduction of Partially Oxidized Samples

An example of the use of TG for the determination of oxidation characteristics is shown in Fig. 1 (curve 1) for the composition $x = 0.67$. In the range 100 to 400°C (region I) the original spinel was oxidized to

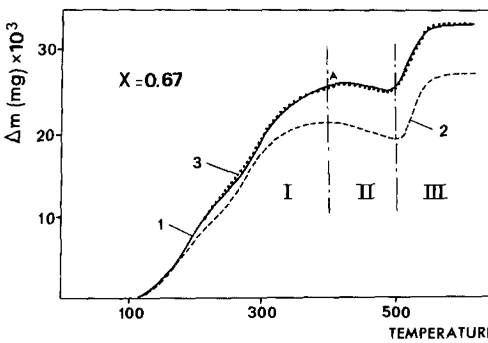

FIG. 1. TG curves for manganese-substituted magnetite with $x = 0.67$ heated in air at 2.5°C/min. 1, freshly prepared sample; 2, sample partially oxidized in air at room temperature for 6 months; 3, sample after reduction at 450°C with 120 Pa hydrogen.

cation-deficient spinel. The weight gain is due to total oxidation of Fe^{2+} (about 240°C) and Mn^{3+} ions (about 290°C) on B-sites and an incomplete oxidation of Mn^{2+} into Mn^{3+} ions (about 375°C). As Mn^{3+} ions exhibit a strong tendency to octahedral coordination, it can be expected that the number of Mn^{3+} ions stabilized in octahedral positions (*13*) will simultaneously lead to the displacement of an Fe^{3+} ion from a B- site to an A-site and that the vacancies will occur largely on B-sites. Above 400°C the compound starts to lose weight (region II), which corresponds to the reduction of Mn^{4+} to Mn^{3+} ions. For the two regions, X-ray diffraction shows a single phase spinel structure. Above 500°C (region III), we again have a weight gain due to oxidation of Mn^{2+} ions that were not completely oxidized at a lower temperature. This oxidation is accompanied by a phase change from a spinel to a corundum structure. The effect of the distribution of Fe^{2+}, Mn^{3+}, and Mn^{2+} ions between B- and A-sites on the oxidation characteristics in region I was demonstrated directly by plotting $d\Delta m/dt$ against temperature (curve 1, Fig. 2) where the variation in intensity of each peak with iron and manganese contents is indicative of the increase in stability toward oxidation and can be envisaged as follows: $|Fe^{2+}–O^{2-}|_B < |Mn^{3+}–O^{2-}|_B < |Mn^{2+}–O^{2-}|_A$ (*10*).

The nature of the TG curve of a sample stored under static air for 6 months is similar (curve 2, Fig. 1): however, compared with a freshly prepared sample (curve 1, Fig. 1), the maximum at point A is diminished as a result of the decrease in the amount of oxidized phase. The analysis of the $d\Delta m/dt = f(T)$ curve (curve 2, Fig. 2) shows that the intensity of the first peak decreases, suggesting a partial oxidation of Fe^{2+} to Fe^{3+} ions. The two other peaks are similar.

These observations indicate that the decrease of the first peak is associated with the oxidation of Fe^{2+} ions when the sample was exposed at room temperature in static air which is consistent with the availability for oxidation of Fe^{2+} ions located on B-sites (*14*).

In order to regenerate the Fe^{2+} ions, the sample stored in air was reduced in hydrogen. However, it has been shown previously (*11, 15*) that during the reduction of γ-Fe_2O_3 to Fe_3O_4, the major difficulty is to

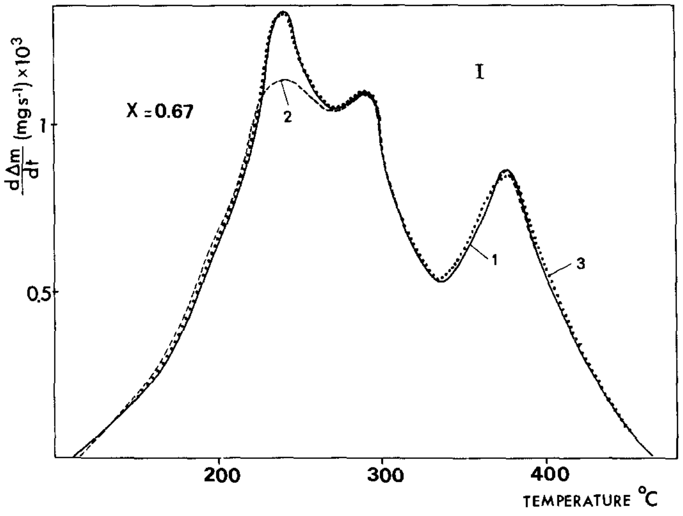

FIG. 2. DTG curves. 1, 2, and 3 as in Fig. 1.

reduce γ-Fe_2O_3 without a trace of metallic iron. The reduction rate, which is very high at the beginning of the process, decreases continuously as the reduction proceeds, approaching zero at a point corresponding to Fe_3O_4. At this point, the gas was pumped out and the sample was rapidly cooled. Further control of the degree of reduction was achieved by chemical and spectrophotometry analyses of the iron in different oxidation states.

In our case the reduction has been carried out at 450°C, using a hydrogen pressure of 120 Pa. X-ray and chemical analyses shows the formation of a stoichiometric spinel corresponding to the ''original state.''

A representative TG trace of the reoxidized sample is shown in Figs. 1 and 2 (curves 3). The sample regained its original oxygen content, shown by the intensity of the first peak being similar to that given for a freshly prepared spinel.

Reduction of Defect Phases Obtained by Treatment with Air at 400°C

Although in region II, oxidation maintains the spinel structure, by analogy with other spinels, resulting in the oxidation of substituted magnetites in which the reduction phenomenon is not present (*6*), we have oxidized the samples at 400°C (plateau of nearly constant weight between regions I and II).

Thermogravimetric Studies

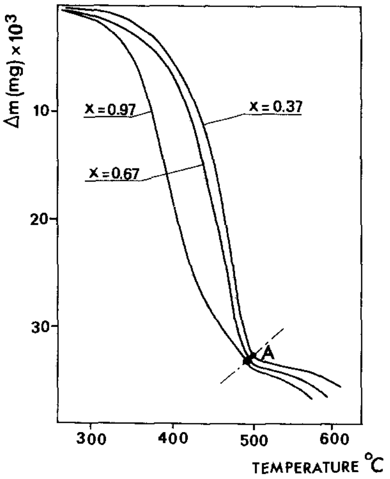

FIG. 3. TG curves for manganese-cation-deficient spinels versus composition x heated with 120 Pa hydrogen at 1.5°C/min.

The TG and differential thermogravimetry (DTG) curves recorded during reduction in hydrogen at a pressure of 120 Pa are shown in Figs. 3 and 4. Whatever the substitution content x, the weight loss (Fig. 1) at point A at the temperature of about 500°C corresponds closely to the weight gain previously obtained at 400°C in Fig. 1 (curve 1). The reduction rate, which is very high before point A, becomes almost nil and the reduction process proceeds very slowly for a temperature interval. When reduction was interrupted at point A and the material was quickly cooled in the reducing atmosphere, X-ray diffraction showed spinel phase only and chemical analysis has confirmed the composition of fresh samples.

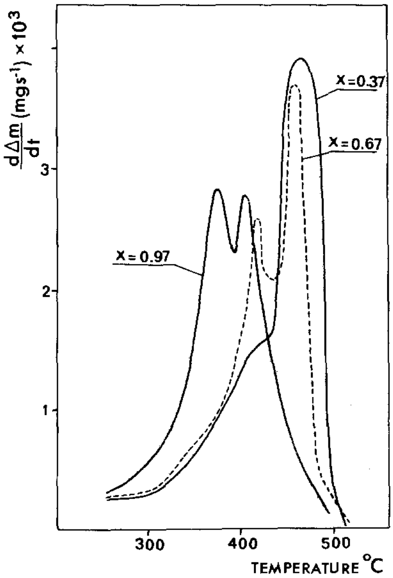

FIG. 4. DTG curves.

For temperatures higher that 500°C, FeO phase is present in the X-ray diffraction patterns of reduced specimens. When the hydrogen pressure is increased above 120 Pa (for example 800 Pa), the FeO phase appears at lower temperature (420°C) and at about 620°C, metallic iron is also formed.

The DTG curves (Fig. 4) show the effect of the substitution extent x on the reduction characteristics. The cation-deficient spinel with $x = 0.37$ exhibits a shoulder at about 420°C and a pronounced peak centered at 470°C. As x increases, the peak at 420°C increases and the intensity of the second peak at 470°C diminishes. It is possible to assume that the low- and high-temperature peaks are associated with the reduction of Mn^{3+} ions and Fe^{3+} ions on B-sites, respectively. It also appears that the availability for reduction of Fe^{3+} ions on B-sites is much less than that of Mn^{3+} ions. This result is consistent with the oxidation–reduction phenomena observed in manganese ferrites (*16*). The reduction of a sample with $x = 0.97$ started at lower temperature but proceeded always through two distinguishable steps, indicated by the maxima in the DTG curve at 380 and 410°C. However, the area of second peak does not agree with the concentration of Fe^{3+} ions and is very much greater than the assumed value. The reason for this is that the intensity of the second peak is probably also caused by the reduction of Mn^{4+} ions.

Electrical Conductivity Studies

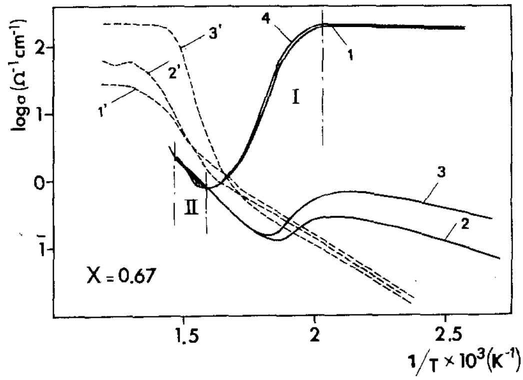

FIG. 5. Plot of log σ against T^{-1} for manganese-substituted magnetite with $x = 0.67$ heated in air at 2.5°C/min. 1, freshly prepared sample; 2, after first reduction with 120 Pa hydrogen; 3, after second reduction with 400 Pa hydrogen; 4, after third reduction with 800 Pa hydrogen. For manganese-cation-deficient spinels heated in hydrogen at 1.5°C/min: 1′, 120 Pa; 2′, 400 Pa; 3′, 800 Pa.

The electrical conductivity behavior during oxidation and reduction is shown in Fig. 5 for samples heated in air from room temperature to 400°C at a constant rate of 2.5°C/min (curves 1, 2, 3, and 4) and then reduced with different hydrogen pressures (120, 400, and 800 Pa) from room temperature to 540°C at a constant rate of 1.5°C/min (curves 1′, 2′, and 3′). As previously reported (*17*) the oxidation process in region I for a freshly synthesized sample (curve 1) can be envisaged as an electron hopping between Fe^{2+} and Fe^{3+} ions as $Fe^{3+} \rightleftharpoons Fe^{2+} + e^-$ and the decrease of conductivity with increase in temperature is due to the oxidation of Fe^{2+} ions and consequently to a decrease of Fe^{2+}–Fe^{3+} pairs because the created vacancies on B-sites do not contribute to the conductivity. The decrease in log σ is then followed by an increase corresponding to complete oxidation to cation-deficient spinels (hatched region II). The activation energy calculated from the slope of the straight line for region II (samples 1 and 4) is around 0.8 eV which is of the order of magnitude reported by Dorris for Mn_3O_4 (*18*). Thus conduction is likely to take place by the hopping of electrons between Mn^{3+} and Mn^{4+} ions on B-sites.

After this oxidation, the sample was reduced with 120 Pa hydrogen. The log σ against T^{-1} K plot (curve 1′, Fig. 5) shows a slow increase in electrical conductivity on heating up to 350°C, followed by a steep increase in the temperature range 350 to 500°C. A further increase in temperature does not show changes in σ. However, this reduction in hydrogen does not reproduce the same initial state as evidenced by a reoxidation of a sample (curve 2, Fig. 5) in a treatment similar to that given in the first oxidation. The region I of the heating curve is not retracted. Thus, region I in the electrical conductivity curve corresponds to an incomplete reduction of Fe^{3+} ions since the decrease in σ would be attributed to some vacancies on B-sites. A second treatment with 400 Pa hydrogen (curve 2′, Fig. 5) did not reproduce the oxidation state of the original sample as indicated by the shape of the reoxidation curve (curve 3, Fig. 5). Finally, it is interesting to note that the reoxidation curve (curve 4, Fig. 5) after the third reduction with 800 Pa hydrogen (curve 3′, Fig. 5) is almost identical to that corresponding to the first oxidation. Conductivity can then take place through electron exchange between Fe^{2+} and Fe^{3+} ions at B-sites since the number of Fe^{2+} ions generated by reduction is maximal. As reported from thermogravimetric data, the reduction temperature of Fe^{3+} ions is higher than that of Mn^{3+} ions.

These experimental results indicate that the reduction characteristics are peculiar phenomena observed between the cation-deficient spinel and the initial phase and that the sensitivity depends strongly on the number of Fe^{2+} ions generated on the grain surface by the reducing gas. One interesting result from this study is that the reduction of Fe^{3+} ions for deficient Mn-substituted magnetites is at a higher temperature than the usual operating temperature for the oxidation of Fe^{2+} ions. However, it is difficult to compare the data because thermodynamically, the oxygen and hydrogen pressures would produce different results. For higher hydrogen pressure, the reduction temperature of Fe^{3+} ions decreases and approaches the oxidation temperature of Fe^{2+} ions in air (*11*).

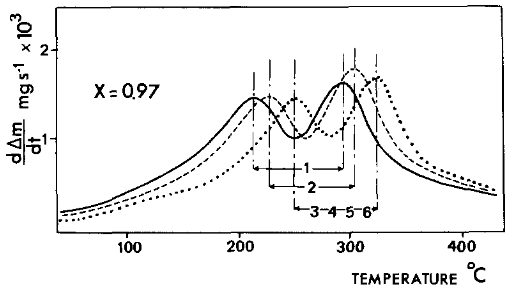

FIG. 6. DTG curves of repeated oxidation in air of a sample with $x = 0.97$ after intermediate reductions with 120 Pa hydrogen.

Reduction–Reoxidation Cycles

Repeated oxidation in air at 400°C with intermediate reductions with 120 Pa hydrogen were performed in order to study the reversibility of the reaction and the time/heating dependence on sintering. The DTG curves recorded during oxidation of a sample with $x = 0.97$ are shown in Fig. 6. Samples oxidized in the first, second, and third cycle proceeded through two distinguishable steps indicated by the maxima at 213 and 292°C for the first cycle, 228 and 304°C for the second cycle, and 250 and 325°C for the third cycle. Further reductions show no change in the oxidation maxima (curves 4, 5, and 6, Fig. 6). The resulting products of all oxidation cycles were identical to that corresponding to the initial sample as confirmed by X-ray analysis. The shift of the peaks toward higher temperatures for samples thermally cycled may be attributed to a sintering and the crystal growth effect as evidenced by electron microscopy when an appreciable variation of morphology by crystallizing is observed. Similar behavior has been observed at low temperatures on manganese ferrite (*19*). As reported in this paper, the relative areas of the peaks would be proportional to the relative quantities of the Fe^{2+} ions and Mn^{2+} ions within the spinel. From the computer fitting it appeared that the area ratios are consistent with the cation distribution. Because the area ratios for oxidation cycles are similar (Fig. 6) we can assume that the original cation distribution at A- and B-sites is conserved during reduction–reoxidation cycles.

Conclusion

These results show that finely grained manganese-substituted magnetites prepared at relatively low temperatures and freshly synthesized are partially oxidized in air at room temperature. In the present investigation a treatment in hydrogen atmosphere, necessary to maintain stoichiometry, allowed an original state to be obtained. Highly oxidized cation-deficient spinels at 400°C in which B-site Fe^{2+} ions will be more rapidly oxidized than A-site Mn^{2+} ions are reduced in hydrogen at 520°C without destroying the spinel structure. Thermogravimetric and electrical conductivity measurements show that Mn^{3+} ions are preferentially reduced to Fe^{3+} ions. This last observation agrees with the oxidation–reduction equilibrium of Mn ions in manganese ferrites.

In order to study the reversibility of the reaction and the temperature–cation distribution dependence, repeated oxidations with intermediate reductions at 520°C have been carried out. No variations in cation distribution between the inequivalent sites of the spinel structure were detected as inferred from areas of DTG peaks. However, it appears that sintering takes place. This kind of fully reversible process is of particular interest in the field of heterogeneous catalysis, since it has been observed that the bulk oxygen of the ferrite catalysts takes part in selective oxidative dehydrogenation of butenes to butadiene (*20*).

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