Availability of Fe^{2+} Ions in Cr- or Al-Substituted Magnetites with Relevance to the Process of Oxidation in Defect Phase γ

B. GILLOT AND F. JEMMALI

Laboratoire de Recherches sur la Réactivité des Solides associé au CNRS, Faculté des Sciences Mirande, B.P. 138–21004 Dijon Cedex, France

AND F. CHASSAGNEUX

Laboratoire de Chimie Minérale, Université Claude Bernard, Lyon 1, 43, boulevard du 11 Novembre 1918, 69621 Villeurbanne, France

AND C. SALVAING AND A. ROUSSET

Laboratoire de Chimie des Matériaux Inorganiques, Université Paul Sabatier, Toulouse III, 118, route de Narbonne, 31000 Toulouse, France

During oxidation of the aluminum- or chromium-substituted magnetites, $(Fe^{2+}Fe^{3+}_{2-x}M^{3+}_x)O^{2-}_4$, with $0.4 < x < 1.8$ in defect phase γ of the same spinel structure, the availability for oxidation of Fe^{2+} ions in the tetrahedral sites (A sites) of the spinel structure is much less than that in octahedral sites (B sites) and in both cases depends on the extent of aluminum or chromium substitution. The influence of cation distribution in A and B sites on the oxidation temperature is shown directly by differential thermogravimetric analysis and by electrical conductivity.

Introduction

Recent studies (*1, 2*) were devoted to the oxidation of fine-grained magnetites substituted by trivalent ions $(Fe^{2+}Fe^{3+}_{2-x}M^{3+}_x)O^{2-}_4$, where $M^{3+} = Al^{3+}$, Cr^{3+}, and $0 < x < 2$. These spinels whose crystallite sizes are less than about 2000 Å could be oxidized to defect phase γ with the same spinel structure. The oxidation temperature and electrical conductivity (*3, 4*) are related to the distribution of Fe^{2+} ions on octahedral sites (B sites) or tetrahedral sites (A sites) of the spinel structure.

The oxidation kinetics performed in a thermobalance under isothermal conditions indicate that the necessary temperature for oxidizing the Fe^{2+} ions to Fe^{3+} ions increases from inverse-spinel-like magnetite $(x < 0.27)$, where all Fe^{3+} ions are on octahedral sites (most oxidation temperatures are in the range 150–250°C), to normal-spinel-like chromite or aluminate $(x > 1.80)$, where all Fe^{2+} ions are on tetrahedral sites (most oxidation temperatures are in the range 400–500°C). The mechanism by which oxidation proceeds has been the subject of some discussion (*5*). During oxida-

tion in air or oxygen, oxygen atoms adsorbed on the grain surface become ionized by acquiring electrons from Fe^{2+} ions diffusing through the crystal. The resulting concentration gradients thus cause the diffusion of Fe^{3+} ions and vacancies into the interior of the grain and the diffusion of Fe^{2+} and M^{3+} ions from the interior. The process is governed by the availability of oxygen at the surface, the energy required to release an Fe^{2+} ion from a lattice site, and the mobility of the diffusion ions.

This discrepancy of reactivity between ferrous ions located, respectively, at B and A sites in spinels has also been shown by electrical conductivity and in this case a different behavior for the $\sigma = f(t)$ curves allows one to differentiate between inverse and normal spinel (3). Inverse spinels such as magnetite, with a high initial conductivity, and which are n-type semiconductors, undergo a large conductivity decrease during oxidation, related to the generation of Fe^{3+} ions and vacancies on octahedral sites, upsetting the electron exchange between the Fe^{2+} and Fe^{3+} ions initially present in equal amounts on octahedral sites. Alternatively, normal spinels such as iron aluminate or chromite, being p-type semiconductors, exhibit an initial increase in conductivity. This is due to the simultaneous presence of Fe^{2+} and Fe^{3+} ions on tetrahedral sites, which allows electron exchange between cations on equivalent sites. Thus, when Fe^{3+} ions prevail, the conductivity decreases as for inverse spinels until the γ compound is obtained.

The purpose of the present work is to determine, by thermogravimetry and electrical conductivity, the availability for oxidation in defect phase γ of Fe^{2+} ions located in the inequivalent sublattices of the Al- or Cr-substituted magnetites whose substitution ratio x is in the composition range $0.4 < x < 1.80$ and therefore which exhibit both Fe^{2+} ions on tetrahedral and octahedral sites. It has been suggested by

O'Reilly and Banerjee (6) for oxidation of titanomagnetites $Fe_{3-x}TiO_4$ $(0 < x < 1)$ that covalent bonding in tetrahedral sites of the structure renders tetrahedrally sited Fe^{2+} less available for oxidation than Fe^{2+} ionically bound in octahedral sites.

Experimental

Samples. The preparation conditions of finely grained spinels, $(Fe^{2+}Fe^{3+}_{2-x}M^{3+}_x)O^{2-}_4$, were given by Rousset (7). In addition to the inverse spinels $(x < 0.40)$ or normal spinels $(x = 2)$ already studied, we prepared various substituted magnetites in which the Fe^{2+} ions are distributed in variable proportions on one sublattice or the other. The techniques used to characterize these samples, namely, chemical analysis, X-ray diffraction, magnetic measurements, and D.T.A., have already been quoted in Ref. (1, 2) and the cation distribution is mentioned in Table I. The lattice parameter, the average particle size, and the oxidation temperature range determined in thermogravimetry at various isothermal temperatures are also listed in Table I.

Measurements. The samples were oxidized in a microbalance Setaram MTB 10-8 with 5 mg of powder under isothermal conditions, or with the temperature increasing at a linear rate. Before every reaction, great care had to be taken while degassing to ensure that the powder was not even partially oxidized. This necessitated a pressure of 10^{-9} atm and a very slow temperature rise during degassing $(t = 500°C)$. These treatment conditions prevent any bulk oxidation if we refer to the weight measurements before and after the reaction, and the determination of the lattice parameter. For isothermal conditions, the fraction of oxidation (a) may be defined as $a = \dfrac{W_t - W_0}{W_\infty - W_0}$, where W_t is the weight of sample at time t, W_0 is the weight at $t = 0$, and W_∞ is the final weight.

The oxidation of these spinels to the defect phase γ was also followed by electrical conductivity. The measuring device and the operating conditions have already been reported (3). The electrical conductivity measurements were carried out by the two-probe method on compressed, highly sintered pellets of about 0.8 cm diameter and 0.2 cm thickness. The grains within the sample were oxidized as freely as those near the outside since the linear variation law predicted for the crystal parameter versus fraction of reaction is rather well verified (1). The measurements for samples exhibiting low resistivity were carried out with the four-probe technique to eliminate contact resistance. Nonohmic behavior and polarization effects were absent.

Results

1—Kinetic Study

Isothermal method. The plots of fraction of reaction a versus time at constant temperature between 170 and 360°C for $x = 0.80$ display a two-stage oxidation process (Fig. 1). The greatest deviation occurs for $a = 0.7$, where only a part of the total Fe^{2+}

ions is readily oxidized (between 170 and 240°C) and some Fe^{2+} ions remain unoxidized at the lower temperature, becoming oxidized at the higher temperature (above 300°C), forming a defect phase as confirmed by X-ray diffraction. The oxidation of octahedral Fe^{2+} ions probably corresponds to the so-called first stage of oxidation. For comparison we also report in Fig. 1 the oxidation kinetics of spinel with approximately all Fe^{2+} ions in octahedral sites ($x = 0.27$) and of spinel with all Fe^{2+} ions in tetrahedral sites ($x = 2$). In both cases the oxidation in defect phase γ shows an oxidation process in one stage and that no further oxidation takes place.

Nonisothermal method. The effect of Fe^{2+} distribution between B and A sites on the oxidation characteristics was demonstrated directly by observing the weight change when the samples were heated at a constant rate of 2.5°C/min from 100 to 700°C. The derivative of the weight–temperature function was determined and plotted as a function of temperature. Figures 2 and 3 show the results of this experiment for chromium-substituted magnetites with $x = 0$, $x = 0.80$, $x = 1.20$, and $x = 2$ and for
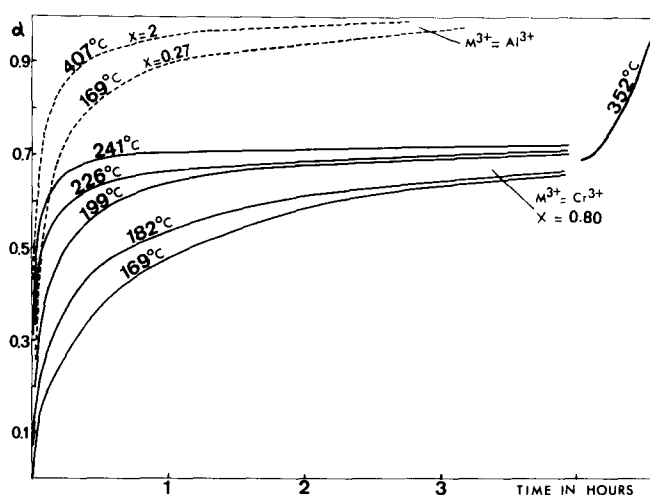

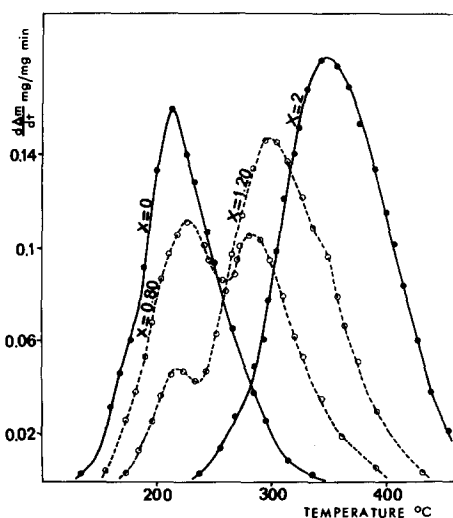FIG. 1. Isothermal curves of the oxidation of process for aluminum- and chromium-substituted magnetites.

FIG. 2. DTG curves for chromium-substituted magnetites heated in oxygen at 2.5°C/min.

aluminum-substituted magnetite for $x = 1.60$ and $x = 2$.

The pure magnetite and chromite or aluminate spinels, containing all Fe^{2+} ions in the octahedral and tetrahedral sites, respectively, exhibit only one peak centered at about 200°C for magnetite, at 400°C for chromite, and at 500°C for aluminate. The spinel for $x = 0.80$, with approximately half the Fe^{2+} ions in each site, has two peaks of similar size (Fig. 2). The spinel for $x = 1.20$ ($M^{3+} = Cr^{3+}$) and $x = 1.60$ ($M^{3+} = Al^{3+}$), with about 30 and 25% Fe^{2+} ions, respectively, in the octahedral sites, shows the development of a second peak centered at about 200°C on the low temperature side of the main peak. The decrease in size of this second peak as x increases is consistent with an increasing number of Fe^{2+} ions in tetrahedral sites, having only limited availability for oxidation in the lower-temperature range. If it is now possible to assume that the low- and high-temperature peaks of the intermediary compositions are associated with the oxidation of Fe^{2+} ions from predominantly B and A sites, respectively, then comparison may be made with the results for Fe_3O_4, $FeCr_2O_4$, or $FeAl_2O_4$, where the Fe^{2+} ions originate exclusively on one site.

2—Electrical Conductivity Study

The oxidation can also be followed by observing the time dependence of electrical conductivity at the oxidation temperature (Fig. 4). For $x = 0.80$ we always observe a large conductivity decrease during oxidation as in inverse spinels. In contrast, for $x = 1.20$ and $x = 1.40$, the conductivity decreases initially with time and then exhibits a maximum as in normal spinels. This behavior can be explained as follows: The Fe^{2+} ions on octahedral sites are oxidized preferentially, producing a decrease of conductivity due to the introduction of vacancies and Fe^{3+} ions on B sites; the electronic exchange between the Fe^{2+} and Fe^{3+} ions is upset. Then, versus time, the Fe^{2+} ions on tetrahedral sites are oxidized, which favors electron exchange between Fe^{2+} and Fe^{3+} ions present on equivalent sites, here tetrahedral sites. Finally, the conductivity decreases as for inverse spinels. For $x = 0.80$ we observe no maximum during oxidation because Fe^{2+} ions in A sites are fewer than
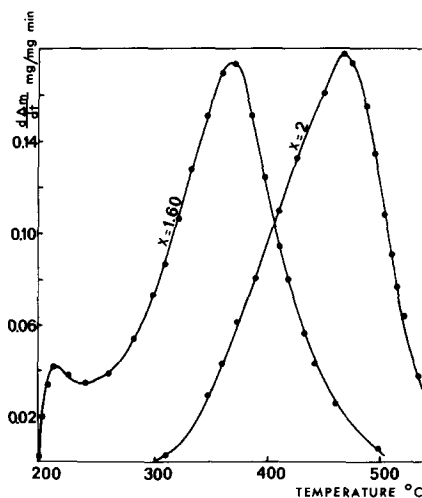

FIG. 3. DGT curves for aluminium-substituted magnetites heated in oxygen at 2.5°C/min.
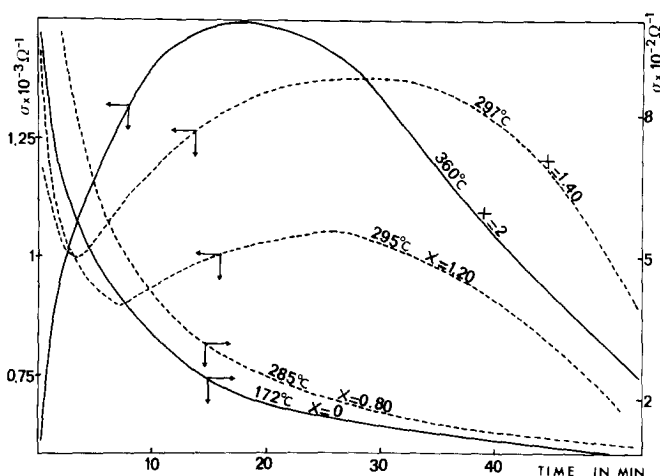
FIG. 4. Evolution of conductivity vs time of the oxidation process for chromium-substituted magnetites.

Fe^{3+} ions. Figure 5 shows the various possibilities of electronic exchange between Fe^{2+} and Fe^{3+} ions depending on the nature of the spinel and fraction of reaction a. Only normal spinels and spinels totally oxidized into the defect phase no longer possess this possibility of exchange and hence have a low conductivity.

the formation of a defect phase γ with the same spinel structure. Consequently, for coarse-grained material (size >0.5 μm), further oxidation retaining the spinel structure may be impossible as the higher temperature and the second peak in DTG is considered to be due to the formation of a multiphase oxidation product of the same

Discussion and Conclusion

The investigation of the oxidation of magnetites substituted by trivalent ions with $0.4 < x < 1.8$ shows that Fe^{2+} ions in octahedral sites are more readily oxidized than Fe^{2+} ions in tetrahedral sites as the degree of oxidation increased. This behavior of Fe^{2+} ions in the spinels, in particular the presence of two peaks for the $d\ \dfrac{\Delta m}{dt} = f(T)$ curves, has been mentioned during the oxidation of titanomagnetites (8, 9) and for other spinel oxides (10) where Fe^{2+} ions are distributed on inequivalent sites. However, in both cases only the oxidation of Fe^{2+} ions on octahedral sites probably corresponds to the so-called first stage of oxidation of magnetite which occurs quickly at relatively low temperature ($<200°C$) with
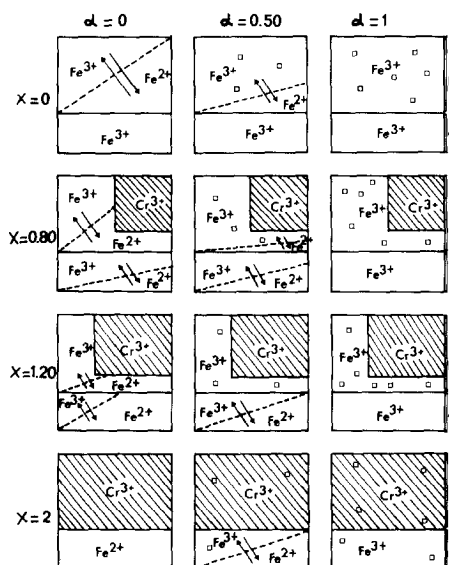

FIG. 5. Scheme of the various Fe^{2+}–Fe^{3+} electronic exchange vs a for different cation distribution.

TABLE I

SAMPLE CHARACTERISTICS

Sample $Fe^{2+}Fe_{2-x}^{3+}M_x^{3+}O_4^{2-}$		Cation distribution between A and B sites	Lattice parameter (Å)	Crystallite size (Å)	Oxidation temperature range (°C)
$M^{3+} = Cr^{3+}$	0	$(Fe^{3+})_A(Fe^{2+}Fe^{3+})_BO_4^{2-}$	8.397	600	150–220
	0.80	$(Fe_{0.4}^{2+}Fe_{0.6}^{3+})_AFe_{0.6}^{2+}Fe_{0.6}^{3+}Cr_{0.8}^{3+})_BO_4^{2-}$	8.386	350	170–250
	1.20	$(Fe_{0.7}^{2+}Fe_{0.3}^{3+})_AFe_{0.3}^{2+}Fe_{0.5}^{3+}Cr_{1.2}^{3+})_BO_4^{2-}$	8.405	780	250–310
	1.40	$(Fe_{0.9}^{2+}Fe_{0.1}^{3+})_AFe_{0.1}^{2+}Fe_{0.5}^{3+}Cr_{1.4}^{3+})_BO_4^{2-}$	8.395	800	280–350
	2	$(Fe^{2+})_A(Cr^{3+}Cr^{3+})_BO_4^{2-}$	8.378	700	330–440
$M^{3+} = Al^{3+}$	0.27	$(Fe^{3+})_A(Fe^{2+}Fe_{0.73}^{3+}Al_{0.27}^{3+})_BO_4^{2-}$	8.373	300	160–210
	1.60	$(Fe_{0.75}^{2+}Fe_{0.25}^{3+})_A(Fe_{0.25}^{2+}Fe_{0.15}^{3+}Al_{1.6}^{3+})_BO_4^{2-}$	8.20	400	300–400
	2	$(Fe^{2+})_A(Al^{3+}Al^{3+})_BO_4^{2-}$	8.149	350	380–490

bulk chemical composition. In our case the two oxidations retain the original spinel structure (1, 2) with only a regular decrease in the lattice parameter with fraction of reaction a in conformity with the smaller ionic radius of Fe^{3+} compared to that of the Fe^{2+} ions. No limit of solid–solid phase is present and the process may be considered as an interdiffusion inside the oxide itself, the only result being a change in stoichiometry with conservation of the oxygen lattice resulting in defect spinels. This is due to the preparation method which governs the crystallite size whose mean diameter lies between 400 and a few thousand angstroms. We have also shown that the oxidation temperature and the stability of defect phases γ resulting from the oxidation of Al- or Cr-substituted magnetites are governed above all by the Al or Cr substitution ratio x and the nature of the substituent (11, 12). The γ phases that are richer in Al are more stable since temperatures of about 900°C are required for the transformation $\gamma Fe_2Al_4O_9 \rightarrow aFe_2Al_4O_9$ and 700°C for the transformation $\gamma Fe_2Cr_4O_9 \rightarrow aFe_2Cr_4O_9$. The result is that the production of a highly oxidized cation-deficient spinel at high temperature is possible under the stabilizing effect of trivalent ions and the DTG peak centered at about 400°C for $FeCr_2O_4$ and 500°C

for $FeAl_2O_4$ can be ascribed to the formation of a cation-deficient spinel oxidation product.

The DTG and electrical conductivity data are in agreement with the relative availability for oxidation of Fe^{2+} ions and with the distribution of cations between tetrahedral and octahedral sites in unoxidized substituted magnetites. The $\sigma = f(t)$ curves clearly show a two-stage oxidation process and the increase of conductivity after the initial fall for $x > 0.80$ indicates the onset of oxidation of Fe^{2+} ions on tetrahedral sites with an Fe^{2+}/Fe^{3+} ratio > 1. It has been suggested by O'Reilly and Banarjee (6) that ions in tetrahedral sites of the spinel structure are strongly bound by covalent bonds, in contrast to the ionic bonding of octahedrally sited ions. It also appears (13) that, to a first approximation, the mobility of tetrahedral site ions is zero and that, initially at least, oxidation will take place at the expense of octahedral Fe^{2+} ions. Also ionic diffusion of Fe^{2+} ions within the tetrahedral sites involves the transport of a large local distortion and mobility will therefore be low.

Freer and O'Reilly (10) have determined by interdiffusion and oxidation experiments the diffusion rates of Fe^{2+} ions from the two cation sites of the spinel structure. It has

been found that the diffusion of Fe^{2+} ions located at B sites may be identified with an activation energy of 0.27 eV and A sites with 0.71 eV. Although these two values for activation energy appear to be significantly lower than those found for oxidation magnetite (0.95 eV) and iron aluminate (2 eV) (*2*), where the cation diffusion always determines the oxidation reaction, with a chemical diffusion coefficient which decreases in the order $FeFe_2O_4 > FeCr_2O_4 > FeAl_2O_4$, these results provide further support that B site Fe^{2+} ions will be more rapidly oxidized than A site Fe^{2+} ions.

References

1. B. GILLOT, J. F. FERRIOT, G. DUPRE, AND A. ROUSSET, *Mater. Res. Bull.* **11**, 843 (1976).

2. B. GILLOT, J. TYRANOWICZ, AND A. ROUSSET, *Mater. Res. Bull.* **10**, 775 (1975).

3. B. GILLOT, *J. Phys. Chem. Solids* **38**, 751 (1977).

4. B. GILLOT, F. BOUTON, F. CHASSAGNEUX, AND A. ROUSSET, *Phys. Status Solidi A* **50**, 109 (1978).

5. B. GILLOT, *Ann. Chim. Fr.* **3**, 209 (1978).

6. W. O'REILLY AND S. K. BANERJEE, *Nature* **211**, 26 (1966).

7. A. ROUSSET AND J. PÂRIS, *Ann. Chim.* **7**, 119 (1972).

8. P. W. READMAN AND W. O'REILLY, *Phys. Earth Planet Inter.* **4**, 121 (1970).

9. R. FROST AND P. L. GAI, *Acta Crystallogr. Sect. A* **36**, 678 (1980).

10. R. FREER AND W. O'REILLY, *Mineral. Mag.* **43**, 889 (1980).

11. A. ROUSSET, J. PÂRIS, AND P. MOLLARD, *Ann. Chim. Fr.* **7**, 119 (1972).

12. F. CHASSAGNEUX AND A. ROUSSET, *J. Solid State Chem.* **16**, 161 (1976).

13. R. J. ARMSTRONG, A. H. MORRISH, AND G. A. SAWAYSKY, *Phys. Lett.* **23**, 414 (1966).