

THERMOANALYTICAL STUDIES ON CATION DISTRIBUTION IN SUBMICRONIC TITANOMAGNETITES*

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(Received June 10, 1986)

Non-isothermal and isothermal TG studies on the cation distribution in submicronic titanomagnetites, $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ with $0 < x < 0.82$ are reported. For $x < 0.61$, these titanomagnetites could be oxidized at temperatures below 500° to titanium-substituted magnetites which have a higher vacancy content than that of $\gamma\text{-Fe}_2\text{O}_3$. The DTA results show that the temperature of oxidation of Fe^{2+} to Fe^{3+} ions is increased, whereas the temperature of phase change is decreased with increasing titanium substitution. The kinetics of oxidation is found to be governed by the law of diffusion for variable working conditions and for different extents of the vacancies created at the solid-gas interface. The diffusion of iron(II) ions located at octahedral sites proceeds with a lower activation energy than that of iron(II) ions located at tetrahedral sites. Diffusion rates were discerned to be composition-dependent and the variations can be identified with the distribution of the iron ions in sublattices.

Recent studies [1-2] were devoted to investigations of the low-temperature ($< 400^\circ$) oxidation of fine-grained magnetites substituted by trivalent ions ($\text{Fe}^{2+}\text{Fe}_{2-x}^{3+}\text{M}_x^{3+}\text{O}_4^{2-}$ ($\text{M}^{3+} = \text{Al}^{3+}, \text{Cr}^{3+}; 0 < x < 2$) and divalent ions ($\text{Fe}_{1-x}^{2+}\text{Fe}_x^{3+}\text{M}^{2+}\text{O}_4^{2-}$ ($\text{M}^{2+} = \text{Co}^{2+}, \text{Zn}^{2+}, \text{Mn}^{2+}; 0 < x < 1$)). The spinels whose crystallite sizes are less than about 200 nm could be oxidized to defect phase γ with the same spinel structure. The oxidations performed in a thermobalance under isothermal conditions indicated that the necessary temperature for oxidizing the Fe^{2+} ions to Fe^{3+} ions increases from spinel-like magnetite, where all Fe^{2+} ions are at octahedral sites (most oxidation temperatures are in the range $150\text{--}250^\circ$), to spinel-like chromite or aluminate, where all Fe^{2+} ions are at tetrahedral sites (most

* Paper presented at the World Conference on Thermal Analysis, Madeira (Portugal), 1986.

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oxidation temperatures are in the range 400–500°). Besides this discrepancy in reactivity between iron(II) ions located at octahedral (B sites) and at tetrahedral (A sites) in spinel, a discrepancy has also been shown for Al- or Cr-substituted magnetites whose substitution ratio x is in the composition range $0.04 < x < 1.70$ and which therefore contain Fe^{2+} ions at both B and A sites [3].

In all cases, during low-temperature oxidations the original spinel structure is retained and the process may be regarded as an interdiffusion inside the oxide itself, the only result being a change in stoichiometry with conservation of the oxygen lattice, resulting in cation-deficient spinels. In particular, the methods developed for the preparation of spinels with submicronic dimensions and in the size range 10 to 200 nm have enabled us to undertake extensive studies on their thermal characteristics and to correlate them with their microstructure. The behaviour of Fe^{2+} ions in the spinel lattice has been the subject of a number of studies involving the oxidation of natural and synthetic titanomagnetites [4–8], where Fe^{2+} ions are located in the unequivalent sublattices of the spinel structure. However, because of the difficulty in preparing titanomagnetites with a grain size less than 10^3 nm, only the oxidation of Fe^{2+} ions at B sites at about 250° preserves the spinel structure. Further oxidation with retention of the spinel lattice may be impossible, as the higher temperatures required to increase tetrahedral Fe^{2+} mobility could result in the decomposition of the cation-deficient spinel and in the formation of multiphase oxidation products.

The oxidation of finely-grained titanium-substituted magnetites of type $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ should allow the production of non-stoichiometric titanomagnetites, in particular at higher temperature. The purpose of this work was to make a systematic study of the process of oxidation of finely-grained titanium-substituted magnetites to cation-deficient spinels, and from very precise thermogravimetric measurements to determine the distribution of iron cations at the A and B sites of the spinel structure. This approach is possible since titanium exists solely in the Ti^{4+} state and only in the octahedral sublattice [9]. The kinetics of oxidation of Fe^{2+} ions located at octahedral and tetrahedral sites is also studied.

Experimental

1 Materials

The conditions of preparation of spinels of type $(\text{Fe}_{2-2x}^{3+}\text{Fe}_{1+x}^{2+}\text{Ti}_x^{4+})\text{O}_4^{2-}$ ($0 < x < 1$) do not differ much from those in the previous method used to prepare M^{3+} or M^{2+} -substituted magnetites [10]. Coprecipitated hydroxide precursors of iron and titanium are subjected to adequate thermal treatment in a H_2 — H_2O

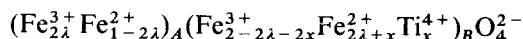
Table 1 Sample-characteristics

Samples	Lattice parameter, nm	Crystallite size, nm	DTA peak temperature in °C	
			oxidation	transformation
$x=0$	0.8397	60	210	—
$x=0.20$	0.8405	100	250	750
$x=0.43$	0.8423	49	254	685
$x=0.61$	0.8467	100	267	675
$x=0.82$	0.8497	100	292 and 401	660

atmosphere at low temperature ($<700^\circ$) to yield the solid solutions $\text{Fe}_3\text{O}_{4(1-x)}(\text{Fe}_2\text{TiO}_4)_x$, which are extremely divided solids and hence highly reactive. Five samples, with $x = 0, 0.20, 0.43, 0.61$ and 0.82 , were selected for these studies.

2 Initial characterization of samples by XRD, electron microscopy and DTA

XRD analysis at room temperature on patterns obtained in vacuum with K_α chromium monochromatized radiation shows that the samples contain only the spinel phase. In addition to the pure magnetite already prepared, we dealt with the various compositions mentioned in Table 1. The synthesized materials show an increase in the lattice parameter with the substitution extent x (Table 1). Although several models have been advanced for the distribution of iron cations in titanomagnetites at various temperatures [11–14], a first structural investigation [15] indicates that the distribution at room temperature can be formulated as follows:



with $\lambda = 0.5$ for $0 \leq x \leq 0.5$, that excluded the presence of Fe^{2+} ions at A sites, and $0 < \lambda < 0.5$ for $0.5 < x < 1$, where the function $\lambda = f(x)$ determined by the Poix method [16] had the shape of a hyperbola.

The morphological study of the samples by means of electron microscopy and X-ray diffraction usually shows spherical crystallites with an average diameter between 70 and 100 nm (Table 1). The DTA of the samples was conducted in the presence of air and with a temperature rise of 600 deg per hour. The diagrams obtained show two exothermic phenomena (Table 1) for $x < 0.61$. The first corresponds to the temperature at which the oxidation of Fe^{2+} ions is maximum; the second is attributed to the transformation of the cation-deficient spinels to a variety of inversion products, hematite, TiO_2 and pseudobrookite. For $x = 0.82$, the second peak at about 400° is due to the oxidation of tetrahedral Fe^{2+} ions.

TG measurements

The samples were oxidized in a Setaram MTB10.8 microbalance under isothermal conditions or with the temperature increasing at a linear rate. The material weighed 6 mg and the powder was spread out so that it would oxidize in the same way as N independent particles with identical mean radius. Before every reaction, great care had to be taken while degassing, to ensure that the powder was not even partially oxidized. This necessitated a vacuum of $< 10^{-4}$ Pa and a very slow temperature rise, so that no weight gain change occurred during the heating period.

The phases present after oxidation were determined by X-ray powder diffraction measurements on samples rapidly cooled from 500° in the TG apparatus. The Fe^{3+} contents of the samples at various levels of oxidation were calculated from the gravimetric data.

Results and discussion

Oxidation of Ti-substituted magnetites to cation-deficient spinels

a) Non-isothermal method—Total oxidation of Fe^{2+} ions

Figure 1 shows the weight gain Δm when the samples were heated in air at a constant rate of 2.5 deg/min from 20 to 700° . As can be seen from this Figure, the oxidation behaviour is influenced by the Ti^{4+} content. Increasing weight gain with

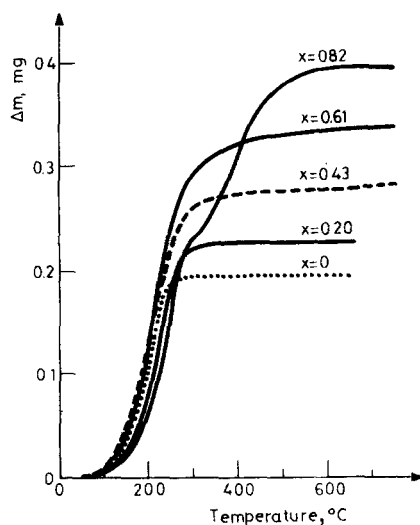


Fig. 1 TG curves for titanium-substituted magnetites heated at 2.5 deg/min

composition x results in an increase in Fe^{2+} content according to the substitution scheme $2\text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + \text{Ti}^{4+}$. Table 2 gives the value of the total weight gain Δm_{exp} for each composition. For comparison we also report Δm_{theor} calculated for the complete oxidation of Fe^{2+} ions in 6 mg of $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$. The obtained value agrees well with the experimental data.

For the composition $x = 0.82$, the weight gain reaches a stable level near 300° , then increases rapidly, and a final oxidation temperature as high as 600° is achieved for this composition. The "plateau" region can be regarded as being caused by the differences in reactivity of the Fe^{2+} ions located in the inequivalent sublattices of the spinel structure, and correspond to the temperatures of the end and beginning of oxidation of Fe^{2+} ions at octahedral sites, respectively. It is of interest to compare the present results with those obtained for $x < 0.82$. When Ti^{4+} ions replace Fe^{3+} ions at B sites in magnetite, no Fe^{2+} ions are displaced from B sites to A sites up to $x \approx 0.30$, and the final oxidation temperature is achieved at 300° . On the other hand, for $x = 0.41$ and $x = 0.60$, small but increasing numbers of Fe^{2+} ions move to A sites and a weight change is observed above 300° .

The effect of the Fe^{2+} distribution between B and A sites on the oxidation characteristics was demonstrated directly by plotting $d\Delta m/dt$ against temperature ($m = \text{mass}$, $t = \text{time}$), which for convenience is usually normalized to the starting weight. Figure 2 shows the results of this experiment as a function of the extent of substitution x . The pure magnetite and the spinel with $x = 0.20$, containing all Fe^{2+} ions at octahedral sites, exhibit only one peak, centred at about 200° . As x increases, the peak at 200° increases and the curve shows the development of a second peak, centred at about 400° , indicating that further oxidation takes place.

The positions of the two maxima shifted towards higher temperatures with increasing amount of Fe^{2+} ions. The size of the second peak, almost non-existent for $x = 0.43$, increases with increase in x , which is consistent with an increasing

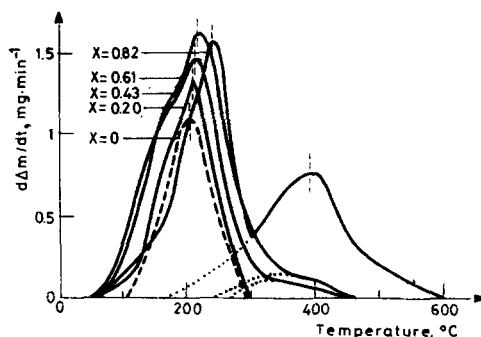


Fig. 2 DTG curves $d\Delta m/dt = f(T)$

number of Fe^{2+} ions at tetrahedral sites, having only a limited availability for oxidation in the lower temperature range.

X-ray diffraction has shown that for $x < 0.61$, one phase with a spinel structure is present, with only a decrease in the lattice parameter with the degree of reaction, in conformity with the smaller ionic radius of Fe^{3+} compared to that of Fe^{2+} . For $x = 0.82$, the sample also contains the spinel phase with a small amount of $\alpha\text{-Fe}_2\text{O}_3$ at temperatures higher than 430° . Comparison may be made with the results for Cr- or Al-substituted magnetites [2] and manganese-substituted magnetites [2], where all Fe^{2+} or Mn^{2+} ions are at tetrahedral sites (most oxidations occur in the range $350\text{--}450^\circ$), and where the covalent bonding at *A* sites renders tetrahedrally-sited Fe^{2+} or Mn^{2+} ions more stable towards oxidation than Fe^{2+} ions ionically bound at *B* sites.

b) Isothermal method—Partial oxidation of Fe^{2+} ions

In order to determine the amounts of Fe^{2+} ions at *B* and *A* sites vs. composition x , the weight gain was followed in air under isothermal conditions. The oxidation of Fe^{2+} ions at *B* sites is achieved at 160° , which requires a reaction time of a few hours for magnetites slightly substituted by titanium, and of several days for the composition $x = 0.82$. For the second stage of oxidation, corresponding to *A* Fe^{2+} ions, the procedure was as follows: After oxidation of the sample at 160° , the gas was pumped out at the end of the run, the temperature was raised to 320° and oxygen was admitted into the thermobalance. Table 2 gives the values of weight gain Δm_B and Δm_A for each site, and Fig. 3 shows the curves obtained. Thus, the cation distribution can be determined from the thermogravimetric data if the coefficients $1 - 2\lambda = a$ and $2\lambda + x = d$ of the lattice formula in the system $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ represented as $(\text{Fe}_b^{3+} \text{Fe}_a^{2+})_A(\text{Fe}_e^{2+} \text{Fe}_d^{2+} \text{Ti}_f^{4+})_B\text{O}_4^{2-}$ are known. These coefficients a and d can be calculated from the ratios $\Delta m_B/\Delta m_{\text{exp}}$, and $\Delta m_A/\Delta m_{\text{exp}}$, where Δm_{exp} represents the weight gain for pure magnetite. The distribution curve of cations at *B* and *A* sites is displayed in Fig. 4. This distribution approaches that deduced via low-temperature extrapolations (20°) from the thermoelectric coefficient measurements of Mason et al. [14].

Table 2 Experimental and theoretical weight gain for Fe^{2+} -ions oxidation in *B* and *A* sites

Samples	Δm_{exp} , mg	Δm_{theor} , mg	Δm_B , mg	Δm_A , mg	<i>B</i> sites $2\lambda + x = d$	<i>A</i> sites $1 - 2\lambda = a$
$x = 0$	0.200	0.204	0.199	—	1	0
$x = 0.20$	0.244	0.250	0.243	—	1.222	0
$x = 0.43$	0.294	0.308	0.270	0.024	1.355	0.123
$x = 0.61$	0.336	0.341	0.276	0.060	1.385	0.301
$x = 0.82$	0.386	0.387	0.224	0.161	1.126	0.807

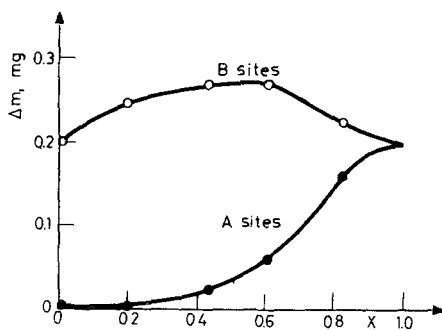


Fig. 3 Distribution of Fe^{2+} cations at *A* and *B* sites

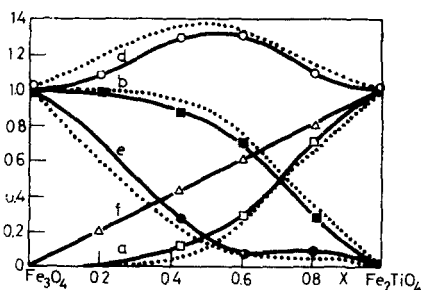


Fig. 4 Cation distribution in $(\text{Fe}_a^{2+} \text{Fe}_b^{3+})_A (\text{Fe}_c^{2+} \text{Fe}_d^{3+} \text{Ti}_f^{4+})_B \text{O}_4^{2-}$ systems, with (A) ——— results from this study, and (B) - - - - after reference [14]

Kinetic study

The purpose of this kinetic study was to measure the activation energy and the chemical diffusion coefficient of Fe^{2+} ions located at *B* sites of titanomagnetites and to compare them with the activation energy and diffusion coefficient of Fe^{2+} ions at *A* sites.

For each site, the oxidation temperature range is selected from the positions of two peaks of the $d\Delta m/dt: f(T)$ curves. As shown in Fig. 5, both oxidation temperatures T_B and T_A increased with increase in the percentage of Ti^{4+} ions.

(.) Kinetics of oxidation of octahedral Fe^{2+} ions

The plots of conversion rate α_B ($\alpha_B = M_t/M_\infty$, with M_t as the amount of Fe^{2+} oxidized to Fe^{3+} ions at *B* sites in time t , and M_∞ the corresponding amount after infinite time) vs. time (Fig. 6) for a pressure of 2×10^4 Pa of oxygen and for different temperatures show that the reaction starts immediately with maximum rate. These curves can be superimposed. A master run roughly in the middle of the series was chosen and a factor A (affinity ratio) was found for each run, such that multiplication of the time scale of the run by A would superimpose it onto the

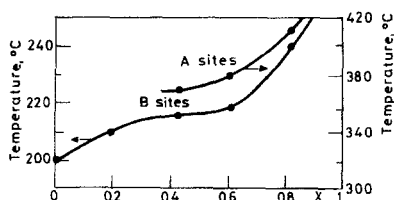


Fig. 5 Oxidation temperatures of Fe^{2+} ions at *B* and *A* sites

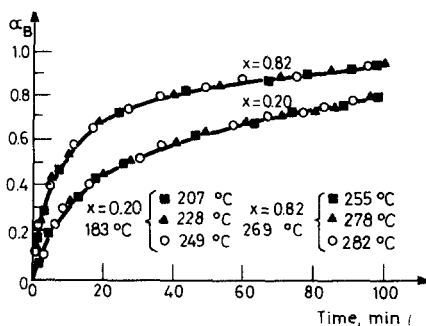


Fig. 6 Superimposition of the oxidation curves $\alpha(t)$ for *B* sites after a transformation $\{\alpha(t) \rightarrow A\alpha(t)\}$. Reference curves were taken at 183° ($x = 0.20$) and 269° ($x = 0.82$)

master run curve. $\log A$ was found to be a linear function of $1/T$. The activation energy increases from pure magnetite to substituted magnetite for $x = 0.82$ (Table 3). As in the case of Al- or Cr-substituted magnetite [17], the kinetics of this oxidation is controlled by the diffusion of vacancies generated at the solid-gas interface. Under these conditions, for spherical particles, we have shown that the experimental curves can be described by the expression:

$$\alpha_B = 1 - 6/\pi^2 \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-n^2 kt} \quad \text{with } k = \frac{\pi^2 \tilde{D}^2}{r^2} \quad (1)$$

where \tilde{D} is the chemical diffusion coefficient and r the main grain radius. For $0.20 < \alpha_B < 0.75$ and for \tilde{D} constant, this may be written as

$$\log(1 - \alpha_B) = \log 6/\pi^2 - kt = f(t) \quad (2)$$

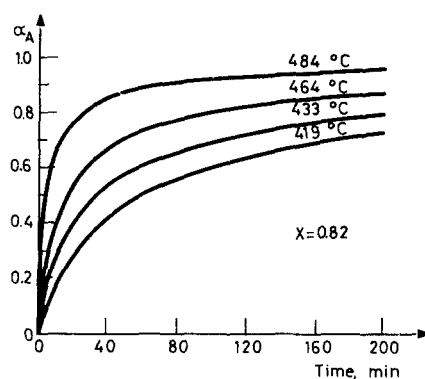
\tilde{D} is then determined directly from the slope of $\log(1 - \alpha_B) = f(t)$. The \tilde{D} values calculated at 300° are given in Table 3.

b) Kinetics of oxidation of tetrahedral Fe^{2+} ions

In this case, the oxidation kinetics was studied on preoxidized titanomagnetites with vacancies uniformly distributed throughout the grain bulk. Figure 7 shows the kinetic curves $\alpha_A = f(t)$ for a sample with $x = 0.82$, where $\alpha_A = \frac{M_t}{M_\infty}$, with M_t the

Table 3 Experimental kinetic results

Samples	Activation energy, kJ mol^{-1}		Diffusion coefficient, $D \text{ cm}^2 \text{ s}^{-1}$ at 300°C	
	<i>B</i> sites	<i>A</i> sites	<i>B</i> sites	<i>A</i> sites
$x=0$	85	—	3.5×10^{-14}	—
$x=0.20$	88	—	1.1×10^{-14}	—
$x=0.43$	127.5	—	9.1×10^{-16}	—
$x=0.61$	131	140	7.8×10^{-16}	3.3×10^{-16}
$x=0.82$	145.1	150.7	1.1×10^{-16}	4.3×10^{-17}

**Fig. 7** Kinetic curves $\Delta m = f(t)$ for tetrahedral Fe^{2+} ions

amount of Fe^{2+} oxidized to Fe^{3+} ions at *A* sites in time t , and M_∞ the corresponding amount after infinite time. The reaction was characterized by an extremely rapid initial stage, declining regularly according to a roughly parabolic law, suggesting a typical diffusion-controlled process. Although a complete analogy with a unique theoretical curve is not observed, the experimental curves can also be represented by the expression (1). A plot of $\log(1-\alpha)$ vs. kt gives a straight line in the region between approximately $\alpha = 0.25$ and 0.60 . The activation energy calculated from a plot of $\log \tilde{D}$ vs. $1/T$ was 140 kJ mol^{-1} for $x = 0.61$, and $150.7 \text{ kJ mol}^{-1}$ for $x = 0.82$ (Table 3). The diffusion coefficients appears to be lower than those found for the oxidation of Fe^{2+} ions at *B* sites. These results provide further support that *B* site Fe^{2+} ions will be oxidized more rapidly than *A* site Fe^{2+} ions.

Conclusions

Titanium-substituted magnetites $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ with $0 < x < 0.82$, prepared at relatively low temperature, are highly reactive with oxygen and could be oxidized at $< 500^\circ$ to defect phases γ with the same spinel structure, with a higher vacancy content compared to that of $\gamma\text{-Fe}_2\text{O}_3$. Although the availability for oxidation of Fe^{2+} ions at A sites is much less than that at B sites, the oxidation of A site Fe^{2+} ions preserves the original spinel structure without the formation of multiphase oxidation products as observed in a number of other studies. Further, when the cation substituting iron in Fe_3O_4 maintains a fixed valence and prefers one sublattice exclusively, the thermogravimetric measurement can be used to determine the cation distribution. This assumes, of course, that B site Fe^{2+} ions are oxidized at lower temperatures than A site Fe^{2+} ions.

For each site, the oxidation kinetics is found to be governed by the law of diffusion, under variable working conditions, of the vacancies generated at the solid-gas interface. The results indicate that the diffusion rates were composition-dependent and that the diffusion of iron(II) ions located at B sites proceeds with a lower activation energy than that of iron(II) ions located at A sites.

References

- 1 B. Gillot, F. Chassagneux and A. Rousset, *J. Solid State Chem.*, 38 (1981) 219.
- 2 B. Gillot, M. El Guendouzi, P. Tailhades and A. Rousset, *Reactivity of Solids*, 1 (1986) 139.
- 3 B. Gillot, F. Jemmali, C. Salvaing and A. Rousset, *J. Solid State Chem.*, 45 (1982) 317.
- 4 W. O'Reilly and S. K. Banerjee, *Nature*, 211 (1966) 26.
- 5 V. Kropacek and M. Lastovickova, *J. Geophys.*, 48 (1980) 40.
- 6 R. Frost and P. L. Gai, *Acta Cryst.*, A 36 (1980) 678.
- 7 P. W. Readman and W. O'Reilly, *Phys. Earth. Planet. Inter.*, 4 (1970) 121.
- 8 R. Freer and W. O'Reilly, *Mineral. Mag.*, 43 (1980) 889.
- 9 Y. Ishikawa, S. Sato and Y. Syono, *Tech. Rep. Inst. for Solid State Physics. Univ. of Tokyo, Series A*, n° 455 (1971).
- 10 P. Mollard, A. Colomb, J. Devenyi, A. Rousset and J. Paris, *I.E.E.E. Trans. Mag. Vol. Mag.*, 11 (1975) 894.
- 11 S. Akimoto, T. Katsura and M. Yoshida, *J. Geomagn. Geoelec.*, 9 (1957) 165.
- 12 L. Neel, *Adv. Phys.*, 4 (1955) 191.
- 13 R. Chevallier, J. Bolfa and S. Mathiew, *Bull. Soc. Franc. Min. Crist.*, 78 (1955) 307.
- 14 A. Trestman-Matis, S. E. Dorris, S. Kumarakrishnan and T. O. Mason, *J. Am. Ceram. Soc.*, 66 (1983) 829.
- 15 B. Gillot, F. Jemmali, L. Clerc and A. Rousset, *C.R. Acad. Sc. Paris, Ser. C, II*, 302 (1986) 211.
- 16 P. Poix, *Liaison interatomique et propriétés physiques des composés minéraux*, SEIDES, Paris (1968) 82.
- 17 B. Gillot, J. Tyranowicz and A. Rousset, *Mat. Res. Bull.*, 10 (1975) 775.

Zusammenfassung — Es wird über nicht-isotherme und isotherme TG-Untersuchungen der Kationenverteilung in submikronen Titanomagnetiten ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ mit $0 < x < 0.82$) berichtet. Titanomagnetite mit $x < 0.61$ konnten unter 500° zu Titan-substituierten Magnetiten oxydiert werden, die eine größere Leerstellenkonzentration als $\gamma\text{-Fe}_2\text{O}_3$ aufweisen. Die DTA-Ergebnisse zeigen, daß die zur Oxydation von Fe^{2+} - zu Fe^{3+} -Ionen notwendige Temperatur mit zunehmender Titansubstitution ansteigt, die Phasenübergangstemperatur dagegen absinkt. Die Kinetik der Oxydation ist unter verschiedenen Arbeitsbedingungen und bei unterschiedlichen Konzentrationen der an der Fest-Gas-Grenzfläche gebildeten Fehlstellen diffusionsbestimmt. Die Aktivierungsenergie der Diffusion von an den oktaedrischen Stellen lokalisierten Fe(II)-Ionen ist geringer als die von tetraedrisch koordinierten Fe(II)-Ionen. Diffusionsgeschwindigkeiten werden als von der Konzentration abhängig erkannt und die Variationen können mit der Verteilung der Eisenionen im Subgitter identifiziert werden.

Резюме — Проведено неизотермическое и изотермическое ТГ исследование распределения катионов в субмикронных титаномagnetитах состава $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ с $0 < x < 0.82$. Титаномagnetиты состава $x < 0.61$ при температурах ниже 500° окисляются до титанозамещенных магнетитов, содержащих более высокую концентрацию вакансий по сравнению с $\gamma\text{-Fe}_2\text{O}_3$. Результаты ДТА исследований показали, что температура окисления двухвалентного железа до трехвалентного увеличивается с увеличением содержания титана, тогда как температура фазового изменения уменьшается. Установлено, что кинетика окисления подчиняется закону диффузии для переменных экспериментальных условий и для различных степеней образования вакансий на границе раздела твердое тело — газ. Диффузия ионов двухвалентного железа, расположенных в октаэдрических узлах решетки, протекает с более низкой энергией активации по сравнению с ионами железа в тетраэдрических узлах решетки. Скорости диффузии зависят от состава веществ, что может быть связано с распределением ионов железа в подрешетках.