Reactivity of Hydrous Ferric Oxide Containing Metallic Cations

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Dedicated to Professor Walter Feitknecht

Summary

Hydrous ferric oxide prepared by precipitation contains the bound water in the form of OH groups. Its dehydration occurs as an endothermic reaction between 100 and 200 °C. The amount of bound water increases with increasing amount of amorphous material within the solid oxide. The crystallization of the amorphous solid which proceeds on ageing in water is retarded by addition of metallic cations to the oxide; especially Cu-ions show a very strong retardation effect.

The reactivity of the oxide containing different kinds of metallic cations and different amounts of the bound water, has been investigated in a number of reactions. The amount of hydrazine decomposed on the oxide increases linearly with the amount of bound water. The rate of dissolution of the oxide in acid solutions obeys the equation, $d[Fe^{3+}]/dt = k\ (H^+)^{0.5}\ (A^-)^m$, where (H^+) and (A^-) denote the concentrations of hydrogen ions and anions and m is a constant. If it is assumed that the bound water forming the Fe–(OH)–Fe bridge provides the active sites this equation may be explained. The rate of the adsorption of a gaseous CO–O_2 mixtures follows the Elovich equation and the initial rate increases with the amount of bound water. Finally, the temperature of the exothermic transformation of magnetite into α-Fe_2O_3 is examined. Cr, Li and Cu-ions showed a accelerating effect on the reaction, and Ti and B-ions a retarding effect.

Introduction

The oxides and hydroxides of iron appear in a variety of structures such as α-Fe_2O_3, γ-Fe_2O_3, FeO, $Fe(OH)_2$, $Fe(OH)_3$, Fe_3O_4, α-FeOOH and γ-FeOOH[1]. These oxides or hydroxides are usually prepared by a precipitation method, in which conditions such as temperature, *p*H, concentration and iron-salt used contribute strongly to structure, crystallinity, particle size and other physico-chemical properties of the resulting product. $Fe(OH)_3$ is always amorphous while the other solid phases are usually crystalline.

It is widely believed that the reactivity of solids depends more or less on the nature and the concentration of lattice imperfections such as point defects, line defects and impurities (structure sensitivity).[2] On the other hand, it has often been observed[3] that different solid catalysts which are claimed to have the same x-ray structure exhibit very different catalytic activities.

In addition, for the anticorrosive passivation film formed on the metal, the stability against corrosion has been found to change with time and temperature of the

[1] R.B. Heslop, *Inorganic Chemistry*, Elsevier, London 1960.
[2] *Reactivity of Solids*, Proceedings of the 4th International Symposium on the Reactivity of Solids, ed. by J.H. De Boer, Elsevier, London 1961. *Reactivity of Solids*, 5th International Sympsium on the Reactivity of Solids, ed. by G.-M. Schwab, Elsevier, London 1965.
[3] T. Takahashi, Thesis, 1962.

passivation[4], even if the passivation is made at the same potential. Moreover, the depolarizability of manganese dioxide in Leclanché cells is not necessarily dependent on the structure of the oxide[5,6]. These facts show that, in addition to the structure sensitive factors, there may be other factors which control the reactivity of solids. Such factors could be generated by transformation processes which lead from the initial amorphous state of a fresh precipitate to the final crystalline state by ageing or heat treatment. From this point of view, it is important to elucidate what kind of factors may determine the reactivity of amorphous solids.

Generally, amorphous solids have been regarded to be more reactive than well crystallized ones. Discussing the reactivity of amorphous solids, the concept of lattice imperfection can not be applied, since the amorphous solids show no long-range order of the atoms.

Recently, SHIBATA and OKAMOTO[7] observed with the aid of a tracer technique that the passive film on stainless steels containing a larger amount of bound water was less stable to the corrosion reaction in acid medium than the passive film containing a smaller amount of bound water. BRENET[8] and GOSH[9] have emphasized that the depolarizability of manganese dioxide is closely associated with the presence of bound water in the form of hydroxyl groups.

The authors[10] have demonstrated that the catalytic decomposition of hydrazine sulphate on hydrous ferric oxide in alkaline solution was enhanced with increasing amount of bound water in the oxide and that the electrical conductivity was increased.

In the present paper, the effect of metallic cations on reactivity of the amorphous ferric oxide and poorly crystalline magnetite is investigated. In the discussion of the results it is shown that the bound water in the iron oxides may play an important role on the reactivity.

Experimental

Materials. Hydrous ferric oxide (Sample a): The ferric hydroxide gel was prepared at 90 °C by mixing 750 ml of 0.067 M–$Fe(NO_3)_3$ with 54 ml of 6N–NH_4OH. The *p*H of the suspension was 9.05. The hydroxide obtained was carefully washed and left to age under water at 25 °C for variable periods. It was first dried at room temperature (48 hrs., 20 mm Hg) and then heated to 100 °C (6 hrs., 20 mm Hg). The samples to be studied were ground (200 to 300 mesh) and calcinated in air at given temperatures. *Sample b* was prepared as above at 30 °C, but 6N–NaOH was used in stead of NH_4OH. The amount of 6N–NaOH was adjusted to give a solution of *p*H ~12.5. The procedure for adding of metallic cations to the oxide was as follows: 0.5 M solutions of $LiNO_3$, $Ti_2(SO_4)_2$, $Cu(NO_3)_2$, $Ni(NO_3)_2$ and $Cr(NO_3)_3$ were mixed with 50 ml of $Fe(NO_3)_3$ solution. The ratio of the two cations was adjusted to the desired concentration of the metallic cation in the oxides. After dilution with water to a volume of 750 ml, the ferric hydroxide was prepared by adding 6M–NaOH. $MoO_3 \cdot H_2O$ which is very little soluble in water, was dissolved in 6N–NaOH. The oxides were aged at 25 °C for 15 days in a solution of *p*H 12.5.

Magnetite: The specimen was prepared according to SUGIHARA[11]: 50 ml portions of 1 M $FeSO_4$ and 2 M $Fe_2(SO_4)_3$ were heated to 95 °C and poured into 125 ml of 6N–NaOH at 95 °C. The resulting black precipitate was washed and dried at room temperature for 24 hrs. in a desiccator and heated at 85 °C *in vacuo* to constant weight. The dried material was ground in an agate mortar (200 to 300 mesh). The addition of metallic cations to the magnetite was achieved by adding various amounts of 10% solutions of $Cr(NO_3)_3$, $Na_2B_4O_7$, $LiNO_3$, $Ti_2(SO_4)_3$ and $Cu(NO_3)_2$.

Differential thermal analysis (DTA) was carried out in air using Al_2O_3 as a standard (Thermoflex 8001, Rigaku Denki Co. Ltd.). The rate of heating was 10 °C/min.

X-ray diffraction: The samples were examined by the powder method with Fe K_α or Co K_α radiation. A diffractometer Geigerflex 2030/p (Rigaku Denki Co. Ltd.) was used.

The decomposition of hydrazine was carried out in a N_2 atmosphere at 35 °C. The oxide (0.5 g of sample a) was immersed in a mixture of aqueous solution of 0.4N–$N_2H_4 \cdot H_2SO_4$ (5 ml) and 0.5N–NaOH (15 ml). After immersion for 24 hrs. the amount of decomposed hydrazine was determined iodimetrically.

Dissolution rate: The dissolution reaction was carried out by immersing the oxide (1.2 g of sample a or b) in 120 ml of the acid solution, which was placed in a 300 ml flask with glass stopper, and stirred at a constant rate. Samples of about 10 ml were withdrawn periodically; the amount of ferric ions was measured colorimetrically using the thiocyanate method.

The adsorption rate of a $CO-O_2$ mixture (2 : 1) was measured at 100 °C and 10 mm Hg using a constant pressure apparatus. Before the adsorption measurement, the specimen (0.3 g of sample a and b) was degassed for 5 hrs. at 100 °C and 10^{-5} mm Hg.

Results and Discussion

Bound water in hydrous ferric oxide

In a previous paper[12] we measured the amount of bound water and determined the structure of hydrous ferric oxides (sample a). The following results were obtained. DTA: Fresh oxide shows an endothermic peak at 170 °C and an exothermic peak at 300 °C, while oxides aged for longer than 15 days showed in addition another endothermic peak at 300 °C. Moreover, the exothermic peak of aged oxide was reduced and shifted to a higher temperature. The sample exposed to water at room temperature showed a large endothermic peak at 100 to 110 °C corresponding to the desorption of the adsorbed water.

X-Ray: Fresh and aged oxides heated to 100 °C showed no x-ray diffraction lines indicating that they

[4] T. SHIBATA, private communication.
[5] M. FUKUDA, *J. Electrochem. Soc. Japan 28* (1960) 67.
[6] J. BRENET, *C. R. Acad. Sci. 246* (1958) 2469.
[7] T. SHIBATA and G. OKAMOTO, *Nature* (1965) 1350, and *3rd International Congress on Metallic Corrosion, 1966*, in press.
[8] J. P. BRENET, *Batteries*, p. 357, Pergamon, London 1963.
[9] S. GOSH, *J. Electrochem. Soc. Japan 34* (1966) 38.
[10] G. OKAMOTO, R. FURUICHI and N. SATO, *Electrochim. Acta 12* (1967) 1289.
[11] M. SUGIHARA, H. SATO and M. SAITO, *J. Chem. Soc. Japan, Ind. Chem. Sect. 65* (1962) 1748.
[12] R. FURUICHI, N. SATO and G. OKAMOTO, *J. Chem. Soc. Japan, Ind. Chem. Sect. 68* (1965) 1175.

are in the amorphous state. At elevated temperature both oxides are converted into α-Fe_2O_3, the conversion starting at 300 °C (fresh oxide) and 200 °C (aged oxide). Crystallisation is also observed after ageing in water for more than 15 days.

TGA: Fresh oxide showed a smooth TGA curve up to 400 °C, while in the case of aged oxide a linear part of the curve appeared in the temperature range between 220 and 300 °C.

The rate of removal of the water from the oxide corresponding to two endothermic peaks at 170 and 300 °C in the DTA curve was represented by a first order equation. The estimated activation energies were 0.3 kcal/mol (170 °C) and 21 kcal/mol (300 °C), respectively. From these facts it was concluded that there are three different kinds of water molecules present in the oxide, each corresponding to a particular endothermic peak in the DTA curve: adsorbed water molecules (110 °C), "bound water" (170 °C) and lattice water (300 °C). The IR-spectrum of the oxide containing bound water shows an absorption band at 3250 cm^{-1} [10]. Moreover, the NMR spectrum[10] of the bound water showed the signal of a one-proton system with considerable broad line width. From the results of the IR and NMR investigation it seems reasonable to conclude that the bound water is present in the form of hydrogen-bonded OH groups[13].

Table 1 contains the values of the amount of bound water and lattice water in the oxide; the values were estimated by comparison between DTA and TGA curves. The amount of bound water is seen to decrease with the time of ageing, while that of lattice water increases.

Table 1. Amount of water in hydrous ferric oxide (sample a)

Water Content (weight-%)	0	Ageing Time (day) 15	28	56
Lattice Water		1.7	2.8	3.0
Bound Water	5.3	4.0	3.1	2.9

In a study of electrical conductivity[10] it was found that the hydrous ferric oxide was a semiconductor of *n*-type and that the logarithm of the conductivity i increases linearly with the amount of bound water x; the relation between the log i at a constant temperature and the activation energy for conduction, E, was found to be

$$\log i = A - B \times E, \qquad (1)$$

where A and B are constants. Since Eq. (1) satisfies MAYER's rule, the bound water present in the form of the OH groups is assumed to form donor centers in the hydrous ferric oxide, which will be represented by $Fe_2O_{3-\frac{x}{2}}(OH)_x$.

[13] O. GLEMSER, *Nature 183* (1959) 943.

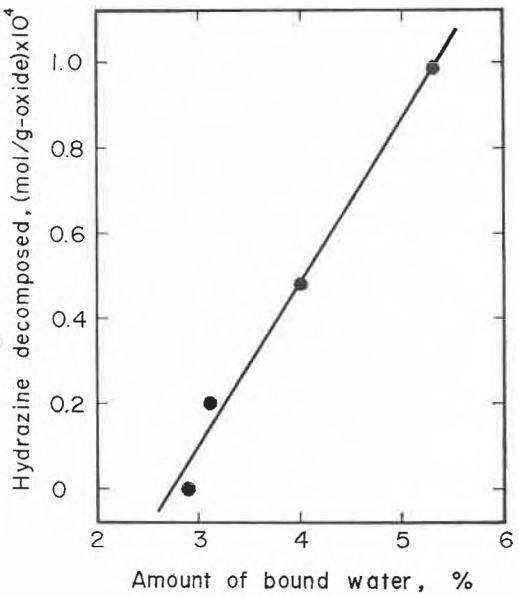

Fig. 1. Relation between the amount of hydrazine decomposed by hydrous ferric oxide (sample a) treated at 110 °C and the amount of bound water

Reactivity of hydrous iron-oxides

(1) Decomposition of hydrazine sulphate[10]: The amount of decomposed hydrazine was measured for both fresh oxides, and aged oxides heated at 110 °C. In Fig. 1 the amount of decomposed hydrazine is plotted as a function of the amount of bound water (Table 1).

It has been reported[5] that hydrazine sulphate in alkaline solution is dissociated, according to

$$(N_2H_4)_2 \cdot H_2SO_4 = 2\,N_2H_5^+ + SO_4^{-2} \qquad (2)$$

TIKKANEN[14] has confirmed by x-ray diffraction that the decomposition of hydrazine by ferric oxide results in the formation of magnetite. It is therefore reasonable to conclude that the active points for the decomposition reaction correspond to the sites of the bound water which forms donor centers in the oxide. Hence, the reaction of hydrazine with the hydrous ferric oxide may be formulated as a coupled reaction including the following steps:

$$N_2H_5^+ = N_2 + 5\,H^+ + 4\,e \qquad (3)$$

$$3\,Fe_2O_{3-\frac{x}{2}}(OH)_x + 2\,H^+ + 2\,e = 2\,Fe_3O_4 + \left(1 + \frac{3}{2}x\right) H_2O \qquad (4)$$

(2) Dissolution reaction in acid solutions: For further examination of the reactivity of hydrous ferric oxide, the dissolution behaviour in acid was investigated. The dissolution rate of sample a aged for different periods is shown in

[14] M.H. TIKKANEN, *Werkstoffe u. Korros. 13* (1961) 351.

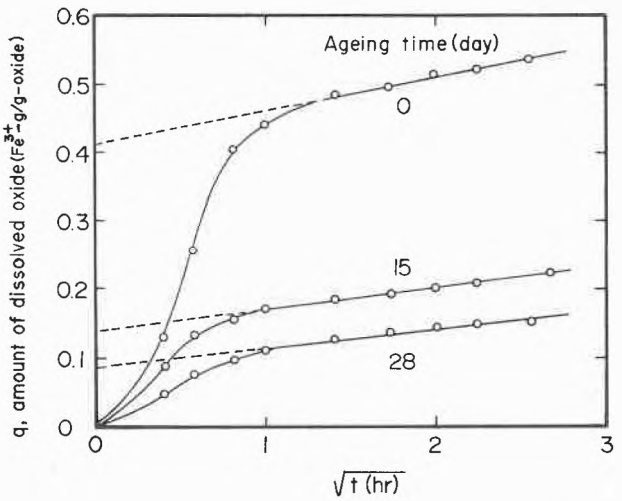

Fig. 2. Effect of ageing time on the dissolution rate of hydrous ferric oxide (sample a) treated at 110 °C, in 5%-H_2SO_4 at 25 °C

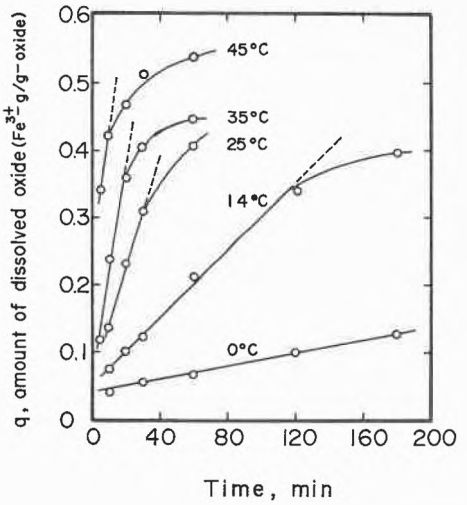

Fig. 3. Effect of temperature on the dissolution rate of fresh oxide (sample a) treated at 110 °C in 1N—H_2SO_4

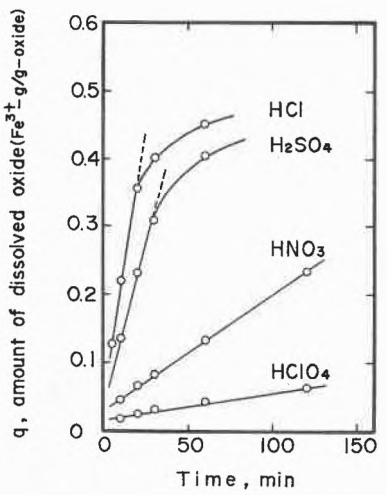

Fig. 4. Rate of dissolution at 25 °C in 1N—HCl, H_2SO_4, HNO_3 and $HClO_4$, of fresh oxide (sample a) treated at 110 °C

Fig. 2, in which the amount of dissolved ferric ion is plotted against the square root of time. It is seen that the curve can be divided into two sections. The initial part does not obey the parabolic law whereas it does so in a latter stage of the reaction. If the term q_0 is defined as the intercept obtained by extrapolating the linear part of the curve and q as the amount of dissolved ferric ion at time t, the following equation is obtained,

$$q = q_0 + k\sqrt{t}, \qquad (5)$$

where k is a constant. It can be seen (Fig. 2) that the values of q_0 decrease with ageing. When the hydrous ferric oxide was converted into α-Fe_2O_3, the value of q_0 was found to become zero. The amount of q_0 is therefore considered to correspond to the amorphous part of the oxide. On the other hand, the linear part of the curve in Fig. 2 obeying the parabolic law suggests that the rate determining process is the diffusion of protons from the solution into the solid phase[15].

In order to obtain the kinetic equation of the dissolution reaction of the amorphous oxide, the dissolution rate of the fresh oxide heated at 110 °C was measured at different temperatures using 1N—H_2SO_4 as a solvent. In the initial stage of the reaction, the dissolution rate is represented by (Fig. 3):

$$d[Fe^{3+}]/dt = k' \ (k' = \text{const}). \qquad (6)$$

Equation (6) applies also for the case that H_2SO_4 is replaced by HCl, HNO_3 or $HClO_4$ (Fig. 4). The slopes of the straight lines in Fig. 4 and hence the rates k', in Eq. (6), shows however, different values. These results indicate that the anion in the acid solution plays an important role in the dissolution of the oxide. On the other hand, as pointet out by Pryor[16], the dissolution reaction consists of the reaction between O^{2-}-ions in the oxide and H^+-ions in the solution. Accordingly, the value of k' in Eq. (6) is expected to depend on the concentration of protons and anions in the solution. To examine the effect of the concentration of anions our measurements were extended to solutions of pH = 0.4, with different amounts of $NaNO_3$, Na_2SO_4 and NaCl and to solutions of pH = 0 containing $NaClO_4$. The results are shown in Fig. 5, where the activity of the anions in the solution was calculated from the mean activity coefficient of the corresponding salts[17]. There is a linear relationship between the logarithm of the dissolution rate and the activity of the present anion (Fig. 5).

[15] R. Furuichi, N. Sato and G. Okamoto, *J. Chem. Soc. Japan, Ind. Chem. Sect. 68* (1965) 1178.

[16] M. J. Pryor and U. R. Evans, *J. Chem. Soc. 3330* (1949).

[17] *Denki Kagaku Binran*, The Electrochemical Society of Japan, 1958.

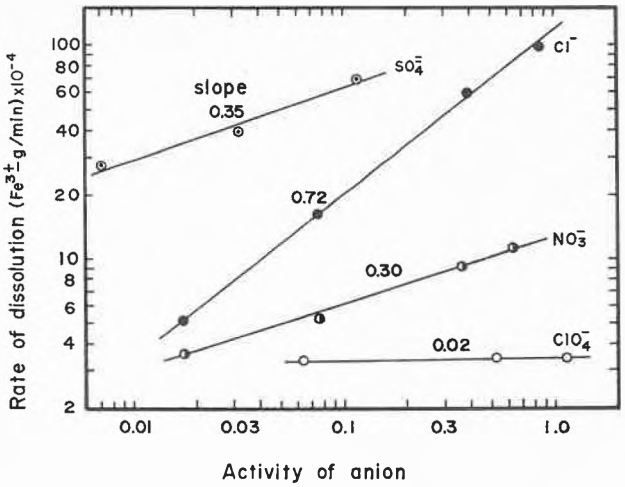

Fig. 5. Relation between the dissolution rate of hydrous ferric oxide (sample a) at 25 °C and the activity of anion in solution

The slope of the straight lines depends on the nature of the anion. For ClO_4^- the slope is comparatively small (0.02). The dissolution rate is therefore assumed to be constant. To study the effect of H^+-concentration pure $HClO_4$ (1.02, 2.02 and 2.85 M) and $HClO_4$ solutions of $pH = 0$, 0.4 and 1.2 containing 0.38 mol/l-Na_2SO_4 were used. Fig. 6 and Fig. 7 show the linear relationship between the logarithm of the rate and the logarithm of the proton activity. The slope is approximately the same in both cases. On the basis of these results, the rate of dissolution is better expressed by Eq. (7) than by Eq. (6):

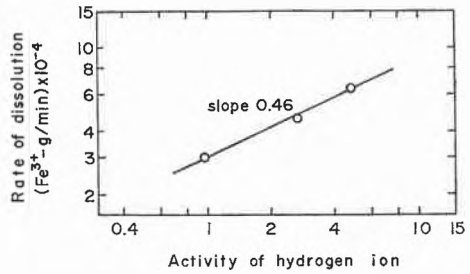

Fig. 6. Effect of hydrogen ion concentration on the dissolution rate of hydrous ferric oxide in pure perchloric acid at 25 °C (sample a)

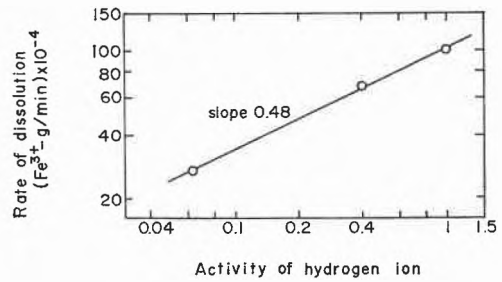

Fig. 7. Effect of hydrogen ion concentration on the dissolution rate of hydrous ferric oxide in perchloric acid solution containing 0.38 M SO_4^{2-} ion at 25 °C (sample a)

$$d[Fe^{3+}]/dt = k\,[H^+]^{0.5}\,[A^-]^m \qquad (7)$$

(k: rate constant, $[H^+]$: H^+-concentration, $[A^-]$: anion concentration, m: slope of the straight lines in Fig. 5.)

MULAY[18] has suggested that the water present in the hydrous ferric oxide gel is responsible for structures such as Fe–(OH)–Fe. Assuming such Fe–(OH)–Fe groups to be present the dissolution reaction can be formulated as

$$[Fe^{III}\text{—}(OH)\text{—}Fe^{III}]_{solid} + H^+ + m'A^- + H_2O \rightleftharpoons \left[Fe^{III}\begin{matrix}(OH_2) & A^-_{m'/2} \\ A^-_{m'/2} & (H_2O)\end{matrix}Fe^{III}\right]_{solid} \qquad (8)$$

$$\left[Fe^{III}\begin{matrix}(OH_2) \\ A^-_{m'/2}\end{matrix}\right]_{solid} + (5 - m'/2)\,H_2O \xrightarrow{\text{rapid}} \left[Fe^{III}\begin{matrix}(OH_2)_{6-m'/2} \\ A^-_{m'/2}\end{matrix}\right]_{solid} \qquad (9)$$

$$\left[Fe^{III}\begin{matrix}(OH_2)_{6-m'/2} \\ A^-_{m'/2}\end{matrix}\right]_{solid} \xrightarrow{\text{slow}} [Fe^{III}(H_2O)_{6-m'/2}\,(A^-)_{m'/2}]_{liquid} \qquad (10)$$

when Eq. (8) is assumed to represent an equilibrium state. From Equations (8), (9) and (10) we obtain:

$$d[Fe^{3+}]/dt = k''K^{1/2}\,[Fe^{III}\text{–}(OH)\text{–}Fe^{III}]^{1/2}\,[H^+]^{1/2}\,[A^-]^{m'/2}[H_2O]^{1/2} \qquad (11)$$

where k'' is a constant and K is the constant derived from Eq. (8):

$$K = [Fe^{III}(H_2O)\,A^-_{m'/2}]^2 / [Fe^{III}\text{–}(OH)\text{–}Fe^{III}]\,[H^+]\,[A^-]^{m'}\,[H_2O] \qquad (12)$$

In Eq. (11), the term $[H_2O]$ is constant, since water is present in a large excess. If $[Fe^{III}\text{—}(OH)\text{—}Fe^{III}]$ is assumed to be constant and all the constant terms in Eq. (11) are represented by k and $m'/2$ by m, Eq. (11) is identical with Eq. (7).

The effect of metallic cations on the dissolution rate (at 25 °C) is shown in Fig. 8. The aged oxides show a lower rate of dissolution than the fresh oxides except for the oxide containing Cr. To clarify the influence of the different cations, the dissolution rate is plotted against $(r_{Me}/r_{Fe^{3+}})$, (Fig. 9). The rate of dissolution increases generally with increasing ionic radii. In the case of aged oxides, however, there is no effect observed for cations smaller than Fe^{3+}.

[18] L.N.MULAY and M.C.NAYLOR, *Advances in the Chemistry of Coordination Compounds*, p. 520, Macmillan, New York 1961.

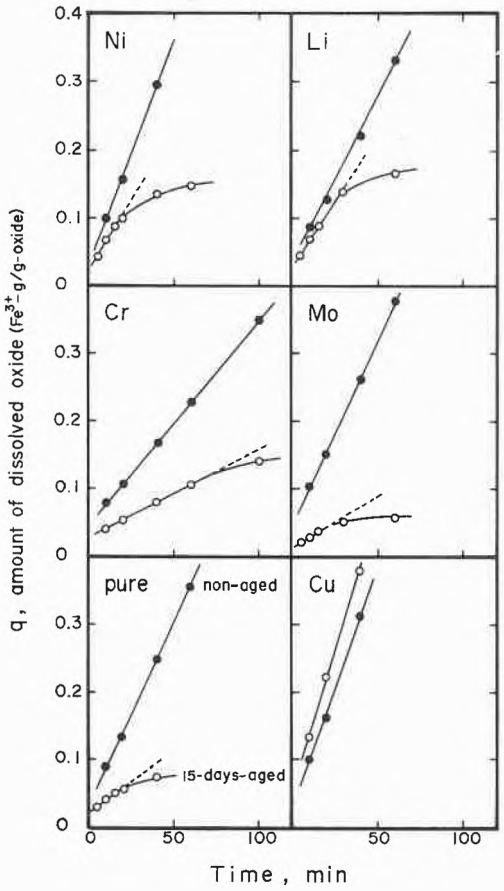

Fig. 8. Rate of dissolution at 25 °C of hydrous ferric oxide (sample b) containing metallic cations. —●— non-aged oxide, —○— 15-days aged oxide

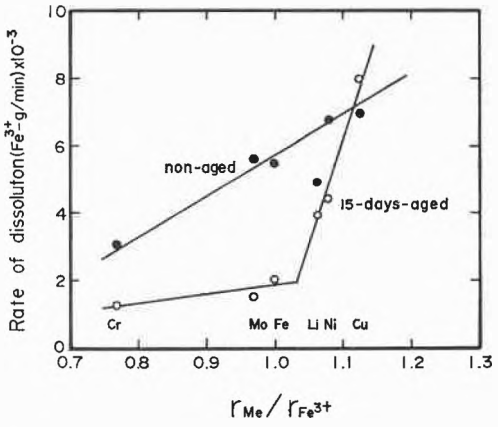

Fig. 9. Relation between the ratio of ionic radius and the dissolution rate of hydrous ferric oxide (sample b) in 1N—H_2SO_4 at 25 °C. —●— fresh oxide, —○— aged oxide

A steep increase is observed for $r_{Me}/r_{Fe^{3+}} > 1$. This phenomenon is interpreted as follows: The large metallic cations exert a greater strain in the polymerized structure and therefore yield a more unstable oxide structure which in turn shows a greater reactivity.

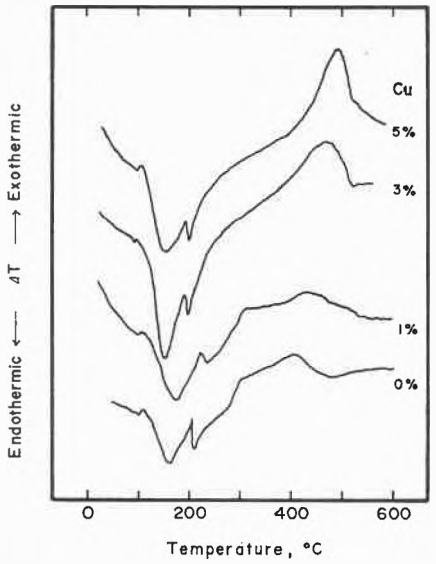

Fig. 10. DTA of non-aged oxide (sample b) containing Cu-ion

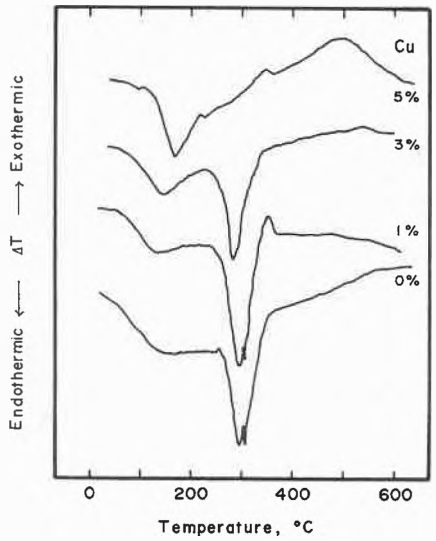

Fig. 11. DTA of 15-days aged oxide (sample b) containing Cu-ion

In Fig. 10 and Fig. 11, DTA curves of fresh and aged oxides (sample b) containing 0, 1, 3 and 5% of Cu-ion are shown. Fresh oxides exhibit the endothermic peak at about 150 °C, which is considered to correspond to the loss of the bound water. In the case of aged oxides (Fig. 11), endothermic peaks can be observed at 300 °C and at 150 °C; the former is thought to correspond to the lattice water and the latter to the bound water. Fig. 12 shows the x-ray patterns (Fe K_α) of fresh and aged oxides containing 0 and 5% Cu-ion heated at 200 °C. The fresh oxides are amorphous. The aged oxide containing 5% Cu is also amorphous wheareas the aged oxide containing no Cu is crystalline. It is concluded that the crystallization is retarded by the addition of more than 3 to 5% Cu. As discussed in Eq. (8), the active sites on the oxide for

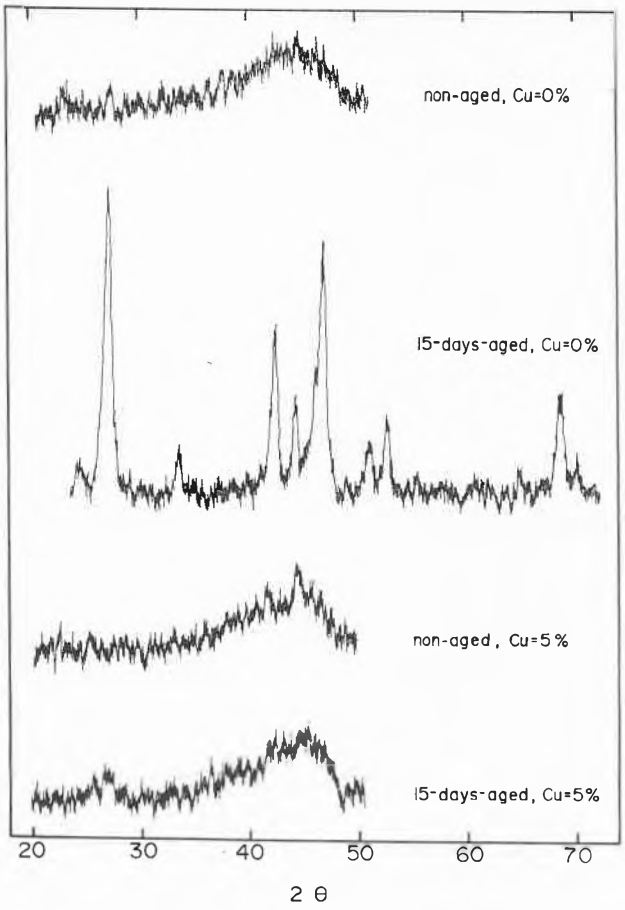

Fig. 12. X-ray diffraction patterns of hydrous ferric oxide (sample b) Target; Fe

the dissolution reaction appear to be the sites associated with the bound water. To confirm this assumption, the rate of dissolution of sample b (5% H_2SO_4, 25 °C) was measured and the amount of bound water of these oxides were estimated from the TGA curves. The results are shown in Table 2.

Table 2. Rate of dissolution and amount of bound water of sample b

Ageing time (day)	15	15	0	15
Cu-ion content (%)	0	2	0	5
Bound water (%)	2.67	3.12	5.02	5.82
Dissolution rate (Fe^{3+}-g/min)	0.24×10^{-2}	0.32×10^{-2}	0.60×10^{-2}	1.0×10^{-2}

It can be seen that the rate of dissolution increases with increasing amount of bound water.

(3) Adsorption of CO–O_2 mixtures: The reactivity of the hydrous oxide in the gas phase reaction was investigated at 100 °C by measuring the rate of adsorption of CO–O_2 mixtures. The adsorption rate of sample a, aged for different periods and heated at 200 °C, is shown

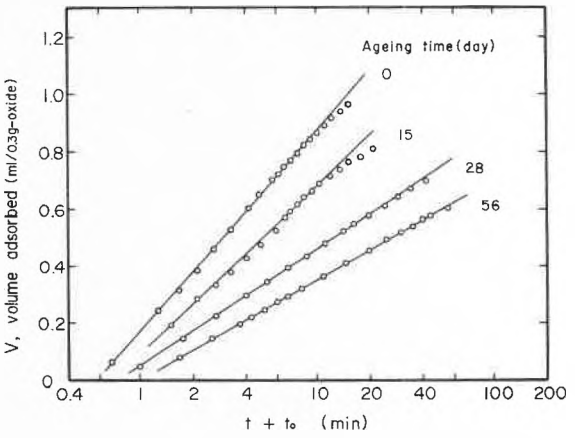

Fig. 13. Effect of ageing time on the adsorption rate of CO—O_2 mixture. Sample a treated at 200 °C. Pressure of CO—O_2 is 10 mm Hg

in Fig. 13. The rate of adsorption can be represented by

$$V = k' \log (t + t_0) + c, \tag{13}$$

where V is the amount of adsorbed gas (ml/0.3 g), t is the time and k', t_0 and c are constants. Eq. (13) is the ELOVICH or ROZINSKY-ZELDOVICH[19] equation. Its differential form is

$$dV/dt = k \exp (-\alpha v), \tag{14}$$

where k is the initial rate of adsorption and α is a constant. Integration of Eq. (14) yields

$$V = (2.303/\alpha) \log (t + 1/\alpha k) - (2.303/\alpha) \log 1/\alpha k. \tag{15}$$

The meaning of the constants in Eq. (13) is revealed by comparing Eq. (13) with Eq. (15). PEERS[20] has interpreted the ELOVICH equation as follows; the number of active sites (n) for the adsorption reaction changes with the amount of adsorbed gas (V) according to

$$n = n_0 \exp (-\alpha V),$$

where α is a constant and n_0 is the number of active sites at $V = 0$. The rate of adsorption is assumed to be proportional to n. According to this interpretation, the initial rate, k, in Eq. (14) should contain the term n_0, the number of active sites on the bare surface. On the other hand, the value of k can be calculated from the slope of line in Fig. 13 and the value of V at $(t + t_0) = 1$. The calculated values of k were found to decrease with increasing ageing time. Since amorphous hydrous ferric oxide is converted into α-Fe_2O_3 during ageing it is believed that the number of active sites for adsorption of CO–O_2 mixed gas depends on the extent of crystalliza-

[19] ROGINSKY and ZELDOVICH, *Acta Physicochim. 1* (1934) 449.
[20] A.M. PEERS, *J. Catalysis 4* (1965) 672.

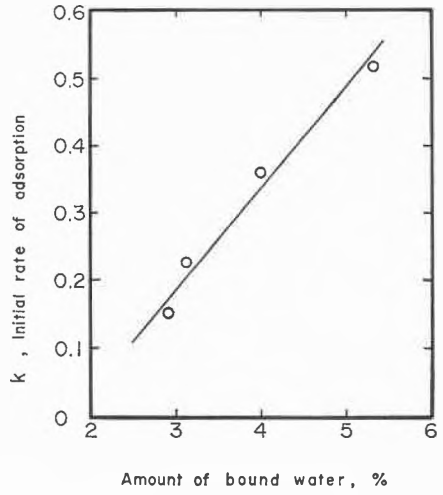

Fig. 14. Relation between the amount of bound water and the initial rate of adsorption

tion. Accordingly, the fact that the initial rate of adsorption, k, decreased with the ageing time suggests a decrease of the number of active sites on the oxide (sample a). If we assume that the active sites exist in the amorphous part of the oxide, the value of n_0 would have to decrease with ageing time. Moreover, the amount of bound water is considered to be proportional to the amount of amorphous oxide. Hence, the number of active sites, n_0, can be assumed to be related with the amount of bound water. A linear relationship is expected to hold between the amount of bound water and the initial rate of adsorption, k. In Fig. 14, the initial rate of adsorption (calculated from the data in Fig. 13) is plotted against the amount of bound water (Table 1). The diagram confirms the linear relation between n_0 and k. Hence the active sites for the adsorption of CO–O_2 mixture consist of the bound water.

The adsorption experiment was carried out also with sample b containing Cu (Fig. 15). Since the rate of adsorption on sample b obeys also the ELOVICH equation [Eq. (13)] the initial rate of adsorption, k, can be calculated as before (Table 3).

Table 3. Initial adsorption rate, k, of CO—O_2 on sample b

Ageing time (days)	15	15	0	15
Cu-ion-content (%)	0	2	0	5
k (ml/min 0.3-g-oxide)	0.064	0.075	0.289	0.987

Comparing of the values of k (Table 3) with the amount of bound water (Table 2) one finds that k increases with the amount of bound water.

The reactivity of hydrous ferric oxide with respect to the adsorption of CO–O_2 mixtures is explained by assuming that the bound water provides the active sites for the CO–O_2 adsorption. The details of the interaction between the active sites and adsorbed gases, however, remain to be studied.

(4) Transformation of Fe_3O_4 → α-Fe_2O_3: The oxidation reaction of Fe_3O_4 to γ-Fe_2O_3 and α-Fe_2O_3 has been studied in details by FEITKNECHT[21]. This reaction is a typical solid state reaction and was used to examine the reactivity of hydrous oxide containing metallic cation. It has been reported[21] that during oxidation of magnetite particles for instance in air two exothermic peaks appear at about 200 and 600 °C; the peak at 200 °C corresponds to the oxidation reaction Fe_3O_4 → γ-Fe_2O_3 and the one at 600 °C to the transformation of γ-Fe_2O_3 → α-Fe_2O_3. FEITKNECHT[21] showed also that magnetite particles larger than 5500 Å in diameter are oxidized directly to α-Fe_2O_3. In the present experiments the temperature change of the exothermic reaction was taken as an indication of the facility of the reaction Fe_3O_4 → α-Fe_2O_3. The diffraction pattern (CoK_α) of the magnetite sample used in our DTA experiment shows rather broad lines (Fig. 16). The DTA curve of the magnetite is shown in Fig. 17. The exothermic peak at 200 °C, which corresponds to the oxidation of Fe_3O_4 to γ-Fe_2O_3, does

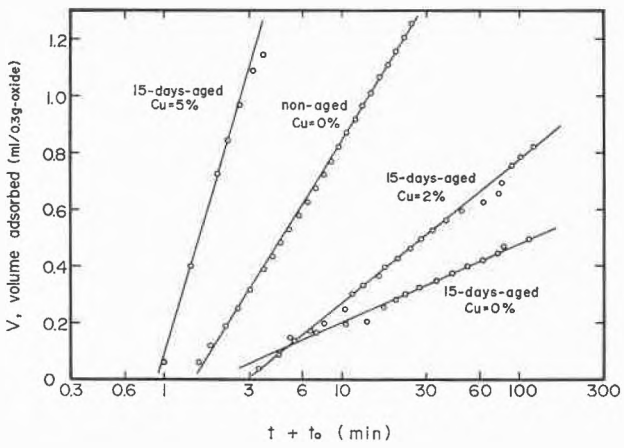

Fig. 15. Rate of adsorption of CO—O_2 mixture on hydrous ferric oxide (sample b) treated at 200 °C. Pressure of CO—O_2 is 10 mm Hg

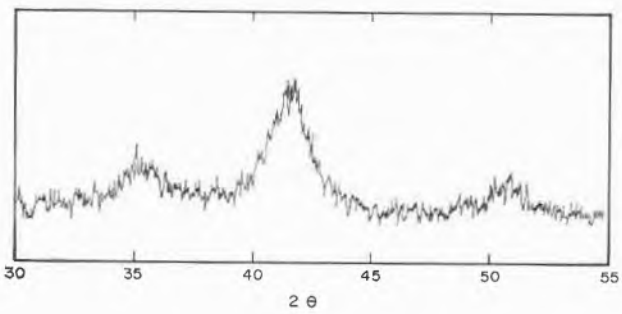

Fig. 16. X-ray diffraction pattern of magnetite. Target; Co

[21] K. EGGER and W. FEITKNECHT, *Helv. Chim. Acta XLV* (1962) 2042; K. J. GALLAGHER, W. FEITKNECHT and U. MANNWEILER, *Nature 217* (1968) 1118.

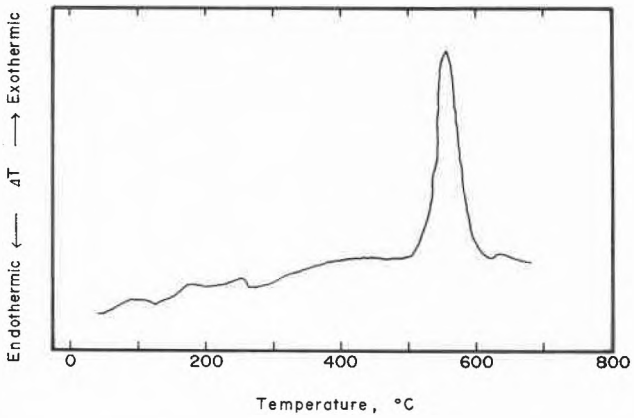

Fig. 17. DTA of magnetite

not appear. The peak due to the transformation into α-Fe_2O_3 appears at 554°C. The reason for the disappearance of the peak at 200°C is not clear at present. In Figures 18a to 18e, the DTA curves of the magnetite samples containing Cu, Cr, B, Li and Ti in the range of 1% to 10% are shown. The temperatures of the exothermic peaks depend on the kind of metallic cation and its concentration (Fig. 19). Cu-, Li- and Cr-containing samples show the minimum of the peak temperature in the range of 2% to 5%, while in the case of Ti and B no decrease of the peak temperature is observed. It is concluded that the former three ions have an accelerat-

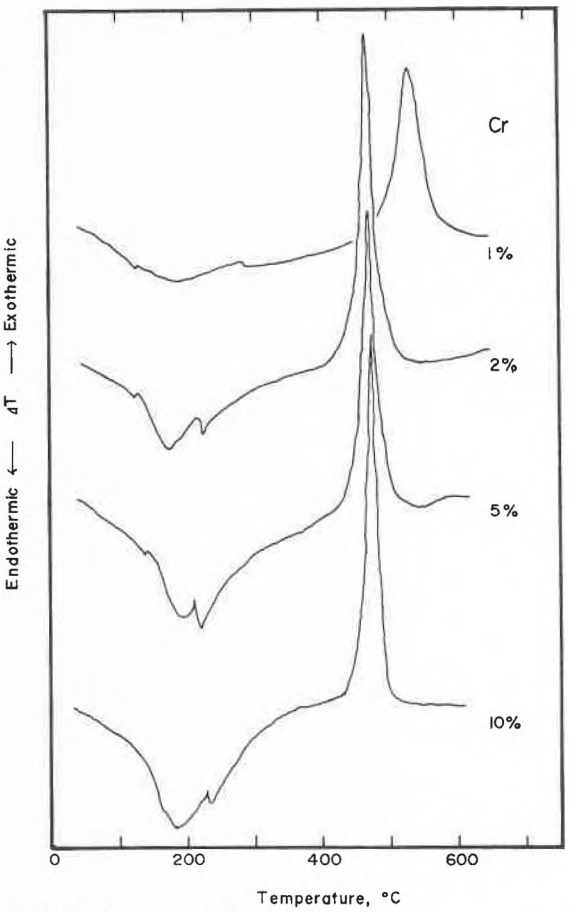

Fig. 18b. DTA of magnetite containing Cr-ion

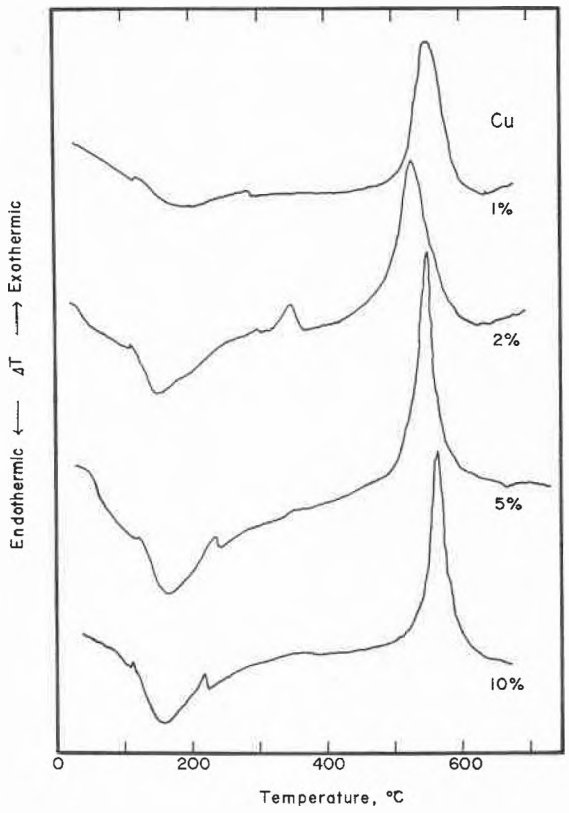

Fig. 18a. DTA of magnetite containing Cu-ion

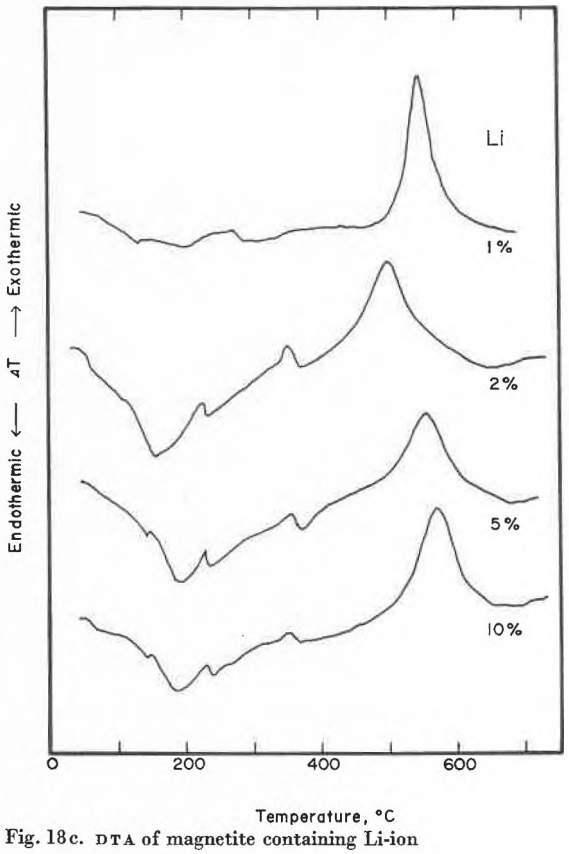

Fig. 18c. DTA of magnetite containing Li-ion

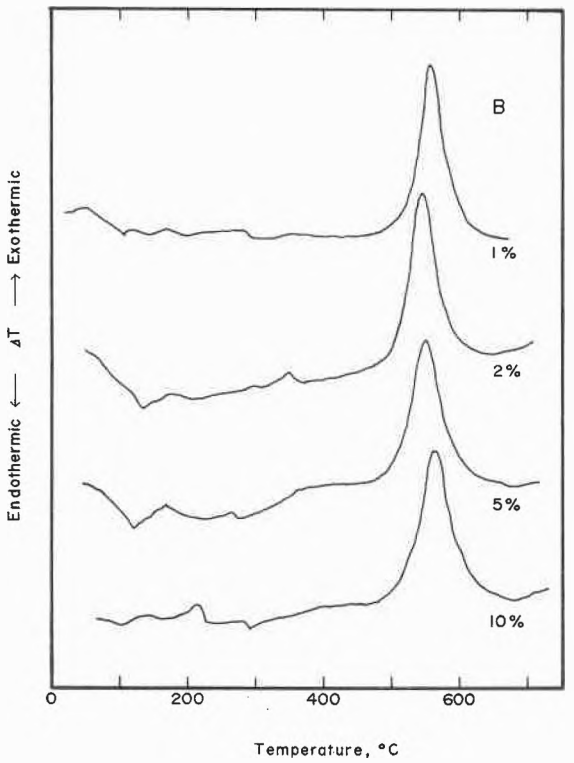

Fig. 18d. DTA of magnetite containing B-ion

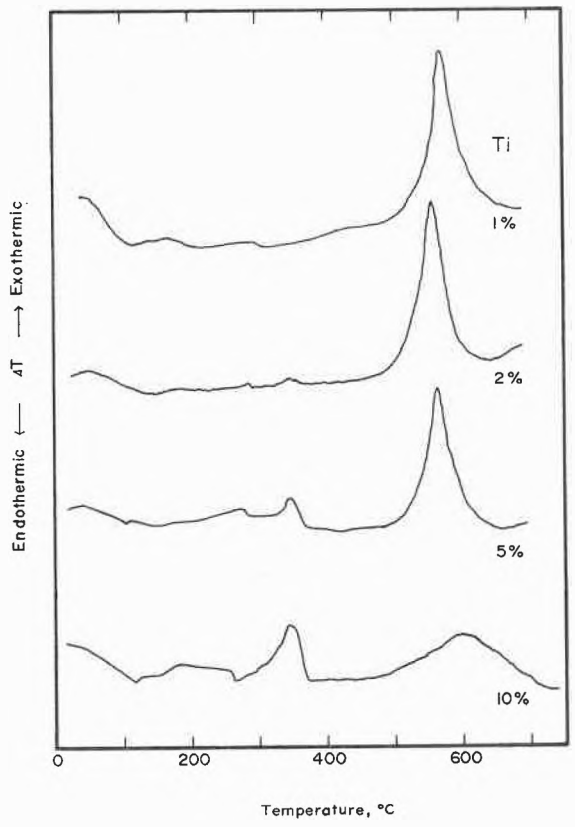

Fig. 18e. DTA of magnetite containing Ti-ion

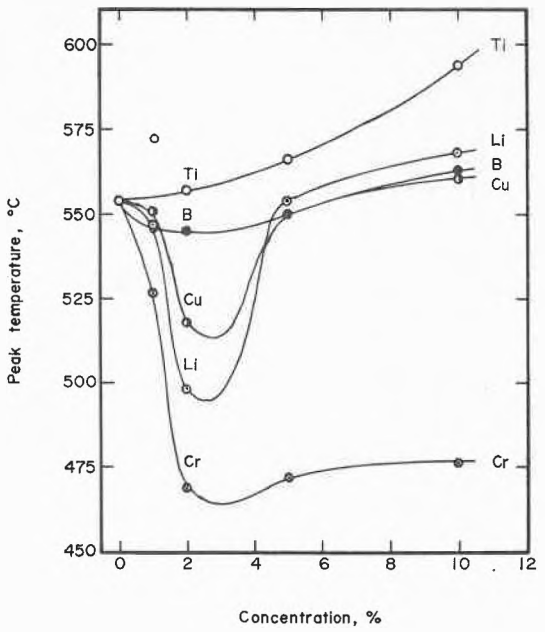

Fig. 19. Relation between the temperature of exothermic peak and the concentration of added metallic cations

ing effect, whereas the latter two ions exhibit a retarding effect on the reaction $Fe_3O_4 \rightarrow \alpha\text{-}Fe_2O_3$. With concentrations of metallic cations higher than 5% the exothermic peak appears at higher temperature than in the case of pure magnetite, except for Cr-containing samples which show an other behavior. The change of the peak temperature by the presence of metallic cations may be explained in terms of the instability of the magnetite structure. KUBO[22] has suggested that ions with a smaller radius than that of Fe^{3+} stabilize the spinel structure of $\gamma\text{-}Fe_2O_3$ by forming a solid solution of Fe_2O_3 and oxides of the small cation, such as As_2O_3. In the present case no correlation was observed between the peak temperature and the ionic radius. Magnetite sample with 1% Cu, 1% Li, Ti and B showing a retarding effect, do not exhibit the endothermic peak between 100 and 200°C. 1% Cr diminished the temperature of the exothermic peak by 20°C and causes a small endothermic peak at about 180°C. Magnetite containing more than 2% of Cu, Li and Cr shows a large endothermic peak. The presence of the endothermic peak at 180°C is considered to be essential for the acceleration effect. Accordingly, the bound water which shows the endothermic peak between 100 and 200°C plays an important role for the reaction $Fe_3O_4 \rightarrow \alpha\text{-}Fe_2O_3$.

Conclusion

Hydrous ferric oxide contains three kinds of water: adsorbed water, bound water and lattice water. The

[22] K. KUBO, M. MITARAI and S. SHIRASAKI, *5th Symposium on Ceramics, Japan*, 1967.

bound water exists in the form of OH groups and its removal is connected with an endothermic peak between 100 and 200 °C. The amount of bound water increases with the amount of the amorphous part of the oxide.The ageing process is retarded by the addition of metallic cations to the oxide. The retardation effect was shown to occur especially in the case of Cu. The mechanism of the retardation effect of metallic cations on the crystallization remains to be explained.

The amount of decomposed hydrazine increases linearly with the amount of bound water. The decomposition can be represented by the reactions:

$$N_2H_5^+ = N_2 + 5H^+ + 4e$$

$$3Fe_2O_{3-\frac{x}{2}}(OH)_x + 2H^+ + 2e = 2Fe_3O_4 + \left(1 + \frac{3}{2}x\right)H_2O$$

The rate of the dissolution in acid solution was found to obey the equation,

$$d[Fe^{3+}]/dt = k[H^+]^{0.5}[A^-]^m.$$

By assuming that the bound water provides the active sites, the rate of the dissolution reaction is explained on the basis of the equations:

$$[Fe^{III}{-}(OH){-}Fe^{III}]_s + H^+ + m'A^- + H_2O \rightleftarrows 2[Fe^{III}(H_2O)A^-_{m'/2}]_s$$

$$[Fe^{III}(H_2O)A^-_{m'/2}]_s + (5 - m'/2)\,H_2O \rightarrow [Fe^{III}(H_2O)_{6-m'/2}(A^-)_{m'/2}]_s$$

$$[Fe^{III}(H_2O)_{6-m'/2}(A^-)_{m'/2}]_s \rightarrow [Fe^{3+}(H_2O)_{6-m'/2}(A^-)_{m'/2}]_l$$

The rate of the dissolution was found to increase with the ionic radius of the metallic cation contained in the oxide.

The rate of the adsorption of CO–O_2 follows the Elovich equation:

$$dV/dt = k \exp(-\alpha V).$$

Since the initial rate of the adsorption, k, increases with the amount of bound water, it is concluded that the active sites for the adsorption are given by the bound water.

Finally, the temperature of the exothermic peak of the transformation of poorly crystallized magnetite into α-Fe_2O_3 was examined. It was found that Cr, Li and Cu accelerate the reaction, whereas Ti and B showed the opposite effect. The magnetite containing accelerating cations exhibits an endothermic peak between 100 and 200 °C, which is due to the removal of bound water.

Acknowledgments

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