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HEAT OF IMMERSION OF IRON(III) OXIDES IN WATER AT 25°C

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ABSTRACT

The heat of immersion in water was measured at 25°C for three iron(III) oxides using a twin-type microcalorimeter. One of the samples was commercial α-Fe_2O_3 (sample C) and the other two (samples M and F) were prepared by calcining magnetite and iron(III) hydroxide in air at various temperatures, T_p, from 300 to 700°C. The samples were evacuated at outgassing temperature, T_o, between room temperature and 500°C at a pressure of 1×10^{-2}–2.7×10^{-2} N m^{-2} for 6 h. The heat of immersion, h_i(J m^{-2}), of samples C and M increased with an increase in T_o and showed the maximum h_i at $T_o = 400$°C, while sample F did not show the maximum up to $T_o = 500$°C. The systematic correlation was not observed between h_i and T_p of sample F. The heat of reproduction of the surface hydroxyl group on sample F was approximately estimated as 6.6×10^4 J mole^{-1} H_2O.

INTRODUCTION

Iron(III) oxide has been used in many solid-state reactions, such as heterogeneous catalytic reactions and ferrite formation reactions. The reactivity of the oxide, which is evaluated from the catalytic activity and the rate of ferrite formation, has been observed to change markedly with its preparation history [1–3]. In the initial period of such a solid-state reaction, the reaction will proceeed at the interface where the iron(III) oxide particle contacts with the reactant present in the system [4]. Therefore, the reactivity of the oxide may be assumed to depend strongly on its surface properties. The heat of immersion of iron(III) oxide has been measured by several investigators to characterize the surface [5–11]. It is expected that the heat of immersion in water will give a measure of the surface property or reactivity of the oxide, since the heat is evolved from the interactions between the oxide surface and water [12]. The present study deals with the effect of outgassing and preparation temperatures on the heat of immersion in water for α-Fe_2O_3 samples, which were prepared by calcining iron(III) hydroxide and magnetite at 300–700°C in air.

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EXPERIMENTAL

Materials

Three α-Fe_2O_3 samples were used: sample C was a commercial reagent from Kanto Chem. Co., sample M was obtained by oxidation of Fe_3O_4 in air, and sample F was prepared from iron(III) hydroxide. Sample C was used in the experiments without further purification. Fe_3O_4 for sample M was precipitated from a mixed solution of $FeSO_4$ and $Fe_2(SO_4)_3$ (mole ratio = 1:2, volume = 0.1 dm^3) by adding NaOH solution (6 mole dm^{-3}) at 95°C. The pH of the solution was 13.6. The Fe_3O_4 precipitate was washed with hot water and dried in a vacuum oven for 12 h at 80–90°C after the preliminary drying at room temperature for 24 h in a vacuum desiccator. Fe_3O_4 was ground in an agate mortar to pass through 200 mesh sieve, and for conversion to α-Fe_2O_3,Fe_3O_4 powders were calcined in air at 500 and 700°C for 3 h. These calcination temperatures will hereinafter be called the preparation temperature, T_p. The α-Fe_2O_3 samples obtained are designated as M-500 and M-700. The Iron(III) hydroxide precipitate for sample F was obtained by mixing $Fe(NO_3)_3$ solution (0.0667 mole dm^{-3}) and NaOH solution (6 mole dm^{-3}) at 90°C. The pH of the solution was in the range 9.4–9.8. The precipitate was treated under the same conditions as those for the Fe_3O_4 precipitate. The hydroxide was heated at T_p = 300, 400, 500, 600 and 700°C for 4 h in air. These α-Fe_2O_3 samples obtained are expressed as F-300, F-400, etc. All samples were kept in a desiccator containing silica gel.

Surface area

The amount of N_2 adsorption was measured volumetrically at the boiling temperature of liquid nitrogen. Samples C, M and F were evacuated at 6.7×10^{-2} N m^{-2} for 2 h at 100°C before the measurement. The BET equation was used to calculate the surface area using 0.162 nm^2 as the cross-sectional area of N_2.

Weight decrease by heating

The Cahn electrobalance model RG was used with a quartz hang-down tube (d = 35 mm). Forty mg of the sample were placed in a quartz basket (10 × 10 mm). Three weights were measured at room temperature: W_{RA} = weight at atmospheric pressure, W_{RV} = weight at reduced pressure of 6.7×10^{-2} N m^{-2}, and W_{RO} = weight in oxygen gas at a pressure of 2×10^4 N m^{-2}. The weight in oxygen at a fixed temperature, T, above 100°C, W_{TO} was measured after the sample was heated up to T°C and kept at this temperature till no change in weight was observed. The heating temperature was from 100 to 500°C. An atmosphere of oxygen was used to prevent the sample from partial reduction due to oxygen release occurring when heated in vacuum [3].

X-Ray diffraction

The Geigerflex type 2004 diffractometer (Rigaku Denki) was operated under the conditions of Co-target, Fe-filter, 35 kV and 10 mA.

Heat of immersion

The measurements were carried out by means of a twin-type microcalorimeter (Oyodenki Kenkyujo type CM-204 S) consisting of sample and reference cells. The cylindrical glass ampoule (10 × 30 mm) was attached to the cells. Prior to the immersion experiments, 0.3–0.6 g of the sample placed in the ampoule was heated at a fixed outgassing temperature (T_0 = 100–500°C) for 6 h at a pressure of 1×10^{-2}–2.7×10^{-2} N m^{-2}. After outgassing, the ampoule was sealed off at this pressure and then set in the sample cell of the calorimeter. Another glass ampoule without sample was also outgassed and set in the reference cell. The volume of wetting water was 0.04 dm^3 and the temperature of immersion was 25°C. When the calorimeter attained thermal equilibrium (about 12 h needed for the equilibrium), two glass ampoules were simultaneously broken in order to immerse the sample in water. In the sample cell, the electrical heater was equipped to give a known amount of electrical energy input. The heat calibrations were carried out by comparing the area of recorded heat curve (temperature difference–time curve) obtained by an electrical energy input with that for the sample. The comparison was performed by weighing the tracing paper cut out in the shape of the recorded heat curve. All measurements were run in duplicate or more.

RESULTS AND DISCUSSION

Preliminary experiments

As mentioned above, the heat of immersion of samples was estimated on the basis of the known electrical energy input. Table 1 shows the change in electrical energy input (0.418–8.368 J) and the corresponding heat curve area measured by weight of tracing paper. In this experiment, the cells contained 0.04 dm^3 of water, but the glass ampoule was not used. The last line in Table 1 indicates that the values obtained under the same conditions (Runs 7 and 8) are within an error of about 1%, while the change in electrical energy input (Runs 3 and 4 and 5–7) and in recorder full scale (Runs 3 and 5) resulted in an error of 4–6%. These values recommend the use of the same

TABLE I

Relation between the area of recorded heat curve and the electrical energy input

	Run No.								
	1	2	3	4	5	6	7	8	9
Electrical energy input (J)	0.418	1.046	2.092	3.138	2.092	5.230	8.368	8.368	8.368
Range of recorder full scale (μV)	50	100	100	100	250	250	250	250	500
Area of heat curve (wt. of tracing paper/g)	0.0522	0.0676	0.1391	0.1969	0.0537	0.1289	0.2115	0.2098	0.1014
Wt. of tracing paper per unit energy input (g J^{-1})	0.1249	0.0646	0.0665	0.0627	0.0257	0.0246	0.0253	0.0251	0.0121

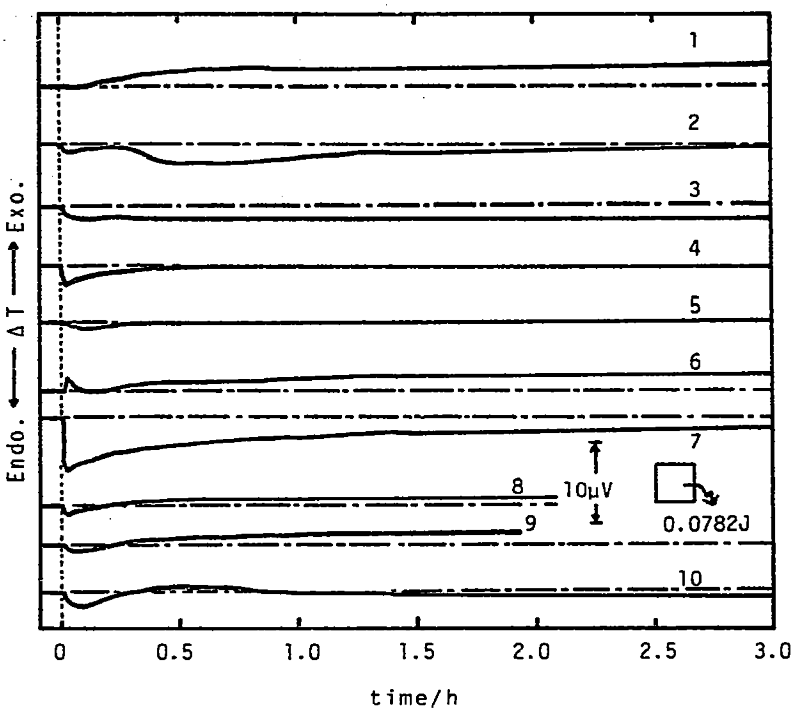
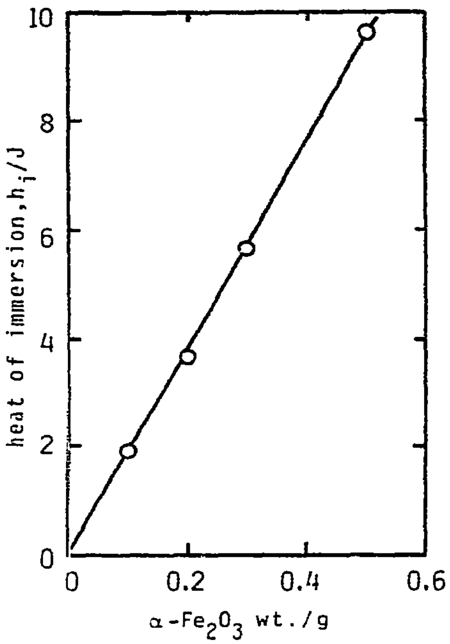


Fig. 1. Results of blank tests of the twin-type calorimeter. Curve 7 is the result for the non-breaking of the glass ampoule set in the sample cell.

conditions for the measurements on samples.

The twin-type calorimeter consists of sample and reference cells which are designed to have identical thermal properties. Therefore, in the "blank test" carried out by simultaneously breaking two empty glass ampoules set in the cells, the recorded heat curve should show a horizontal straight line, if the breaking of the two ampoules occurred in the same mode. Figure 1 shows the heat curves of the blank tests. The curves in Fig. 1 indicate the irregularities in the initial 1–1.5 h and become the straight lines at 1.5 or 2 h after the breaking at time = 0. Furthermore, the straight lines show a small disagreement with the base line (the broken line in Fig. 1) except for curves 4 and 5. These facts may be due to differences in the breaking mode of the two ampoules and in the thermal properties of the two cells. In the experiments for the iron(III) oxide samples, the base line of the recorded heat curve was determined by extending the recorded straight line, which appears 2–4 h after the breaking, to time = 0. This procedure contains the error of heat value corresponding to the irregularities observed during the initial period in Fig. 1. This error, except for curve 7, is estimated to be about 0.08 J from a comparison of the area of 0.0782 J shown in Fig. 1. Curve 7 shows the initial large endothermic deflection due to non-breaking of the glass ampoule in the sample cell.

The heat of dissolution of NaCl in water at 25°C has been reported as $4.230 \pm 0.004 \times 10^3$ J mole^{-1} [13]. Two dissolution experiments were carried



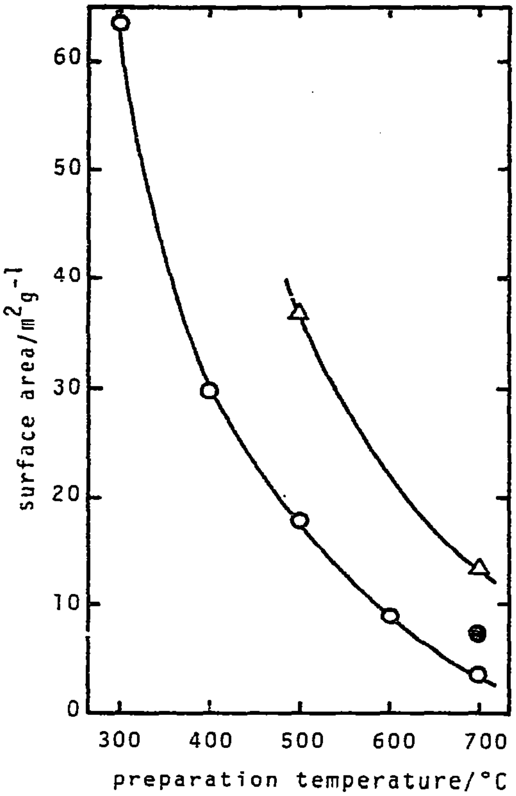


Fig. 2. The change in heat of immersion with weight of sample M-500.

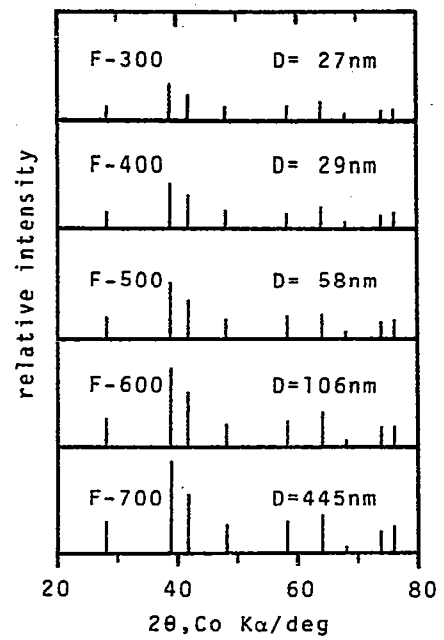
Fig. 3. The change in surface area with preparation temperature of iron(III) oxide samples. ○, Sample F; △, sample M; ●, sample C.

out using 0.250 g of reagent-grade NaCl (Kanto Chem. Co.) for each experiment. The results are 4.13×10^3 and 4.02×10^3 J mole^{-1}. These are 2.5 and 5% smaller than the value cited above, but they may be regarded as permissible experimental errors for the apparatus used.

Finally, the relation between the heat of immersion and sample weight was measured using 0.1, 0.2, 0.3 and 0.5 g of sample M-500. The result in Fig. 2 shows a straight line starting at the origin. The average deviation of the measured points from the line is found to be within about ±0.1 J. On the basis of this value, the measurements were carried out using a sufficient amount of sample to give an output heat of more than 1 J. However, the size of the glass ampoule limited the weight of sample to a maximum of 0.6 g. Thus some samples prepared at high temperatures showed the relatively large error due to a small immersion heat per unit weight of sample.

Effect of outgassing temperature and preparation temperature

Figure 3 shows the specific surface area of samples C, M and F. The abscissa indicates the preparation temperature of the oxides, T_p. The area of



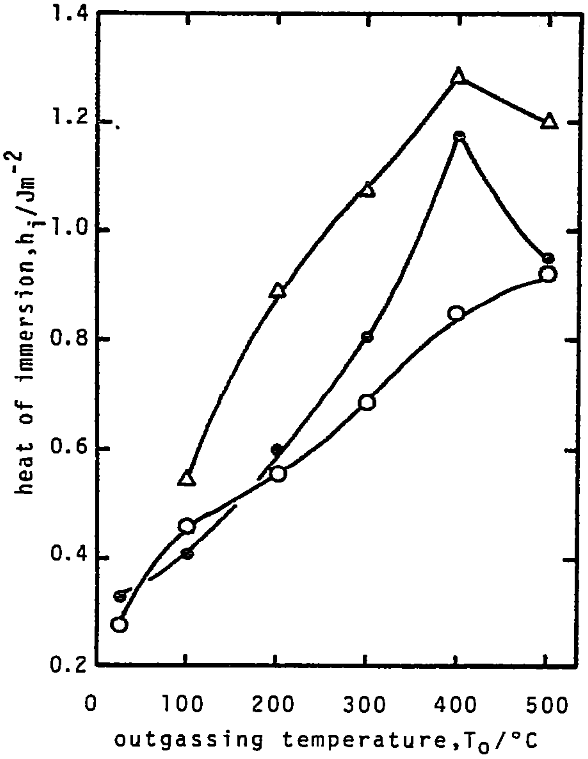


Fig. 4. X-Ray diffraction patterns and crystallite size (D) of samples F. The D value was calculated for (104) line at $2\theta=38.9°$.

Fig. 5. The relation between h_i and T_o. △, Sample M-700; ●, sample C; ○, sample F-700.

sample C is shown at 700°C, though its T_p value is unknown, since the commercial oxide reagent can be assumed to be prepared at high temperatures. The surface areas of samples F and M are found to decrease with an increase in T_p.

Figure 4 indicates X-ray diffraction patterns of five F samples. The intensity of the diffraction lines increases with increasing T_p, which shows an increase in the crystallinity of iron(III) oxide. The value of D in Fig. 4, the crystallite size calculated by the Scherrer equation for the α-Fe_2O_3 (104) line at $2\theta = 38.9°$, increases from 27 nm for F-300 to 445 nm for F-700 with the progress of crystallization of the oxide.

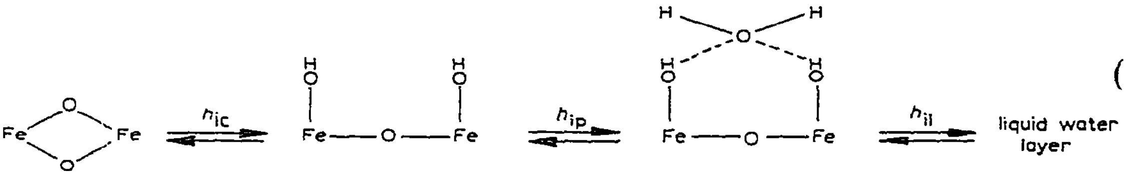
Table 2 shows the change in heat of immersion, h_i(J m^{-2}), with T_p and outgassing temperature, T_o, for samples C, M and F. The maximum T_o was limited to 500°C, because of the use of a glass ampoule. The h_i values were calculated on the basis of the specific surface area shown in Fig. 3. For the calculation, it was assumed that the surface area does not change during out-gassing treatment, if T_o is lower than T_p. It is found from Table 2 that the h_i values of samples C, M and F differ from each other at the same T_o (effect of preparation histories), the increase in T_o results in an increase in h_i

TABLE 2

Heat of immersion of iron(III) oxides in water at 25°C, h_i(J m^{-2})

Sample	Outgassing temperature (°C)					
	Room temp.	100	200	300	400	500
C	0.328	0.409	0.598	0.804	1.173	0.949
M-500		0.515	0.617	0.731	0.805	0.778
M-700		0.545	0.890	1.073	1.283	1.201
F-300	0.319	0.407	0.572	0.703		
F-400	0.366	0.482	0.618	0.773	0.944	
F-500	0.322	0.421	0.533	0.674	0.863	0.885
F-600	0.274	0.298	0.519	0.636	0.729	0.766
F-700	0.273	0.460	0.558	0.687	0.850	0.923

of all samples, and the maximum h_i appears at $T_o = 400$°C for samples C and M. Figure 5 shows typical results; similar results have been reported previously [6,14], and may be explained as follows: (1) the surface hydroxyl group is formed on the oxide by chemisorption of water in air, (2) the hydroxyl group is desorbed in the from of H_2O by outgassing treatment under vacuum and the amount of H_2O desorbed increases with T_o, and (3) when the outgassed oxide is immersed in water at 25°C, the following three processes take place: (a) reproduction of the surface hydroxyl group by chemisorption, (b) physisorption, and (c) formation of a liquid water layer on the oxide [8,15,16]. These processes can be expressed as



(1)

where h_{ic} and h_{ip} are the heat of chemisorption and physisorption, respectively. The heat of immersion, h_i, is shown by eqn. (2)

$$h_i = h_{ic} + h_{ip} + h_{il} \tag{2}$$

where h_{il} is the surface enthalpy of liquid water at 25°C which is 0.118 J m^{-2} [17]. It has been considered from the above schema that the increase in h_i with T_o is due to an increase in the number of reproduced hydroxyl groups and that the maximum h_i appearing in the h_i–T_o relation is due to stabilization of the surface structure of the oxide occurring at a higher T_o than a limited temperature, and this surface stabilization leads to a marked delay in the rate of reproduction of hydroxyl groups. Figure 5 suggests that samples C and M-700 are stabilized above 400°C while the stabilization of sample

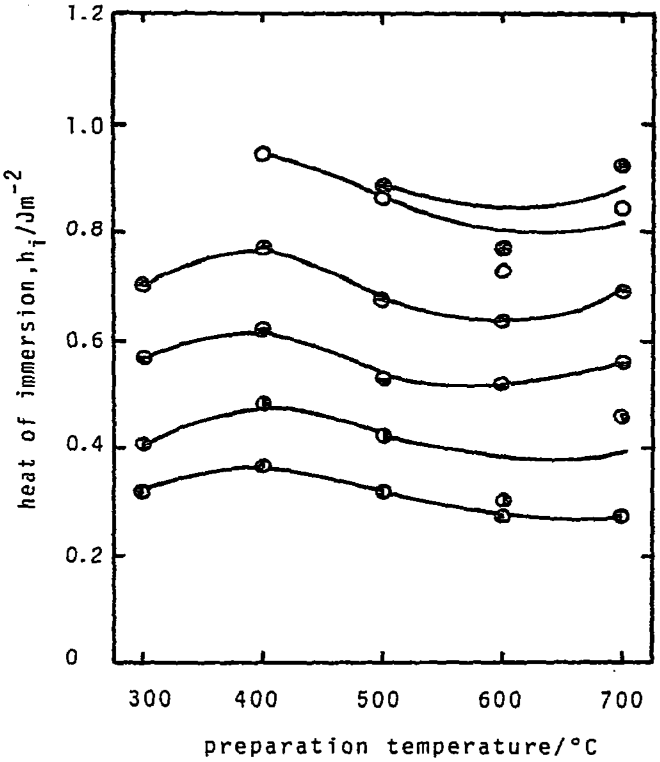


Fig. 6. The relation between h_i and preparation temperature. Outgassing temperature: ◐ = room temperature; ◑ = 100°C; ⊖ = 200°C; ⊜ = 300°C; ○ = 400°C; ⊛ = 500°C.

F-700 occurs at temperatures higher than 500°C below which the maximum h_i is not observed. Morimoto et al [6] reported the maximum h_i value to be obtained at $T_o = 600°C$ for their α-Fe_2O_3 sample. The T_o showing the maximum h_i may be taken as one measure of representing a surface property of the oxides with different preparation histories.

Figure 6 shows h_i values of the F samples as a function of T_p with the parameter of T_o. At all T_p, h_i increases with T_o. On the other hand, the h_i value does not change systematically with the variation of T_p, though a broad peak is seen at $T_p = 400°C$. This may suggest that the surface activity evaluated from the heat of immersion does not change with T_p. A similar result has been reported by Ishikawa et al. [9].

Figure 7 shows the weight decrease of samples F-300, 400, 500 and 600 assigned to unit surface area, which may correspond to the amount of desorbed water by heating. Solid marks plotted at room temperature correspond to the physisorbed water and the condensed water in pores, A_p(mg m^{-2}), which was calculated from the weight difference of $W_{RA} - W_{RV}$, where W_{RA} and W_{RV} are the weight in air and in vacuum at room temperaure, respectively. The A_p value increases with T_p from 0.32 for F-300 to 0.9 mg m^{-2} for F-600. Zettlemoyer and McCafferty [7,15] found that the

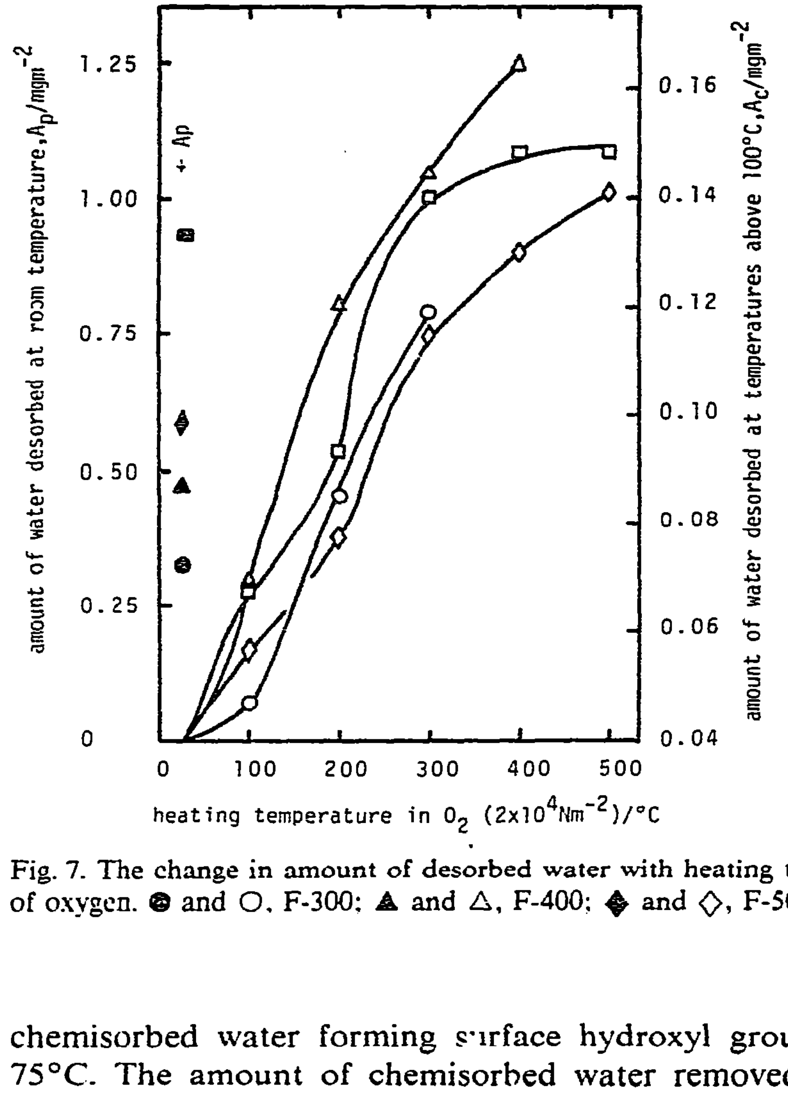


Fig. 7. The change in amount of desorbed water with heating temperature in an atmosphere of oxygen. ● and ○, F-300; ▲ and △, F-400; ◆ and ◇, F-500; ■ and □, F-600.

chemisorbed water forming surface hydroxyl groups was removed above 75°C. The amount of chemisorbed water removed by heating up to any temperatures *T*, A_c(mg m^{-2}), was estimated, after the physisorbed water had been eliminated by outgassing the sample in vacuum at room temperature, by measuring the weight difference between W_{RO} and W_{TO}; the former is the weight of sample at room temperature and the latter is that at *T*°C (100–500°C) in O_2 (2×10^4 N m^{-2}). The A_c value of F-700 could not be determined. The atmosphere of oxygen was used to prevent removal of oxygen from the oxide [3]. The A_c value (open symbols in Fig. 7) of each sample increases with increase in heating temperature, but does not show a correlation to T_p of the sample. It is roughly estimated that A_c increases from 0.05 mg m^{-2} at 100°C to 0.16 mg m^{-2} at 500°C. By using these values and assuming that 1 mole of water corresponds to 2 moles of hydroxyl groups, the number of surface hydroxyl groups removed at 100 and 500°C can be calculated as 3.3 and 11 OH nm^{-2}, respectively. These numbers will not be in conflict with 8–13 OH nm^{-2} reported as the maximum number of surface hydroxyl groups on α-Fe_2O_3 [18,19]. From Fig. 6, the average h_i value at

T_o = room temperature is 0.3 J m^{-2} and that at $T_o = 500°C$ is 0.9 J m^{-2}. The difference between the two values (0.6 J m^{-2}) is considered to correspond to the heat of reproduction of surface hydroxyl group of 11 OH nm^{-2} ($= 1.8 \times 10^{18}$ mole m^{-2}). This heat is calculated as 6.6×10^4 J $mole^{-1}$ H_2O, which may be comparable to 4.3×10^4–4.9×10^4 J $mole^{-1}$ H_2O reported as the heat of surface hydration [6].

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