Variations of Heat of Immersion of Ferric Oxyhydroxides in Water with Structural Changes by Heating

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The relationship between the activity of ferric oxyhydroxides (α-, β-, and γ-FeOOH) and structural changes has been investigated by determining the heat of immersion in H_2O and H_2O vapor adsorption. For each ferric oxyhydroxide, the monolayer capacity of H_2O adsorption and the heat of immersion decreased with the progress of transformation into α-Fe_2O_3. Above the transformation temperature the heat of immersion increased with the outgassing temperature. The heat of immersion of α-Fe_2O_3 obtained by outgassing each ferric oxyhydroxide at 400 and 500 °C increased with the accompanying increase in crystallite size. β-FeOOH showed higher heat of immersion and larger monolayer capacity per unit surface area than other ferric oxyhydroxides. It is presumed that the higher heat of immersion and larger monolayer capacity observed for β-FeOOH are ascribed to micropores in β-FeOOH crystals produced by the removal of molecular water originally contained.

Although ferric oxyhydroxides and oxides are commonly known as significant corrosion products of iron, the surface property in view of the structure of these compounds still remains unclarified. The surface activity of ferric oxyhydroxide, for instance, is expected to vary with the degree of its structural transformation into other compounds. Jurinak[1] reported that the adsorptive activity of α-FeOOH to H_2O suddenly decreases at the transformation temperature into α-Fe_2O_3. The present authors have studied the SO_2 adsorption on ferric oxyhydroxides[2] and ferric oxides at various outgassing temperatures[3] in order to show that β-FeOOH chemisorbs a larger amount of SO_2 than other ferric oxyhydroxides and that the amount of chemisorbed SO_2 by each ferric oxyhydroxide, regarded as a measure of reactivity, decreases with the progress of transformation into α-Fe_2O_3.

It appears that a knowledge of the interaction between H_2O and ferric oxyhydroxides is essential to understand the surface properties of ferric oxyhydroxides as main corrosion products of iron. Several investigators[4–6] have suggested that the surface activity of ferric oxides, evaluated by the heat of immersion in water and H_2O vapor adsorption, depends upon the temperature of heat treatment and the number of hydroxyl groups on the surfaces of resulting ferric oxides. We found that the heat of immersion of ferric oxides of different particle size (50 to 650 Å in diameter) is independent of particle size.[7] However, there has been no investigation into the change of heat of immersion of ferric oxyhydroxides with structural transformation. In the present work, the heat of immersion in water and H_2O adsorption isotherms are determined and discussed for α-, β-, and γ-ferric oxyhydroxides with outgassing at various temperatures up to 500 °C in order to confirm the change of activity towards H_2O with the structural changes.

Experimental

Materials. The preparation of ferric oxyhydroxides has been described in detail[3]. α-FeOOH(α-1) was prepared by the hydrolysis of 0.1 M ferric oxalate solution at 100 °C with the initial pH 6.6. More crystalline α-FeOOH(α-2) was obtained by the hydrolysis of ferric sulfate solution at 50 °C with the adjusted pH 13.6. β-FeOOH(β-1) prepared by hydrolysing 0.1 M ferric chloride solution containing urea at 100 °C is more crystalline than other β-FeOOH(β-2) obtained by heating 0.1 M ferric chloride solution at 75 °C. Crystalline γ-FeOOH(γ-1) was prepared by the oxidation of ferrous hydroxide suspension with $NaNO_3$, and amorphous γ-FeOOH(γ-2) by the oxidation of ferrous sulfate solution in the presence of $Na_2S_2O_3$.

Procedure. The heat of immersion in water was measured at 30.0 °C by means of a twin-type microcalorimeter (Oyodenki Kenkyujo, CM-204S) consisting of a pair of calorimeters, one of them being the reference. Prior to the immersion experiments, approximately 200—300 mg of the sample was heated up to 110, 150, 200, 300, 400, and 500 °C at a heating rate of 8 °C/min in a glass ampule under 10^{-5} Torr and outgassed for 5 hr at each temperature. After outgassing, the glass ampule was sealed off in a vacuum and set in the calorimeter. When the calorimeter attained thermal equilibrium, the ampule was broken in order to immerse the sample in water.

The water adsorption experiment was performed gravimetrically at 30.0 °C by means of a quartz spring balance.

The surface area of the sample was determined by a conventional volumetric method by nitrogen adsorption according to the BET method. The pretreatment of the sample in the H_2O adsorption and surface area determinations was identical to that in the heat of immersion measurement.

The X-ray diffraction patterns were obtained by the powder method with a diffractometer (Rigaku Denki Co., 2001) by use of Mn-filtered Fe*K*α at 30 kV and 10 mA.

Results and Discussion

The X-ray diffraction patterns of ferric oxyhydroxides are shown in Fig. 1.

The changes of X-ray diffraction patterns of α-2, β-1, and γ-1 with outgassing at various temperatures

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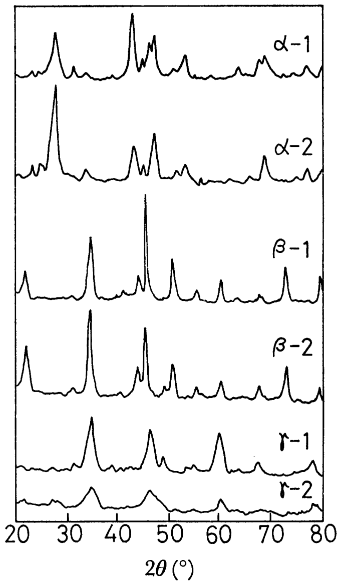

Fig. 1. X-ray diffraction patterns of ferric oxyhydroxides.

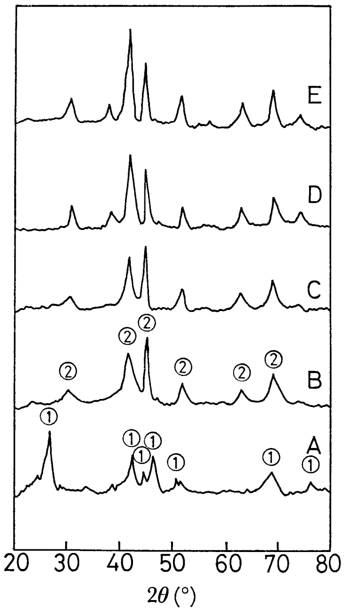

Fig. 2. X-ray diffraction patterns of α-2 at various outgassing temperatures: ①, α-FeOOH; ②, α-Fe_2O_3; A, 150 °C; B, 200 °C; C, 300 °C; D, 400 °C; E, 500 °C.

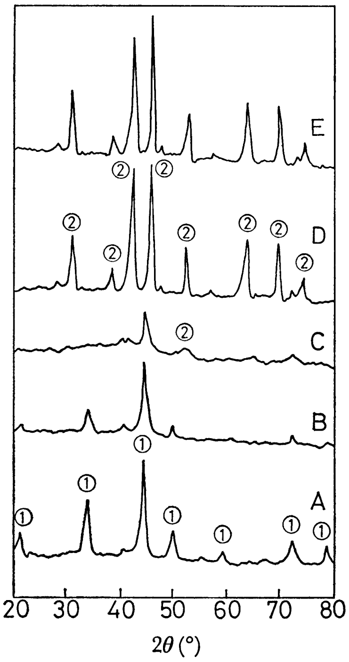

Fig. 3. X-ray diffration patterns of β-1 at various outgassing temperatures: ①, β-FeOOH; ②, α-Fe_2O_3; A, 150 °C; B, 200 °C; C, 300 °C; D, 400 °C; E, 500 °C.

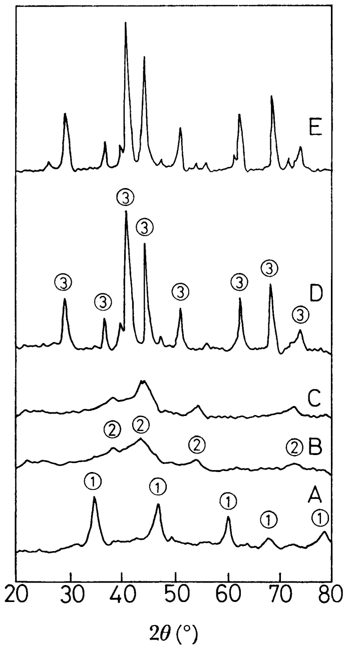

Fig. 4. X-ray diffraction patterns of γ-1 at various outgassing temperatures: ①, γ-FeOOH; ②, γ-Fe_2O_3; ③, α-Fe_2O_3; A, 150 °C; B, 200 °C; C, 300 °C; D, 400 °C; E, 500 °C.

are shown in Figs. 2, 3, and 4 respectively, illustrating the mode of transformation of each ferric oxyhydroxide into α-Fe_2O_3 at particular temperature ranges. α-FeOOH is transformed into α-Fe_2O_3 at 200 °C. β-FeOOH changes to an amorphous mixture, composed of β-FeOOH and α-Fe_2O_3, in the temperature range 200—300 °C, and is further transformed into the crystalline α-Fe_2O_3 above 400 °C. γ-FeOOH is transformed into γ-Fe_2O_3 at 200 °C and is converted into crystalline α-Fe_2O_3 at 400 °C. These results show that all ferric oxyhydroxides are transformed into α-Fe_2O_3 above 400 °C.

The weight loss accompanying the change of ferric oxyhydroxide to α-Fe_2O_3 is 10% corresponding to the dehydration formula; $2FeOOH \rightarrow Fe_2O_3 + H_2O$. To obtain the variations of weight loss with outgassing temperature (Fig. 5), the samples were subjected to heat treatment in the same manner as those in the H_2O adsorption and the heat of immersion measurements. For α-2 and γ-1, the weight loss increases with the rise of temperature up to 200 or 300 °C, followed by almost constant weight above 300 °C. The total weight loss at 500 °C corresponds to 11.2 and 12.8% for γ-1 and α-2, respectively. These values are somewhat larger than the theoretical value (10%), because of the dehydration of adsorbed water and the "bound"

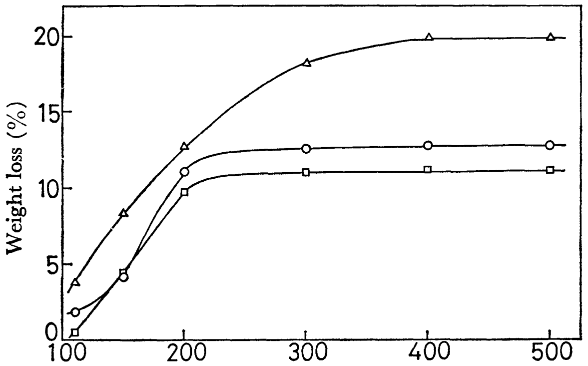

Fig. 5. Relation between weight loss and outgassing temperature: ○, α-2; △, β-1; □, γ-1.

water supposedly contained in the ferric oxyhydroxide crystals.[8] Although the X-ray diffraction patterns obtained for these samples (α-2 and γ-1) remain almost unchanged up to 150 °C, an approximate 4.5% weight loss is observed. This indicates that α-2 and γ-1 are partially transformed into amorphous ferric oxide below 150 °C. On the other hand, the weight loss of β-1 increases with the rise in outagssing temperature up to 400 °C, reaching a total weight loss of 20% at 500 °C. This large weight loss is due to the removal of chlorine and molecular water originally contained in β-FeOOH crystals.[3]

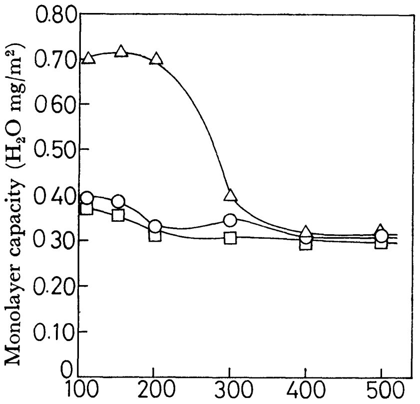

Fig. 6. Effect of outgassing temperature on monolayer adsorption capacity: ○, α-2; △, β-1; □, γ-1.

H_2O adsorption isotherm is the BET-II type for each sample. The monolayer capacity (A_m) of H_2O adsorption per unit BET surface area, calculated from the N_2 adsorption isotherm, is shown in Fig. 6 as a function of outgassing temperature. The A_m values of α-2 and γ-1 decrease with the rise in temperature up to 200 °C and become nearly constant above 400 °C, whereas A_m of β-1 below 200 °C is considerably high but decreases abruptly in the temperature range 200—300 °C. Above 400 °C, where transformation into α-Fe_2O_3 occurs, the A_m value of β-1 becomes equal to that of α-2 and γ-1. The large A_m of β-FeOOH seems to be due to the formation of micropores in crystals with the release of molecular water by outgassing. The crystal structure of β-FeOOH proposed by Mackay[9] has micropores parallel to c-axis as shown in Fig. 7. The diameter of these micropores is estimated to be 2.54 Å from the effective diameter of the hydroxyl group (1.35 Å) and the distance between hydroxyl groups (5.24 Å). On the other hand, the diameter of N_2 molecule and H_2O molecule is 3.5 and 2.5 Å, respectively. H_2O molecule has a strong dipole moment, whereas N_2 molecule has only a quadrupole moment. Thus, it is plausible that the micropores are more accessible to H_2O molecules than to N_2 molecules. According to X-ray diffraction results (Fig. 3) in which the β-FeOOH crystal turns into an amorphous state in the temperature range 200—300 °C, the decrease in A_m of β-FeOOH in the course of outgassing below 300 °C seems to be due to the destruction of β-FeOOH structure having the micropores.

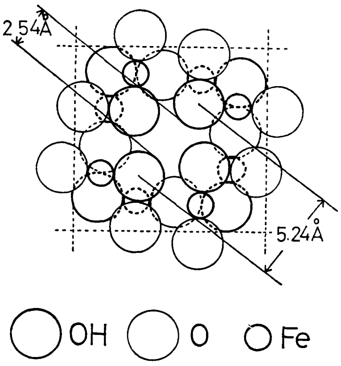

Fig. 7. Projection of the crystal structure of β-FeOOH on (001). β-FeOOH has a tetragonal lattice with the following unit cell dimensions: $a=b=10.48$ Å, $c=3.02$ Å.

The decrease in A_m of α-FeOOH or γ-FeOOH below 200 °C might be attributed mainly to the removal of surface hydroxyl groups. The heat of immersion (ΔH_I) per unit surface area of α-FeOOH is shown in Fig. 8 against outgassing temperature. The decrease in ΔH_I below 150 °C is considered to be due to the removal of the hydroxyl groups acting as hydrophilic sites on the ferric oxyhydroxide surface. In contrast

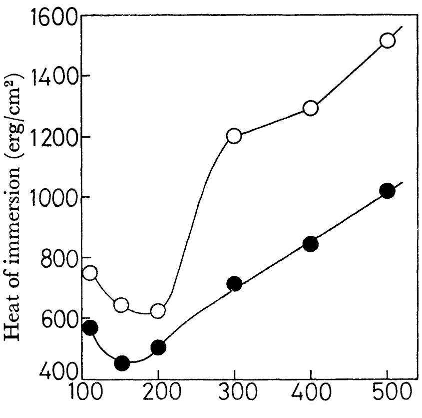

Fig. 8. Effect of outgassing temperature on the heat of immersion of α-FeOOH: ○, α-1; ●, α-2.

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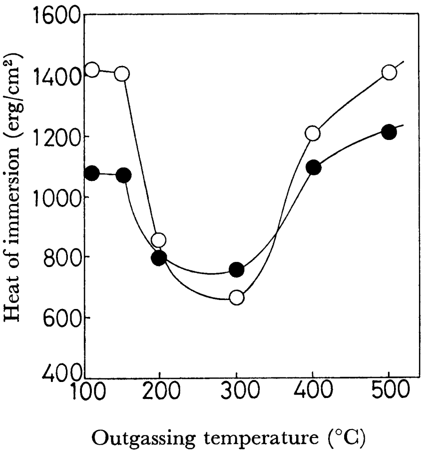

Fig. 9. Effect of outgassing temperature on the heat of immersion of β-FeOOH; ○, β-1, ●, β-2.

to this, the increase in ΔH_I above 200 °C seems to be caused by rehydration of the α-Fe_2O_3 surface, the dehydrated surface being readily rehydrated to be covered again with hydroxyl groups during the immersion process in water.[5] γ-FeOOH shows the same tendency as α-FeOOH. As illustrated in Fig. 9, β-FeOOH shows a larger ΔH_I than that of other ferric oxyhydroxides below 150 °C, the ΔH_I value falling sharply in the temperature range 150—200 °C. Above 300 °C, ΔH_I increases with temperature probably by surface rehydration as with other ferric oxyhydroxides.

It is apparent that α-Fe_2O_3 samples obtained by outgassing α-2, β-1, and γ-1 at 400 and 500 °C were almost completely dehydrated, since they show a constant weight loss above 400 °C as shown in Fig. 5. The heat of immersion (ΔH_I) for these samples therefore includes the heat evolved with the rehydration of dehydrated α-Fe_2O_3 surface. The heat of rehydration depends upon the stability of the oxygen bridge such as $-\mathrm{Fe}\langle\begin{smallmatrix}\mathrm{O}\\\mathrm{O}\end{smallmatrix}\rangle\mathrm{Fe}-$ which is formed on dehydration. The stability of the oxygen bridge is considered to be related to the crystallinity of α-Fe_2O_3. The crystallite size as a measure of crystallinity was calculated by the Scherrer equation for the α-Fe_2O_3 (104) pattern at 2θ of 41.9° in X-ray diffraction diagrams. ΔH_I was plotted against crystallite size (Fig. 10) to show that it increases with increase in crystallite size. This could be explained by assuming that the oxygen bridge of less crystalline α-Fe_2O_3 is so unstable as to be rehydrated with evolution of less heat than that of more crystalline α-Fe_2O_3.

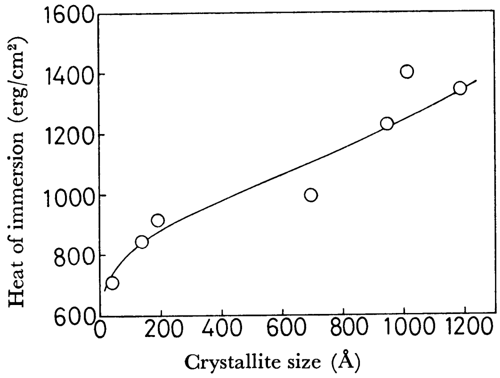

Fig. 10. Relation between crystallite size and the heat of immersion.

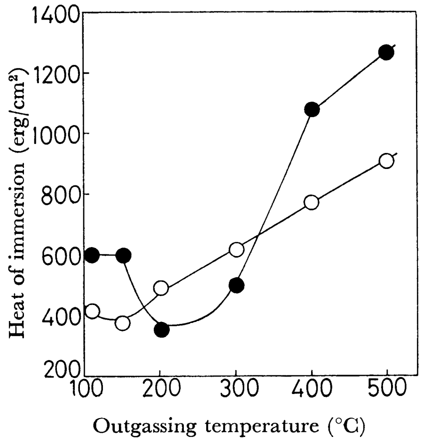

Fig. 11. The heat of immersion per unit H_2O surface area: ○, α-2; ●, β-1.

The large ΔH_I of β-FeOOH below 150 °C (Fig. 9) seems to be associated with the microporous structure of β-FeOOH. The depression of ΔH_I in the temperature range 150—200 °C is caused by the destruction of the microporous structure of β-FeOOH. The heat of immersion in water, per unit surface area obtained by N_2 adsorption, shows a large value caused by the existence of the micropores into which H_2O molecules are adsorbed more easily than N_2 molecules. To exclude the micropore effect on the heat of immersion, calculation based on the surface area estimated from H_2O adsorption, using 10.6 Å for the sectional area of an adsorbed water molecule, was attempted. However, β-FeOOH still showed a higher heat of immersion than other ferric oxyhydroxides up to 150 °C (Fig. 11). It is concluded, therefore, that β-FeOOH is more reactive to H_2O as compared with other ferric oxyhydroxides.