Role of Chlorine in β-FeOOH on Its Thermal Change and Reactivity to Sulfur Dioxide

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The state of Cl in β-ferric oxide hydroxide (β-FeOOH) was examined by X-ray diffraction, IR absorption, chemical analysis, DTA, and TGA. The adsorption of SO_2 was determined as a measure of the surface activity. No influence of Cl contained in the crystal appeared in the X-ray diffraction patterns and surface area. The absorption bands at 640 and 840 cm^{-1} in IR spectra showing the deformation vibration of OH group diminished with the decrease of Cl content. It was shown that the path for β-FeOOH to transform into α-Fe_2O_3 by heating differentiates from the sample including more than 11.5% Cl/Fe to one including less than 11.5% Cl/Fe. This critical Cl content is equal to the amount of Cl when Cl fills up the characteristic tunnels existing in the β-FeOOH crystal. Cl in β-FeOOH interferes both its transformation into α-Fe_2O_3 and the recrystallization of resultant α-Fe_2O_3. These effects were explained by the stabilization of the β-FeOOH structure by Cl in tunnels and the bonding between Cl and Fe. The amount of chemisorbed SO_2 was lowered by Cl which was adsorbed on outer surfaces.

It has been known that β-FeOOH is formed in the presence of Cl^- ions. It results in the fact, for example, that the corrosion products of steel, formed in marine environments, contain β-FeOOH amounting to 20—30 %.[1] The β-FeOOH sample prepared by the hydrolysis of an $FeCl_3$ solution also contains a certain amount of Cl and the Cl content varies with the conditions of preparation and subsequent treatments.[2] Mackay[3] asserted that β-FeOOH has the hollandite ($BaMn_8O_{16}$) or α-MnO_2 structure[4] and presumed that Cl^- ions and H_2O molecules fill the positions which in hollandite are occupied by Ba^{2+} ions and that Cl^- ions are replaced by H_2O molecules on washing, accompanied by the conversion of OH^- to O^{2-} to maintain the electrical neutrality. This structure of β-FeOOH was confirmed recently by means of neutron diffraction.[5] Chlorine in β-FeOOH is believed to affect some properties of β-FeOOH, *e.g.*, the thermal transformation into α-Fe_2O_3 and the surface activity. Hofer, Peebles, and Deiter[6] investigated the catalytic activity of various ferric oxides and oxide hydroxides in the Fisher-Tropsh synthesis but concluded that β-FeOOH is inactive. However, the present authors found that β-FeOOH shows higher reactivity to SO_2[7] and higher heat of immersion in water[8] than those of α-FeOOH and γ-FeOOH.

In the present work, β-FeOOH samples containing different amounts of Cl were examined by X-ray diffraction, infrared absorption, thermal analyses (DTA and TGA), chemical analysis, and the adsorption of SO_2 to reveal the influence of Cl on the reactivity of crystal surface.

Experimental

Materials. β-FeOOH was precipitated by heating 0.1 M $FeCl_3$ solution for 5 hr at 96—99 °C. The resultant precipitate was washed by the following method in order to change the Cl content. The sample A-1 was obtained by washing the precipitate with distilled water until no Fe^{3+} ions were detected, and A-2 by electrodialyzing the sample A-1 at 10 V/cm for 10 hr. A-3 was obtained by washing the original precipitate with 1 M NH_4Cl solution till free of Fe^{3+} ions, with 1 M NH_4OH solution to remove Cl^- ions, and finally with distilled water. The electrodialysis of A-3 at 10 V/cm for 10 hr gave A-4. A-5 was obtained by dispersing A-3 in 1 M NH_4OH for 3 day, followed by filtering and washing with distilled water. Another kind of β-FeOOH was prepared by heating 500 ml of 0.1 M $FeCl_3$ solution containing 30 g urea at 96—99 °C for 5 hr. The sample U-1 was obtained by washing the resultant precipitate with distilled water (500 ml) till free of Fe^{3+} ions and U-2 with 4 l distilled water. Each sample was dried in an air oven for 2 hr at 100 °C.

Procedure. The SO_2 adsorption was measured at 30.0 °C by use of a quartz spring balance. The samples were pretreated by outgassing under 10^{-5} Torr for 14 hr at 110 °C. The BET surface area was determined by N_2 adsorption measurement at liquid nitrogen temperature. The X-ray diffraction examination was carried out by the powder method by use of Mn-filtered FeKα at 30 kV and 10 mA. The differential thermal analysis (DTA) was done in air using α-Al_2O_3 as a reference sample at a heating rate of 10 °C/min, and the thermogravimetric analysis (TGA) by means of a quartz spring at a heating rate of 10 °C/min. Infrared absorption spectra were taken by the KBr disk method with JASCO IR-G spectrophotometer. Cl and Fe contents of the sample were determined according to the procedures described in the previous paper.[9]

Results

The Cl content expressed in atomic % Cl/Fe (Table 1) could not be reduced below 7% by the washing procedures used in this work. The X-ray diffraction patterns and the surface area were almost identical regardless of the Cl content. IR spectra (Fig. 1) changed with the Cl content; the absorption bands at 640 and 840 cm^{-1} shifted to higher frequencies and their absorbance increased with the Cl content. Müller[10] reported that β-FeOOH prepared from $FeCl_3$ solution shows IR spectra having two bands at 690 cm^{-1} and 840 cm^{-1} due to the OH deformation vibration, but the 840 cm^{-1} band disappears on treating with alkali bicarbonate or carbonate. In our spectra, the 640 cm^{-1} and 840 cm^{-1} bands diminished with the removal of Cl. It is accordingly speculated that the bands at 640 cm^{-1} and 840 cm^{-1} are due to the deformation vibration of the OH^- which become O^{2-} to maintain the electrical neutrality when Cl^- ion is replaced by H_2O molecule.

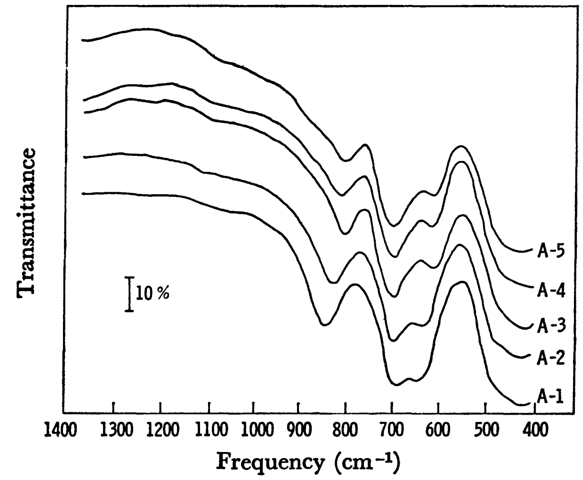

Fig. 1. Variations of IR spectrum with Cl content.

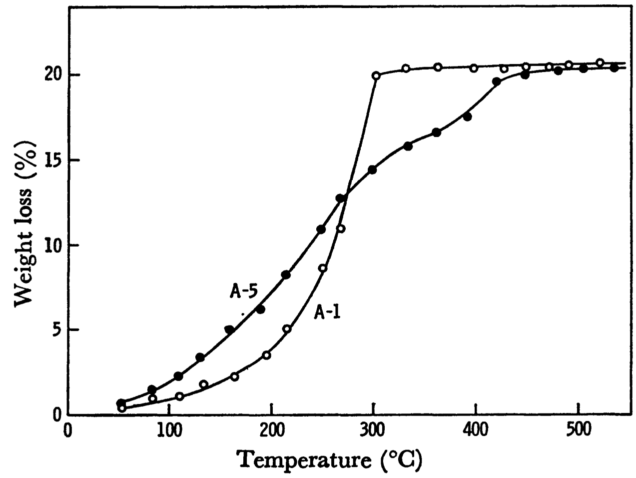

Fig. 2. TGA curves of A-1 and A-5.

TGA curves of samples A-1 and A-5 are shown in Fig. 2. The weight loss up to 270 °C of A-5 sample of 7% Cl/Fe was larger than that of A-1 of 17% Cl/Fe, but a gradual weight loss up to 420 °C was observed for A-5. The weight loss is considered to be caused by the dehydration of hydroxyl group ($2FeOOH \rightarrow Fe_2O_3 + H_2O$), the release of HCl, and the sublimation of $FeCl_3$. Then, the water content was calculated by subtracting the amount of released Cl and Fe from the weight loss between 110 and 500 °C in TGA curves. The water content thus obtained (Table 1) was still larger than the theoretical dehydration value (10.1 wt %). This result indicates that β-FeOOH embraces some more water molecules in addition to hydroxyl groups which produce the "crystallization water" on dehydration.[11] As Mackay suggested,[3] this excess water seems to exist in tunnels parallel to the c-axis of the crystal. The amount of these water molecules, calculated by subtracting the theoretical dehydration value (10.1 wt %) from the water content, increases with the decrease of Cl content (Table 1). This result shows that Cl in β-FeOOH is replaced by H_2O molecule in the course of washing with water. The larger weight loss of A-5 below 270 °C will be due to the release of such water molecules.

TABLE 1. SURFACE AREA AND COMPOSITION OF SAMPLES

Sample	Surface area (m^2/g)	Cl (Cl/Fe, %)	Fe (mmol/g)	H_2O molecule (wt %)	H_2O molecule (H_2O/Fe, %)
A-1	35	17	11.1	12.5	12.5
A-2	34	12	11.5	12.7	13.1
A-3	32	7.7	10.7	13.5	18.2
A-4	32	7.4	11.4	13.8	18.6
A-5	32	7.0	10.6	13.8	20.0
U-1	33	10	10.7	12.9	15.0
U-2	31	9.4	10.6	13.0	15.7

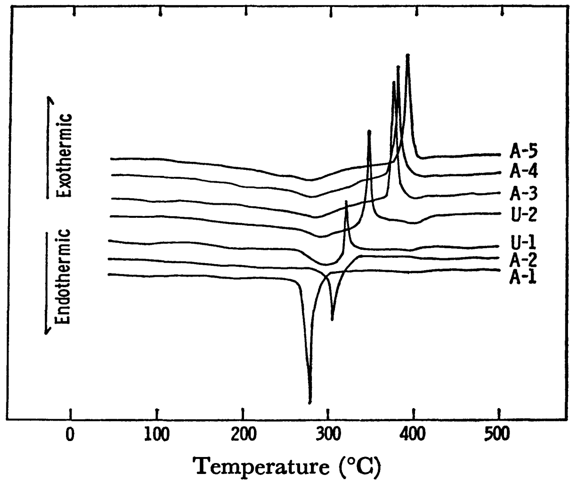

Fig. 3. Variations of DTA curve with Cl content

Variations of DTA curve with the Cl content are illustrated in Fig. 3. The sample A-1 of 17% Cl/Fe showed an endothermic peak at 280 °C, whereas A-5 of 7% Cl/Fe showed a broad endothermic peak at 275 °C and a sharp exothermic peak at 390 °C.

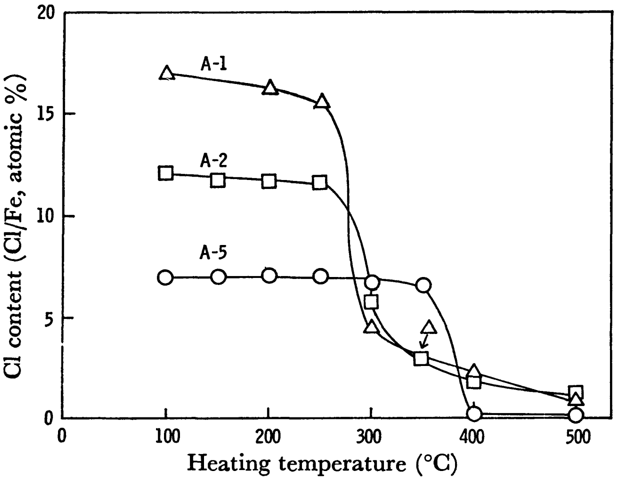

Fig. 4. Relation between Cl content and heating temperature.

The curves expressing the relationship between the Cl content and heating temperature (Fig. 4) showed the steep drop of Cl content at different temperatures. This temperature fell with the increase in the original Cl content. The sublimation of $FeCl_3$ was observed for A-3, A-4, and A-5 and the evolution of HCl was observed for A-1 and A-2 at each temperature corresponding to the sudden decrease of Cl.

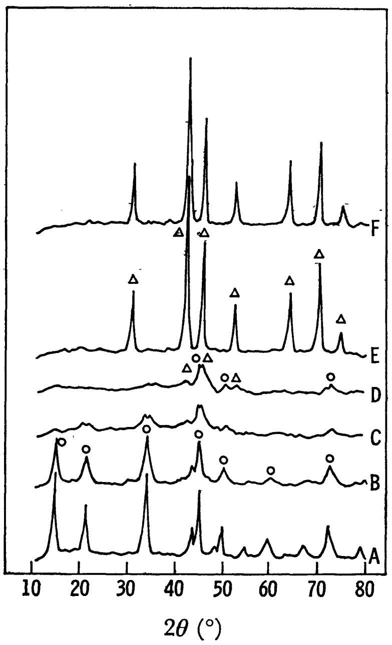

Fig. 5. X-ray diffraction patterns of A-1 at various heating temperatures: ○, β-FeOOH; △, α-Fe_2O_3; A, 100 °C; B, 200 °C; C, 300 °C; D, 350 °C; E, 400 °C; F, 500 °C.

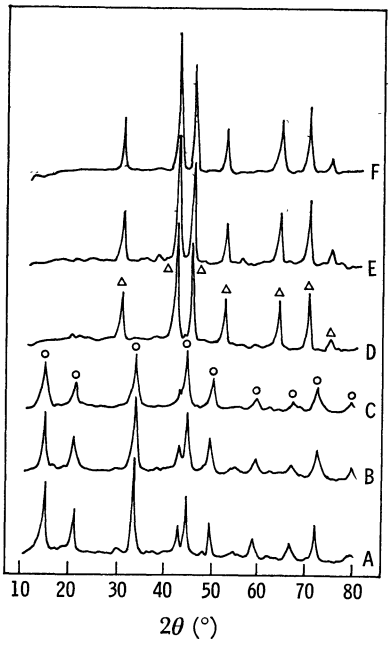

Fig. 6. X-ray diffraction patterns of A-5 at various heating temperatures: ○, β-FeOOH; △, α-Fe_2O_3; A, 100 °C; B, 200 °C; C, 250 °C; D, 300 °C; E, 400 °C; F, 500 °C.

Variations of X-ray diffraction patterns of A-1 and A-5 with heating up to various temperatures are shown in Figs. 5 and 6. A-1 was converted into an amorphous mixture of β-FeOOH and α-Fe_2O_3 at the temperature range 300—350 °C, whereas A-5 was transformed from β-FeOOH to α-Fe_2O_3 at 300 °C. Above 400 °C all the samples were completely transformed into α-Fe_2O_3. The crystallite size, calculated by the Scherrer equation for the (301) pattern of β-FeOOH at 2θ of 50.2 ° and

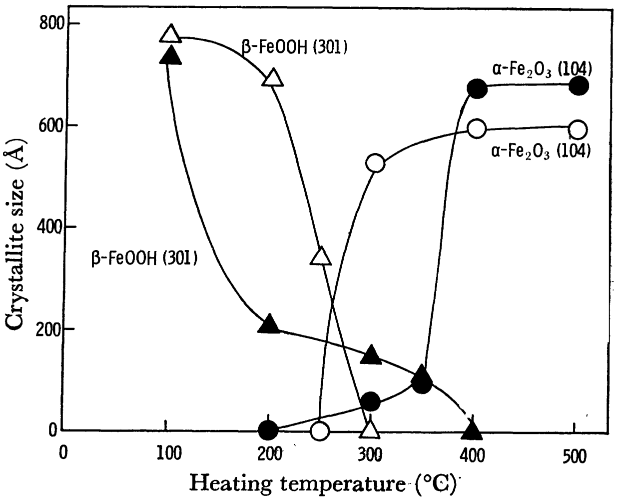

Fig. 7. Relation between crystallite size and heating temperature: △ and ○, A-1; ▲ and ●, A-5.

for the (104) pattern of α-Fe_2O_3 at 2θ of 41.9 °, is given in Fig. 7 for A-1 and A-5 as the function of heating temperature. The β-FeOOH structure of A-5 must be more liable to be destroyed on heating than that of A-1.

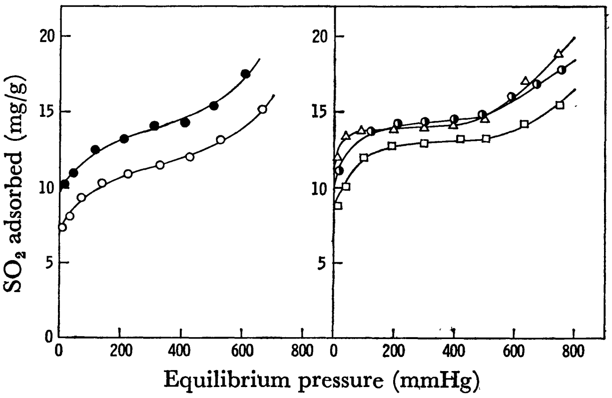

Fig. 8. SO_2 adsorption isotherms: ○, A-1; ●, A-2; △, A-3; ◑, A-4; □, A-5.

TABLE 2. AMOUNTS OF ADSORPTION (A_m and A_c) OF SO_2 ON β-FeOOH AND THE C CONSTANT OF THE BET EQUATION

Sample	Cl content (Cl/Fe, %)	A_m (mg/m²)	A_c (mg/m²)	A_c/A_m	C constant
A-1	17	0.31	0.25	0.8	390
A-2	12	0.38	0.34	0.9	390
A-3	7.7	0.40	0.40	1.0	520
A-4	7.4	0.44	0.43	1.0	720
A-5	7.0	0.45	0.46	1.0	1100

All the SO_2 adsorption isotherms are the BET-II type as shown in Fig. 8. However, the C constant of the BET equation, representing the adsorption strength in the first adsorption layer, increases with the decrease of Cl content. The monolayer adsorption capacity (A_m) calculated by the BET equation and the amount of the chemisorbed SO_2 (A_c) determined by the desorption under 10^{-5} Torr at 30.0 °C for 24 hr increased as the Cl content lowered (Table 2). The A_c/A_m ratio also increased up to unity as the Cl content decreased. These results indicate that the adsorption force for A-3, A-4, and A-5 is stronger than that for A-1 and A-2.

Discussion

Structure of β-FeOOH and the existence of Cl. The unit cell of β-FeOOH crystal contains two tunnels parallel to the c-axis (Fig. 9), in which water molecules and Cl^- ions can be accomodated.[3] If we assume that the unit cell includes one Cl^- ion, the Cl content is $1/8=12.5\%$ Cl/Fe, since a unit cell has eight Fe atoms. The H_2O/Fe ratio (Table 1) and the atomic ratio $(Cl+H_2O)/Fe$ obtained by the chemical analysis and TGA are plotted against the Cl content in Figs. 10 and 11, respectively. The values of $(Cl+H_2O)/Fe$ (Fig. 11) and H_2O/Fe (Fig. 10) amount to about 25% and 12.5%, respectively, at 12.5% Cl/Fe on each abscissa corresponding to the Cl content postulated from crystal structure as discussed above. It is therefore likely that tunnels and outer surfaces are to be filled up with Cl^- ions and H_2O molecules of equal amounts. As the crystal surfaces of β-FeOOH consist of a—c or b—c planes, the amount of Fe existing in the surface, estimated from the surface area obtained by N_2 adsorption and the unit cell area of a—c or b—c plane (31.7 Å^2), is 6.5% of the total Fe atoms. Therefore, the amount of Fe in the bulk is 93.5%. The Cl content in the crystal, which is overwhelmingly the amount of Cl in tunnels, is calculated as 11.7% Cl/Fe from the Cl/Fe ratio 12.5% and the Fe content 93.5%. The ratio $(Cl+H_2O)/Fe$ for the samples containing more than 12 or less than 9 atomic % is over 25% as shown in Fig. 11. As the tunnels in the 17% Cl/Fe sample are filled with H_2O molecules and Cl^- ions, the Cl^- ions of 17 minus 11.7% appear to exist on the crystal surfaces. The large value of $(Cl+H_2O)/Fe$ for the 7% Cl/Fe sample is considered to be due to the accumulation of H_2O molecules in the tunnels by replacing Cl^- ions.

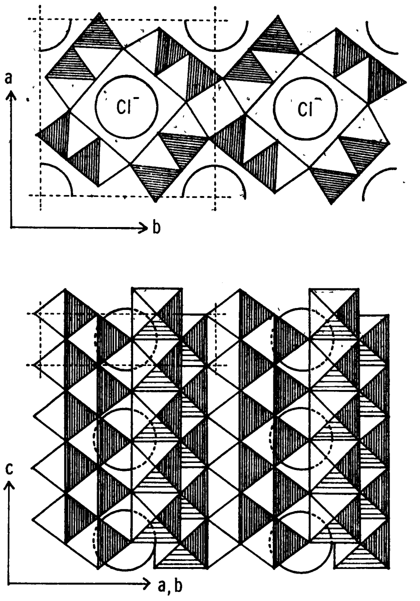

Fig. 9. Crystal structure of β-FeOOH. O^{2-} and OH^- ions are to be imagined at the corners of each octahedron and an Fe^{3+} ion at its center. β-FeOOH has a tetragonal lattice with the following unit cell dimensions: $a=b=10.48$ Å, $c=3.02$ Å.

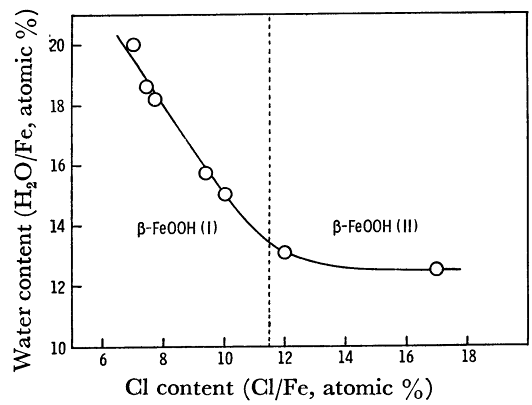

Fig. 10. Variation of H_2O content with Cl content.

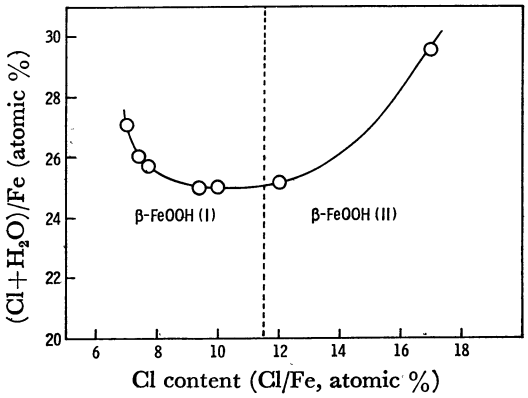

Fig. 11. Variation of $(Cl+H_2O)/Fe$ with Cl content.

The broad endothermic DTA peaks at 275—295 °C observed for A-3, A-4, A-5, U-1, and U-2 correspond to the conversion of β-FeOOH to the mixtures of β-FeOOH and α-Fe_2O_3. The sharp exothermic peaks at 345—390 °C correspond to the recrystallization of less-crystalline α-Fe_2O_3 produced from β-FeOOH at lower temperatures. On the other hand, A-1 and A-2 show only one endothermic DTA peak in the temperature region around 300 °C. It is confirmed by the X-ray diffraction and the chemical analysis of Cl that in cases of A-1 and A-2 the transformation of β-FeOOH into α-Fe_2O_3, the crystallization of resultant α-Fe_2O_3, and the Cl elimination occur simultaneously around 300 °C. The peak temperatures in those DTA curves are plotted against the Cl content in Fig. 12, where the following three areas are defined; the region of β-FeOOH, region of a mixture of β-FeOOH and α-Fe_2O_3, and region of α-Fe_2O_3. The three lines intersect each other at a point of 11.5% Cl/Fe. The Cl content of 11.5% Cl/Fe is nearly equal to the amount of Cl filling up the tunnels (11.7%). The samples containing Cl of less than 11.5% Cl/Fe and more than 11.5% Cl/Fe are denoted in Figs. 10, 11, and 12 as β-FeOOH(I) and β-FeOOH(II), respectively. The α-Fe_2O_3(II) transformed from β-FeOOH(II) contains an appreciable amount of Cl and is less crystalline than the α-Fe_2O_3(I) transformed from β-FeOOH(I).

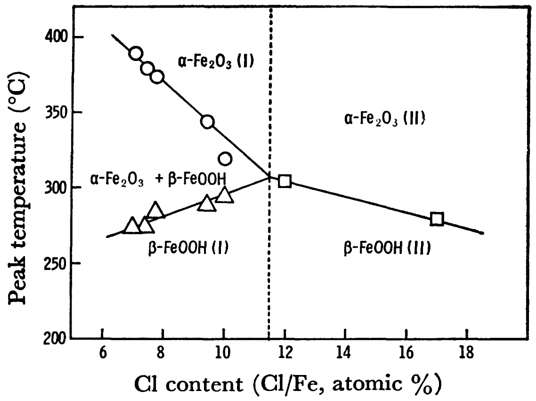

Fig. 12. Relation between peak temperature of DTA curve and Cl content in the original crystals: ○, exothermic peak; △ and □, endothermic peaks.

Cl in β-FeOOH(I). TGA curves (Fig. 2) show that H_2O molecules in the tunnels in A-5 (β-FeOOH(I)) are easily released by heating at temperature below 250 °C, so that the β-FeOOH structure of A-5 is more easily destroyed by heating than that of A-1 (β-FeOOH(II)) as shown in Fig. 7. β-FeOOH(I) is not completely transformed into α-Fe_2O_3 until Cl is removed as $FeCl_3$, though it changed into the mixture of less-crystalline β-FeOOH and α-Fe_2O_3. This fact suggests the roles of Cl in β-FeOOH: Cl inhibits both its transformation into α-Fe_2O_3 and the recrystallization of less-crystalline α-Fe_2O_3. The inhibitory effect of Cl on the transformation into α-Fe_2O_3 will be due to the stabilization of the β-FeOOH structure by Cl. The recrystallization of α-Fe_2O_3 seems to be obstructed by the bonding between Cl and Fe.

Cl in β-FeOOH(II). Fig. 7 indicates that A-1 (β-FeOOH(II)) is thermally more stable than A-5 (β-FeOOH(I)) up to 250 °C, probably because Cl^- ions on the surface interfere the release of H_2O molecules. However, the transformation of β-FeOOH(II) into α-Fe_2O_3 occurs abruptly at the temperature of release of Cl. The evolution of HCl was observed at the transformation temperature of β-FeOOH(II) into α-Fe_2O_3. It is presumed from this fact that Cl^- ions on the surface produce HCl on heating according to the formula; $OH^- + Cl^- \rightarrow O^{2-} + HCl$. The resulting HCl may accelerate the formation of α-Fe_2O_3 by destructing β-FeOOH crystal structure.

SO_2 adsorption. The monolayer adsorption capacity (A_m) and the amount of chemisorbed SO_2 (A_c) decrease with the increase of Cl content. Furthermore, A_c/A_m value approaches unity and the C constant in the BET equation increases as the Cl content decreases. From these results, we can conceive that Cl in β-FeOOH interferes the SO_2 adsorption, especially the chemisorption of SO_2. The chemisorption sites for SO_2 are presumably the O^{2-} ions in β-FeOOH. The surface is covered with Cl^- ions as the Cl content increases, The estimation of the surface coverage with Cl^- ions. using the diameter of Cl^- ion (3.6 Å) and the surface area obtained by N_2 adsorption, shows that the surface of the 17% Cl/Fe sample is completely covered by the monolayer of Cl^- ions, and suggests that the chemisorption does not occur. However, Table 2 indicates that the sample of 17% Cl/Fe chemisorbs a considerable amount of SO_2, which is nearly equal to half A_c of 7% Cl/Fe sample adsorbing no Cl^- ions on the surface. This conflict can be understood by assuming that SO_2 binds with a half O^{2-} ions, pushing Cl^- ions aside. According to the structure of a—c or b—c plane constituting the crystal structure, there are two kinds of surface O^{2-} ions; O^{2-} ion bound with one Fe atom and O^{2-} ion bound with two Fe atoms. The former O^{2-} ions are considered to have stronger affinity with sulfur in SO_2 than the latter O^{2-} ions.

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