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DTA STUDY ON α-Fe_2O_3 FORMATION FROM Fe(III)-HYDROXIDES CONTAINING FOREIGN METALLIC IONS

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ABSTRACT

The formation of α-Fe_2O_3 from Fe(III)-hydroxides containing the different metallic ions (Me) was studied with DTA, TG and XRD; Me^{2+}'s were Mg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} and Me^{3+}'s were Al^{3+} and Cr^{3+}. The mixing of Me was carried out by three procedures: co-precipitation, gel-mixing and mortar-mixing. Sample-F of Fe(III)-hydroxide containing no Me was prepared from $Fe(NO_3)_3$ and NaOH solutions at pH=12. The sample showed an endothermic DTA peak at Td=100°C due to the dehydration and an exothermic peak at Tc=414°C corresponding to the formation of α-Fe_2O_3. The co-precipitation samples containing 10 mol% of Me showed Tc=527°C for Cu^{2+}, 528°C for Co^{2+}, 550°C for Zn^{2+}, 554°C for Mg^{2+}, 559°C for Ni^{2+}, 473°C for Al^{3+}, and 480°C for Cr^{3+}. The Tc value increased with an increase in the amount of Me mixed between 0 and 10 mol%. The different mixing procedures for 10 mol% of Cu^{2+} were observed to give Tc=527°C for co-precipitation, 517°C for gel-mixing, and 414 and 494°C for mortar-mixing. These results suggest that (1): the foreign Me's forming ferrite retard the formation of α-Fe_2O_3 more than Me's forming solid solution with α-Fe_2O_3 and (2): the mixing procedure affects the degree of incorporation of Me in the Fe(III)-hydroxide.

INTRODUCTION

The thermal dehydration of Fe(III)-hydroxide is used as an industrial process for the production of α-Fe_2O_3 powder. In the present experiments, the transformation of Fe(III)-hydroxides from amorphous state to α-Fe_2O_3 was studied with DTA, TG, and XRD. Inouye et al.[1] showed that Cu^{2+} ion mixed in α-FeOOH retarded its transformation to α-Fe_2O_3. In a previous paper [2], we observed a similar fact. This paper presents the retardation effect of seven foreign matallic ions

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(Me=Mg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Al^{3+}, and Cr^{3+}) on α-Fe_2O_3 formation.

EXPERIMENTAL

Materials. Pure Fe(III)-hydroxide (sample-F): Fe(III)-hydroxide gel (Fe-gel) was prepared at 30°C from solutions of 0.1M-$Fe(NO_3)_3$ and 6M-NaOH at pH=12. The sample-F was obtained from Fe-gel by drying for 8 hr at 80°C after washing.XRD of the sample-F showed no diffraction line at 2θ=20-80°. Foreign Metallic Ion Containing Hydroxide: the mixing of foreign metallic ion (Me) was carried out with the following procedures: (1) co-precipitation: 6M-NaOH solution was mixed with 0.1M-$Fe(NO_3)_3$ solution containing Me-salt at a fixed Me/(Fe+Me) mol ratio. The volume of the NaOH solution was adjusted to give pH=12±0.2 of the supernatant solution at 30°C after precipitate was settled. The reagents of Me-salts were analytical grade sulfates of Mg^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} and nitrates of Cu^{2+}, Al^{3+}, and Cr^{3+} ; (2) gel-mixing:slurries of Fe-gel and Cu(II)-hydroxide gel (Cu-gel) were mixed at pH=12 and then stirred for 15 min. The Cu-gel was prepared from 0.1M-$Cu(NO_3)_2$ solution and 6M-NaOH solution at 30°C; (3) mortar-mixing: the sample-F (500 mg) and a desired amount of $Cu(OH)_2$ or CuO was mixed in an agate mortar for 30 min. $Cu(OH)_2$ precipitate was prepared from an ammoniacal 0.1M-$Cu(NO_3)_2$ solution (280 ml) and 6M-NaOH solution (8.5 ml). The precipitate was washed with water (2 l) and dried at room temperature under a vacuum of 20-30 mmHg. XRD showed the lines of $Cu(OH)_2$. CuO(A) and CuO(B) were obtained by heating of $Cu(OH)_2$ in air at 110°C for 5 hr and 400°C for 1 hr, respectively.

DTA and TG. The apparatus of Model 8085 from Rigaku Denki (Tokyo Japan) was operated in air at 10°C/min. The sample weight was 20 mg and α-Al_2O_3 powder (20 mg) was used as reference material. The size of platinum sample container was 5 mm dia. and 2.5 mm hight. Temperature was measured with Pt-13%Rh thermocouple.

XRD. A Geigerflex Type 2001 diffractometer (Rigaku Denki) was used for powder XRD of the samples. The diffraction conditions were: target, Co; voltage, 35 kV; current, 10 mA.

BET. The specific surface area was estimated by the BET method from the amount of N_2 adsorbed at liquid nitrogen temperature.

RESULTS AND DISCUSSION

Figure-1 shows DTA and TG curves of sample-F, which does not contain the foreign metallic ion. DTA curve has an endothermic peak at 100°C and a sharp exothermic peak at 414°C. The TG curve shows that the weight decrease starts around 40°C and ends near 400°C. The total weight decrease is 14.8 wt.%. The XRD was carried out for samples heated to temperatures shown by arrows on the DTA curve. Sample-F gave XRD lines of α-Fe_2O_3 above 300-350°C and the intensity increased with heating temperature. The crystallite size estimated from half-line width of (104) plane [3] increased from 23 nm to 93 nm for the sample obtained at 400°C and 600°C, respectively. The BET surface area decreased gradually from 285 m^2/g for non-heated sample-F to 175 m^2/g for the sample heated to 350°C and then decreased markedly at higher tempeartures (48.5 m^2/g at 450°C). These results suggest that the sample-F is amorphous ferric hydroxide ($Fe_2O_3.1.5H_2O$) below 300-350°C and the dehydration occurs at 40-400°C which is followed by the crystallization to α-Fe_2O_3 occurring in the temperature range where the exothermic peak appears, and the crystallinity increases with the temperature.

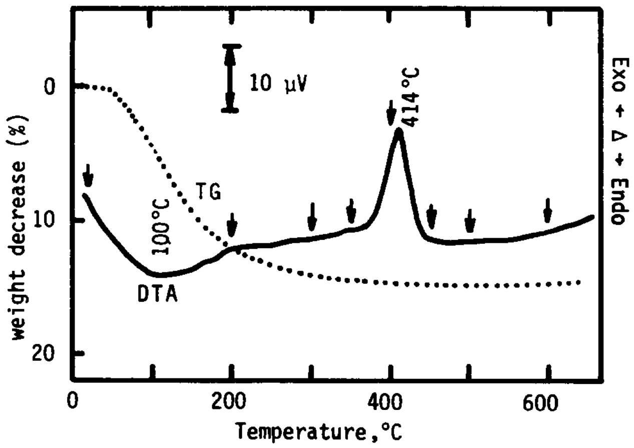

Fig. 1 DTA and TG curves of pure Fe(III)-hydroxide (sample-F). ϕ=10°C/min, static air

Figure-2 shows DTA curves of samples containing 10 mol% of Me, which were prepared with the co-precipitation procedure. The exothermic peak corresponding to the formation of α-Fe_2O_3 is observed at Tc=527-559°C for the samples containing Me^{2+} and at Tc=473-480°C for Me^{3+}, which are higher by 60-140°C than Tc=414 °C for the sample-F. These Tc values imply that Me^{2+} ion has a larger retardation effect than Me^{3+} ion. The XRD data for samples taken out in the course of heating process indicated that the co-precipitation samples containing Me^{2+} form a small amount of $MeFe_2O_4$ in addition to α-Fe_2O_3 and those containing Me^{3+} show only XRD lines of α-Fe_2O_3, but 2θ is shifted to higher angles. From these results, the difference in the retardation effect of Me^{2+} and Me^{3+} is considered to be due to that Me^{2+}'s react with α-Fe_2O_3 to form the oxide of spinel structure and Me^{3+}'s form the solid solution with α-Fe_2O_3. In Fig.2, the curve for Al^{3+}-containing sample shows two extra exothermic peaks at 211°C and 272°C. It was indicated by XRD that the sample was still amorphous after heated to 400°C. The reactions corresponding to these two peaks are unknown at present.

Figure-3 shows DTA curves of the samples containing 10 mol% Cu^{2+}, which were prepared with different mixing procedures. Curve-C was obtained for co-precipitation sample, curve-G was for gel-mixing sample, and curves-M1, M2 and M3 were for mortar-mixing samples containing $Cu(OH)_2$, CuO(A) and CuO(B), respectively.

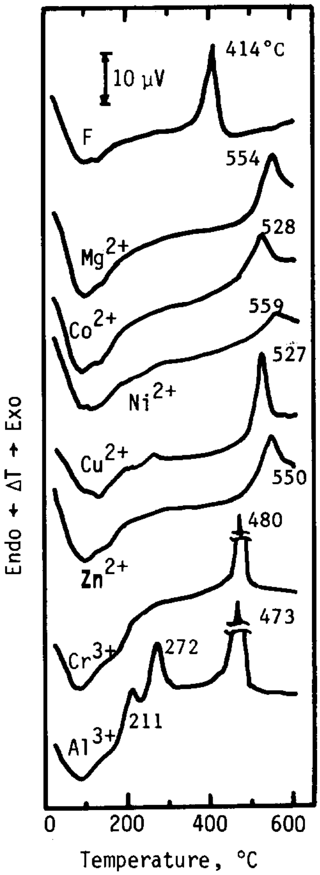

Fig.2 DTA curves of Fe(III)-hydroxides containing 10 mol% of Me^{2+} mixed by co-precipitation procedure. F:sample-F, ϕ=10°C/min, static air

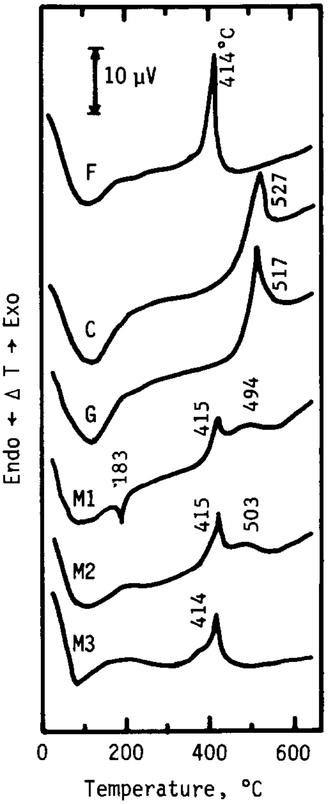

Fig.3 DTA curves of Fe(III)-hydroxides containing 10 mol% Cu^{2+} prepared with different mixing procedures.

F: sample-F,
C: co-precipitation,
G: gel-mixing,
M1,M2 and M3: mortar-mixing with $Cu(OH)_2$, CuO(A) and CuO(B)

Curve-C and G show Tc=527°C and 517°C. These values indicate that the retardation effect of Cu^{2+} mixed by co-precipitation procedure is similar to that by the gel-mixing procedure. Curve-M1 shows an endothermic peak at 183°C in addition to that at 100°C. XRD and DTA of pure $Cu(OH)_2$ suggested that the former corresponds to dehydration of $Cu(OH)_2$ to CuO. The exothermic peak temperatures (Tc=414-415°C) of curves-M1, M2 and M3 are equal to that of the sample-F (pure Fe(III)-hydroxide, Tc=414°C, curve-F). Furthermore, the formation of α-Fe_2O_3 was confirmed by XRD of the samples heated to 415°C. Accordingly, it is considered that the pure Fe(III)-hydroxide remains in the mortar-mixing samples prepared from sample-F and $Cu(OH)_2$ or CuO. Curves-M1 and M2 show small broad exothermic peaks at 494°C and 503°C. XRD showed an increase in the diffraction line intensity of α-Fe_2O_3 in the range of 450 °C to 600°C. This fact indicates that the broad exothermic peaks are also corresponding to the formation of α-Fe_2O_3. These DTA and XRD results suggest that the mechanical mixing with a mortar leads to inhomogeneous interaction between the particles of sample-F and $Cu(OH)_2$ or CuO; Cu^{2+}-oxide incorporates with the outer surface layer of sample-F particle, but can not with the inner part of the par-

Table 1

DTA peak temperature (Tc) of α-Fe_2O_3 formation, amount of water by TG, and the oxides formed for the co-precipitation samples.

Me mixed	Fe/(Fe+Me) mol %	Tc °C	H_2O wt.%	oxide formed after heating at 600°C
non	0	414	14.8	α-Fe *
Cu^{2+}	1	454	12.4	α-Fe
	3	485	17.6	α-Fe
	5	507	13.6	α-Fe, CuO
	10	527	13.8	α-Fe, CuO
	15	541	14.0	α-Fe, CuFe**, CuO ?
Mg^{2+}	1	414	18.7	α-Fe
	3	474	18.4	α-Fe
	5	500	13.6	α-Fe, MgFe ?
	10	554	19.8	α-Fe, MgFe
Co^{2+}	1	427	19.3	α-Fe
	3	466	9.6	α-Fe
	5	488	13.2	α-Fe, CoFe
	10	528	17.2	α-Fe, CoFe
Ni^{2+}	1	435	15.0	α-Fe
	3	499	10.8	α-Fe
	5	524	13.4	α-Fe, NiFe ?
	10	559	17.1	α-Fe, NiFe
Zn^{2+}	1	432	18.7	α-Fe
	3	472	17.2	α-Fe
	5	509	12.5	α-Fe, ZnFe
	10	550	18.8	α-Fe, ZnFe
Al^{3+}	10	473	-	α-Fe
Cr^{3+}	10	480	-	α-Fe

* α-Fe = α-Fe_2O_3, **MeFe = $MeFe_2O_4$

ticle,thus the exothermic peaks at 414°C and 415°C correspond to α-Fe_2O_3 formation from pure Fe(III)-hydroxide present in the inner part and the peaks at 494°C and 503°C correspond to that from the outer surface layer. Further, Fig.3 shows that curve-M3 for CuO(B) does not give the broad exothermic peak near 500 °C and the curve-M1 for $Cu(OH)_2$ gives a large area of the exothermic peak compared with curve-M2 for CuO(A). This may imply that the degree of interaction between Cu^{2+} incorporated in the surface layer and Fe(III)-hydroxide decreases in the order of $Cu(OH)_2$ > CuO(A) > CuO(B).

In Table 1 are listed Tc values of co-precipitation samples of different mixing ratios of Me, the oxides detected by XRD of samples after heating to 600°C and the amount of water estimated by TG. The amount of water is seen to be independent of the mixing ratio and the kind of Me. The change in Tc value shown in the table indicates an increasing retardation effect of Me's with their mixing ratio. The all Me^{2+}'s are found to form $MeFe_2O_4$ after heating to 600°C when the mixing ratio exceeds 5 mol% except for Cu^{2+}. These facts suggest that the co-precipitation procedure leads to the formtion of amorphous hydroxide containing Me which is not a simple mixture of amorphous Fe(III)-hydroxide·and Me-hydroxide, but is in an intermediate state for ferrite formation [4]. Tn the cases of Al^{3+} and Cr^{3+}-containing co-precipitation samples, the formation of Al_2O_3 and Cr_2O_3

was not observed. Thus, these foreign metallic ions are supposed to occupy the sites of Fe^{3+} and form solid solution of hydroxide. It is considered that the movement of Fe^{3+} and O^{2-} ions in heating process is more restricted in the intermediate state and in the solid solution than in the pure amorphous Fe(III)-hydroxide.

CONCLUSION

The foreign metallic ions (Me^{2+} and Me^{3+}) mixed in Fe(III)-hydroxide retard the formation of α-Fe_2O_3 in heating process. Me^{2+} ions which form $MeFe_2O_4$ having spinel structure retard the formation more than Me^{3+} ions which form solid solution with α-Fe_2O_3. The mixing procedures of co-precipitation and gel-mixing have a higher retardation effect than mortar-mixing.

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REFERENCES

1. K.Inouye, S.Ishii, K.Kaneko and T.Ishikawa, Z. anorg. allg. chem., 391 (1972) 86.
2. R.Furuichi, N.Sato and G.Okamoto, Chimia, 23 (1969) 455.
3. L.Alexander, J.Appl. Phys., 25 (1952) 155.
4. T.Sato, M.Sugihara and M.Saito, Kogyo Kagaku Zassi, 65 (1962) 748.