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THE EFFECT OF Cr^{3+} AND Fe^{3+} IONS ON THE TRANSFORMATION OF DIFFERENT ALUMINUM HYDROXIDES TO α-Al_2O_3

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ABSTRACT

The α-transformation of pseudoboehmite, boehmite and bayerite containing Cr^{3+} and Fe^{3+} ions at concentrations of 0, 4.8, 9.1 and 16.7 mole%, which were prepared by coprecipitation, was investigated by means of TG, DTA, X-ray diffraction and diffuse reflectance spectra. It was found that the added metal ions influenced remarkably the temperature and sequence of the transformation to α-Al_2O_3. The effect depended on the state of existence of the ions, which varied with the kind of aluminum hydroxide. In pseudoboehmite and boehmite containing Cr^{3+} ion, the α-transformation [via η (or γ) $\rightarrow \delta \rightarrow \theta \rightarrow \alpha$-$Al_2O_3$] was inhibited by the stabilization of θ-Al_2O_3. The stabilization of θ-Al_2O_3 was considered to be due to the formation of Cr^{6+} ion, which resulted from the oxidation of part of the Cr^{3+} ions incorporated in aluminum hydroxides during the dehydration in air. On the contrary, in bayerite containing Cr^{3+} ion the α-transformation (via $\eta \rightarrow \alpha$) was accelerated; the added Cr^{3+} ion was not incorporated in the bayerite structure and was crystallized separately as α-Cr_2O_3 on heating. This α-Cr_2O_3 particle in a nascent state appeared to act as an active nucleus to the crystallization of α-Al_2O_3. On the other hand, in all aluminum hydroxides containing Fe^{3+} ion, the α-transformation [via η (or γ) $\rightarrow \delta \rightarrow \alpha$] was remarkably accelerated. Since the added Fe^{3+} ion was not incorporated in all aluminum hydroxides and was crystallized as α-Fe_2O_3 on heating, the same accelerating mechanism as in the bayerite containing Cr^{3+} ion is assumed to operate.

Moreover, the effect of α-Cr_2O_3, mixed mechanically with transition aluminas (η-, γ- and δ-Al_2O_3) in different molar ratios on the α-transformation was also investigated for a comparison with the results obtained in aluminum hydroxides containing Cr^{3+} ion prepared by coprecipitation.

INTRODUCTION

The temperature of the transformation of aluminum hydroxides or transition aluminas to α-Al_2O_3 (hereafter called α-transformation below) is influenced by many factors such as their particle size and shape, calcining atmosphere, additives, impurities, etc. Some of these factors have already been investigated by several workers [1]. In a previous paper [2], the present authors showed that the hydrothermal conditions for the preparation of boehmite influenced not only its dehydration kinetics and mechanism, bu also the transformation temperature of the resultant γ-Al_2O_3 to α-Al_2O_3. I has also been found that the reactivity of transition aluminas [3] an amorphous aluminas [4], which were prepared by thermal decomposition o the sulfate, nitrate and chloride of aluminum, for α-transformation an $ZnAl_2O_4$ formation was influenced by a small amount of anions containe in aluminas. Although Al_2O_3–Cr_2O_3 and Al_2O_3–Fe_2O_3 systems are important in the technology of inorganic [1] and catalytic chemistry [5], th effect of Cr^{3+} and Fe^{3+} ions, which have a similar ionic radius and electrica charge to Al^{3+} ion, on α-transformation has not been fully investigated. It i generally agreed that the addition of Fe^{3+} ion by both coprecipitation [6,7 and mechanical mixing [8] accelerates α-transformation, while some discrepancies in the effect of Cr^{3+} ion have been reported. For example, Okad and Kuwazima [9] have shown that the addition of Cr^{3+} ion by coprecipitation stabilized θ-Al_2O_3 and inhibited α-transformation at a concentratio below 5 wt.% Cr_2O_3, whereas α-transformation was accelerated above 1 wt.% Cr_2O_3. Bye and Simpkin [7] obtained a similar result, i.e. α-transformation was inhibited at 2 and 4 wt.% Cr^{3+} ion and was accelerated at 8 wt. Cr^{3+} ion added by coprecipitation. On the contrary, the addition of Cr_2O oxide by mechanical mixing is reported to have no effect [10] or to promot [8] α-transformation. The effect of the difference in the addition method o the metal ion, i.e. coprecipitation and mechanical mixing, on α-transformation has not been investigated systematically until now. Even in the coprecipitation system [7,9], the mechanism by which the effect of Cr^{3+} ion on th α-transformation varies with its concentration has not been fully understood It is considered that the effect of coprecipitated Cr^{3+} ion depends on th kind of aluminum hydroxide as a starting material, its crystallinity, the stat of ion existing in it, etc.

In order to elucidate these problems, the effect of Cr^{3+} and Fe^{3+} ions o the temperature and sequence of the transformation from pseudoboehmit boehmite and bayerite coprecipitated with these ions to α-Al_2O_3 was investigated in detail. Furthermore, the effect of α-Cr_2O_3 mechanically mixe with transition aluminas (η-, γ- and δ-Al_2O_3) in different molar ratios o α-transformation was also investigated and compared with results obtaine in the coprecipitation system.

EXPERIMENTAL

Three kinds of aluminum hydroxides containing Cr^{3+} and Fe^{3+} ions, i. pseudoboehmite ($Al_2O_3 \cdot n\ H_2O$, $1.3 < n < 1.8$) [11], boehmite ($Al_2O_3 \cdot H_2O$ and bayerite ($Al_2O_3 \cdot 3\ H_2O$), were prepared using the same techniques a those for pure aluminum hydroxides [12]. Pseudoboehmite was prepared b adding 10 wt.% $Al(NO_3)_3$ solutions containing $Cr(NO_3)_3$ or $Fe(NO_3)_3$ a concentrations of 0, 4.8, 9.1 and 16.7 mole% to 4 M NH_4OH, with stirring, at room temperature until the pH reached about 8.7. The precipitates obtained were filtered immediately without ageing, washed, and dried in air at 130°C for 24 h. Bayerite was obtained by ageing gels precipitated at about 10°C and pH = 11.3 by a process similar to that for pseudoboehmite. After ageing in the mother liquor at 15°C for 24 h, the gels were filtered, washed and then dried in a vacuum drying oven at 50°C for 21 h. Boehmite was hydrothermally synthesized from pseudoboehmite, obtained as described above, in an autoclave under the conditions of 88 kg cm^{-2} vapor pressure, 300°C for 5 h. All aluminum hydroxide samples were sieved to obtain -300 mesh fraction and were used in the TG–DTA experiment and in the isothermal experiment, which was carried out in a horizontal electrical furnace at 800–1200°C in air or in vacuum.

In order to investigate the effect of α-Cr_2O_3 mixed mechanically on the α-transformation, the samples used were prepared as follows. η-Al_2O_3 was obtained by calcining the pure bayerite mentioned above at 700°C for 3 h. γ- and δ-Al_2O_3 were obtained by calcining the pure boehmite at 700 and 1000°C for 3 h, respectively. α-Cr_2O_3 was prepared by calcining commercial reagent at 1300°C for 2 h. Each transition alumina (η-, γ- and δ-Al_2O_3) and α-Cr_2O_3 were sieved to obtain -300 mesh fraction and were mixed in different molar ratios (0–50.9 mole%). All reagents used were of GR grade and were supplied by Kanto Chemical Co. Inc.

Simultaneous TG–DTA measurements were carried out using a Rigaku Denki Model 8085 thermoanalyzer at a heating rate of 10°C min^{-1} in air. The weight loss in TG and the peak temperature in DTA were reproduced within $\pm$ 3% and ± 2°C, respectively.

X-Ray diffraction for aluminum hydroxides and their dehydration products was conducted with Ni-filtered CuK_α radiation (25 kV, 10 mA) using a Geigerflex 2141 (Rigaku Denki Co.) or with Fe-filtered CoK_α radiation (35 kV, 10 mA) using a Geigerflex 2001 (Rigaku Denki Co.).

The diffuse reflectance spectra were obtained with a Hitachi 330 spectrophotometer using alumina as reference in the wavelength range 300–800 nm at room temperature.

The specific surface area was determined by measuring nitrogen adsorption isotherms at -196°C.

RESULTS AND DISCUSSION

X-Ray diffraction and DTA of aluminum hydroxides containing Cr^{3+} and Fe^{3+} ions

Figure 1 shows the X-ray diffraction patterns and DTA curves for pseudoboehmites with and without the addition of Cr^{3+} and Fe^{3+} ions. The

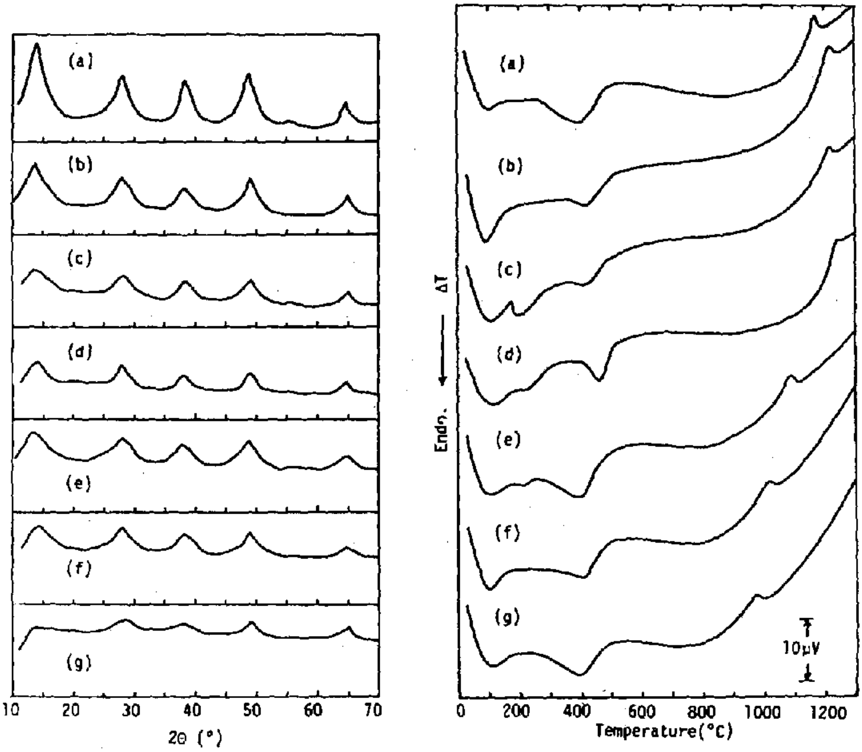

Fig. 1. X-Ray diffraction patterns and DTA curves for pseudoboehmites containing Cr^{3+} and Fe^{3+} ions. (a) Pure pseudoboehmite; (b) +4.8 mole% Cr^{3+}; (c) +9.1 mole% Cr^{3+}; (d) +16.7 mole% Cr^{3+}; (e) +4.8 mole% Fe^{3+}; (f) +9.1 mole% Fe^{3+}; (g) +16.7 mole% Fe^{3+}.

X-ray diffraction patterns of pseudoboehmites containing Cr^{3+} and Fe^{3+} ions (Fig. 1b–g) are very similar to that of pure pseudoboehmite (Fig. 1a), but they become broader with increasing Cr^{3+} or Fe^{3+} ion content. As shown in the DTA curve (Fig. 1a), pure pseudoboehmite has two broad endothermic peaks at 100 and 400°C which correspond to the desorption of adsorbed water and the dehydration of pseudoboehmite, and a small exothermic peak at 1170°C which corresponds to the transformation of a resultant transition alumina to α-Al_2O_3, respectively. The peak temperature of the dehydration of pseudoboehmite at 400°C tends to shift to higher temperatures with increasing Cr^{3+} ion content, while it did not change in the case of pseudoboehmites containing Fe^{3+} ion. On the other hand, the temperature of the exothermic peak corresponding to α-transformation shifted to higher temperatures on the addition of Cr^{3+} ion and to lower temperatures on the addition of Fe^{3+} ion. Because the X-ray diffraction patterns of pseudoboehmites containing Cr^{3+} and Fe^{3+} ions are very broad, it is difficult to determine from the shift of diffraction lines whether or not the metal ions coprecipitated are incorporated in the pseudoboehmite struc-

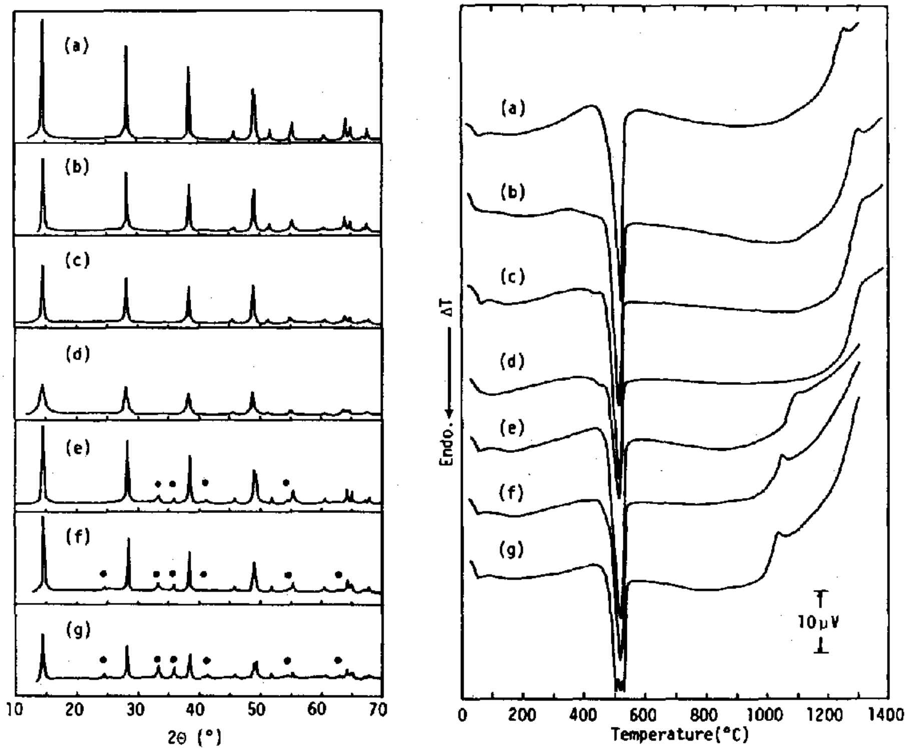

Fig. 2. X-Ray diffraction patterns and DTA curves for boehmites containing Cr^{3+} and Fe^{3+} ions. ●, α-Fe_2O_3. (a) Pure boehmite, 23 m^2 g^{-1}; (b) +4.8 mole% Cr^{3+}, 40 m^2 g^{-1}; (c) +9.1 mole% Cr^{3+}, 40 m^2 g^{-1}; (d) +16.7 mole% Cr^{3+}, 67 m^2 g^{-1}; (e) +4.8 mole% Fe^{3+}, 24 m^2 g^{-1}; (f) +9.1 mole% Fe^{3+}, 21 m^2 g^{-1}; (g) +16.7 mole% Fe^{3+}, 22 m^2 g^{-1}.

ture. However, the fact that the peak temperature of dehydration changes on the addition of Cr^{3+} ion and does not change on the addition of Fe^{3+} ion may suggest that Cr^{3+} ion is incorporated in the structure of pseudoboehmite and Fe^{3+} ion is not.

Figure 2 shows the X-ray diffraction patterns and DTA curves of boehmites with and without the addition of Cr^{3+} and Fe^{3+} ions, which were obtained by the hydrothermal synthesis of pseudoboehmites shown in Fig. 1. The values of the specific surface areas of these samples are given in the legend of this figure. The changes in the angular position of the diffraction lines of boehmites with Cr^{3+} and Fe^{3+} ion content are summarized in Table 1. In the systems containing Cr^{3+} ion (Fig. 2b–d), the presence of boehmite alone is detected, and the diffraction lines become broader and the specific surface area increases with increasing Cr^{3+} ion content. These facts indicate the decrease in crystallinity of boehmite. Besides, as shown in Table 1, (020), (021) and (041) lines of boehmite shifted to lower diffraction angles with increasing Cr^{3+} ion content, indicating expansion of the boehmite lattice due to the incorporation of Cr^{3+} ion (Goldschmidt's ionic radius

TABLE 1

The change in 2θ angle [a] of (020), (021) and (041) or (130) lines of boehmites shown in Fig. with Cr^{3+} and Fe^{3+} ion content

	(020)	(021)	(041), (130)
Boehmite	14.48	28.23	38.40
+4.8 mole% Cr^{3+}	14.45	28.20	38.38
+9.1 mole% Cr^{3+}	14.42	28.10	38.30
+16.7 mole% Cr^{3+}	14.42	28.05	38.25
+4.8 mole% Fe^{3+}	14.47	28.22	38.40
+9.1 mole% Fe^{3+}	14.48	28.23	38.40
+16.7 mole% Fe^{3+}	14.46	28.22	38.40

[a] With the experimental error of about ±0.03°.

is 0.65 Å for Cr^{3+} ion and 0.57 Å for Al^{3+} ion). On the other hand, in th systems containing Fe^{3+} ion (Fig. 2e–g), the diffraction patterns reveal th presence of boehmite and α-Fe_2O_3. Regardless of the change in Fe^{3+} io content, the diffraction lines of boehmite were relatively sharp and showe no shift in position (Table 1). The specific surface area values of thes samples were also nearly constant. These facts indicate that the added Fe^3 ion (Goldschmidt's ionic radius is 0.67 Å) was not incorporated in th boehmite structure, but was separated as α-Fe_2O_3. The position of the line of α-Fe_2O_3 shifted to higher diffraction angles by the lattice contraction du to the incorporation of Al^{3+} ion; the diffraction lines at $2\theta(°) = 33.17$, 35.5 and 40.85 for pure α-Fe_2O_3 shifted to 33.40, 35.95 and 41.20 for α-Fe_2C containing Al^{3+} ion (Fig. 2e–g).

As shown in the DTA curve (Fig. 2a), pure boehmite has an endothermi peak at 519°C and an exothermic peak at 1254°C, which correspond to th dehydration of boehmite and the transformation of the resultant alumina t α-Al_2O_3, respectively [2]. The peak temperature of the endotherm shifted t lower temperatures with increasing Cr^{3+} ion content [for example, fro 519°C in (a) to 509°C in (d)], while it did not change in the system containing Fe^{3+} ion. On the other hand, the peak temperature of th exotherm due to the α-transformation shifted to higher temperatures in th systems containing Cr^{3+} ion and to lower temperatures in the system containing Fe^{3+} ion, respectively.

Figure 3 shows the TG curves for boehmites with and without th addition of Cr^{3+} and Fe^{3+} ions. The weight loss of pure boehmite shown i curve (a) was observed as 15.3 wt.% in the temperature range RT–1300°C which agrees well with the theoretical value of water content of boehmi (15.0 wt.%). The weight loss for boehmites containing Fe^{3+} ion decrease with increasing Fe^{3+} ion content, i.e. 14.9, 13.5 and 11.0 wt.% for curves (e (f) and (g), respectively. This is consistent with a relative increase in th

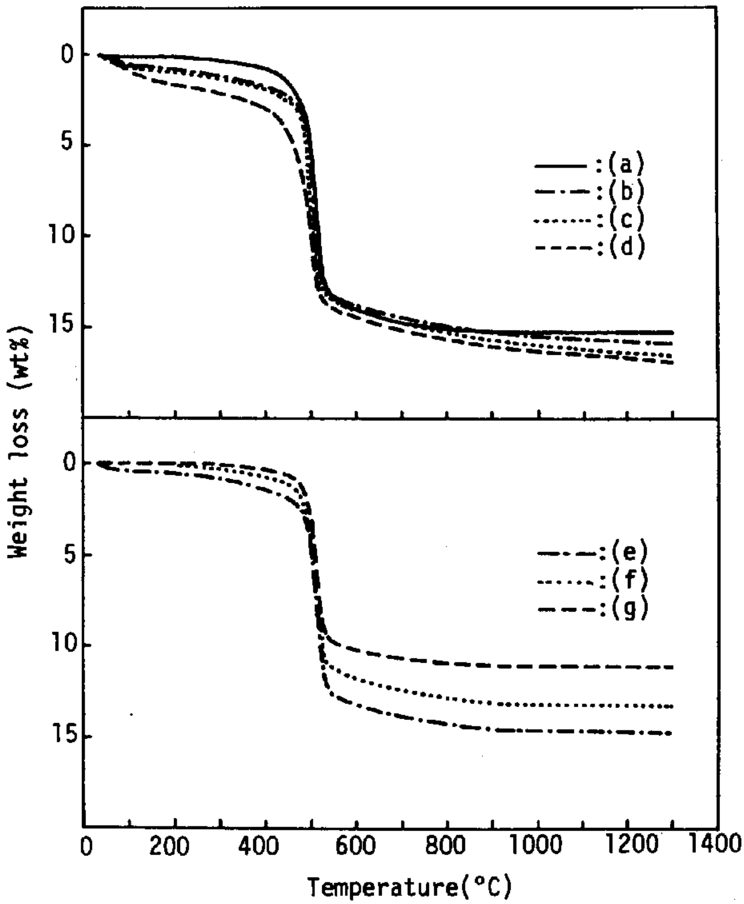

Fig. 3. TG curves for boehmites shown in Fig. 2(a–g).

amount of α-Fe_2O_3 coexisting with boehmite as shown in Fig. 2(e–g). On the other hand, the boehmites containing Cr^{3+} ion shown in curves (b)–(d) give some weight loss even below 200°C in contrast to pure boehmite. This weight loss will correspond to the desorption of the physically adsorbed water on the surface of boehmite, which results from increasing surface area in the system containing Cr^{3+} ion as shown in Fig. 1. Therefore, compared with the weight loss in the temperature range 200–1300°C except below 200°C, the values of 15.6, 15.2 and 15.4 wt% were observed for boehmites containing 4.8, 9.1 and 16.7 mole% Cr^{3+} ion [(b)–(d)], respectively. These values may agree with the theoretical water content of boehmite. However, no weight loss was observed for pure boehmite above 900°C, while for boehmites containing Cr^{3+} ion [(b)–(d)], the weight loss of ca. 0.7 wt.% was observed in the temperature range 900–1300°C. It is known that Cr^{3+} ion in aluminum hydroxide is readily oxidized to Cr^{6+} ion on dehydration [13]. Therefore, it can be considered that the weight loss above 900°C observed in

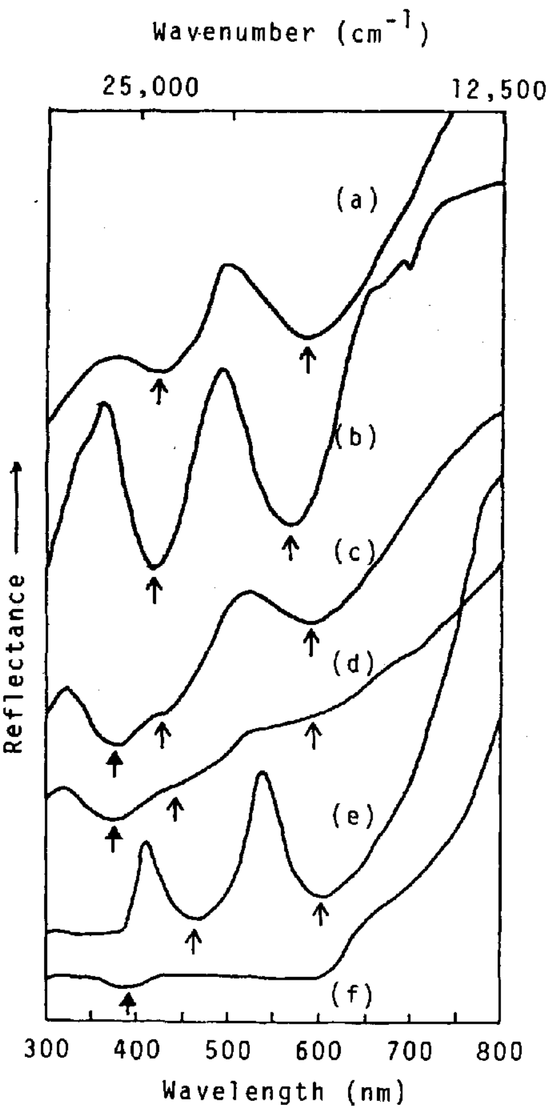

Fig. 4. Diffuse reflectance spectra of aluminas obtained by heating boehmite containing 16.7 mole% Cr^{3+} ion in vacuum (a) and in air (b–d) at various temperatures. (a) 1000°C, 3 h in vacuum (10^{-3} mm Hg); (b) 1370°C; (c) 1100°C; (d) 600°C; (e) α-Cr_2O_3; (f) CrO_3. (a) was heated in the horizontal furnace and (b–d) in the DTA apparatus. The aluminas obtained were identified by X-ray diffraction as (a) θ- and δ-Al_2O_3; (b) α-Al_2O_3; (c) θ-Al_2O_3; and (d) η-Al_2O_3.

the boehmites containing Cr^{3+} ion is not due to the dehydration of boehmite, but due to the evolution of oxygen according to the reaction [7,13]

$$4\,Cr^{6+} + 6\,O^{2-} = 4\,Cr^{3+} + 3\,O_2 \qquad (1)$$

In this study, the formation of Cr^{6+} ion was detected by diffuse reflectance spectra and chemical analysis.

Figure 4 shows the diffuse reflectance spectra of four aluminas, which were obtained by heating boehmite containing 16.7 mole% Cr^{3+} ion up to 600, 1100 and 1370°C in air in the DTA apparatus, and at 1000°C for 3 h in vacuum (10^{-3} mm Hg) in a horizontal electrical furnace. The phases obtained at 600, 1100 and 1370°C in air and at 1000°C in vacuum were identified by X-ray diffraction as η-Al_2O_3, θ-Al_2O_3, α-Al_2O_3 and a mixture of θ- and δ-Al_2O_3 containing Cr^{3+} ion, respectively, which are, in other words, called Al_2O_3–Cr_2O_3 solid solution. The spectra of α-Cr_2O_3 and CrO_3 are also shown in Fig. 4 for comparison. The samples obtained by heating at a temperature lower than 1370°C showed the broader spectra. In general, it is known that a disordered lattice structure renders the spectra broad and less well resolved than an absorption from a well-crystallized lattice [5]. The absorption peaks or shoulders appearing at 420–450 nm and at 570–600 nm in (a)–(d), which are denoted by arrow (↑), correspond closely to those of α-Cr_2O_3 shown in (e). These bands, therefore, can be ascribed to the presence of Cr^{3+} ion, and their position is observed to shift somewhat to a

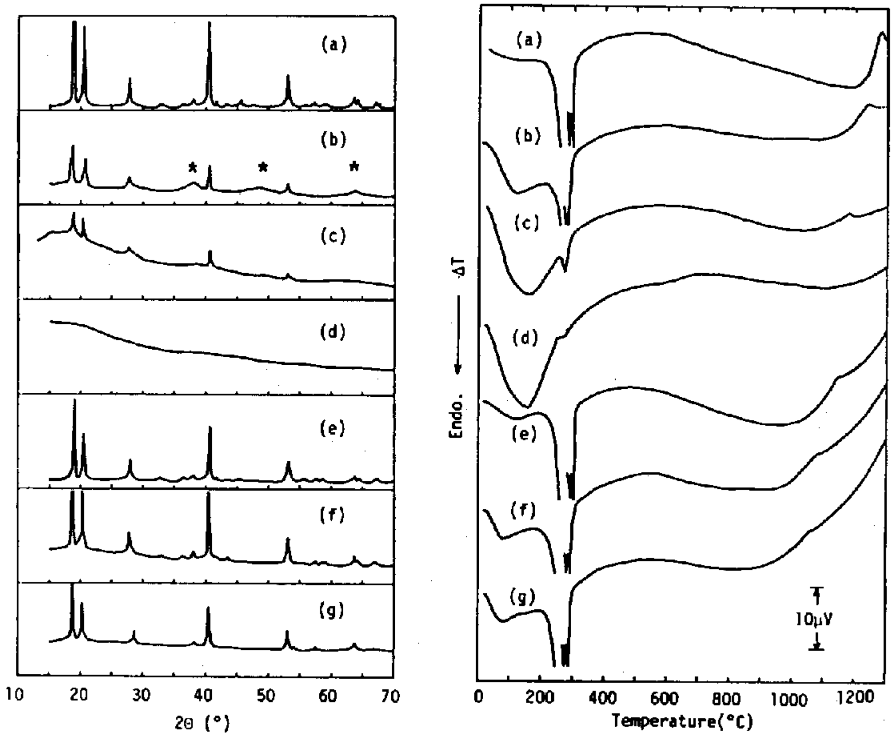

Fig. 5. X-Ray diffraction patterns and DTA curves for bayerites containing Cr^{3+} and Fe^{3+} ions. *, Pseudoboehmite. (a) Pure bayerite; (b) +4.8 mole% Cr^{3+}; (c) +9.1 mole% Cr^{3+}; (d) +16.7 mole% Cr^{3+}; (e) +4.8 mole% Fe^{3+}; (f) +9.1 mole% Fe^{3+}; (g) +16.7 mole% Fe^{3+}.

shorter wavelength than that of α-Cr_2O_3. This may be due to the lattice expansion that results when Cr^{3+} ions are incorporated in an alumina lattice [5]. Moreover, the spectra in (c) and (d) show another absorption band near 370 nm which is denoted by ↑. This band can be ascribed to the presence of Cr^{6+} ion because it also appears in the case of CrO_3 shown in (f). The presence of Cr^{6+} ion in alumina was also detected qualitatively by diphenylcarbazide method. However, the band due to Cr^{6+} ion was no longer detectable in α-Al_2O_3 heated at 1370°C shown in (b). This will suggest that the $\eta \rightarrow \delta \rightarrow \theta \rightarrow \alpha$-$Al_2O_3$ transformation is accompanied by progressive reduction of Cr^{6+} to Cr^{3+} ion according to reaction (1) described above. The alumina obtained by heating in vacuum, shown in (a), also showed absorption bands only due to Cr^{3+} ion.

Figure 5 shows the X-ray diffraction patterns and DTA curves of bayerites with and without the addition of Cr^{3+} and Fe^{3+} ions. X-Ray diffraction of the sample containing 4.8 mole% Cr^{3+} ion (b) reveals the presence of bayerite and pseudoboehmite. With increasing Cr^{3+} ion content, however, the crystallization of bayerite is remarkably inhibited, and the sample containing 16.7 mole% Cr^{3+} ion (d) was in an amorphous state. On the other hand, X-ray diffraction of the samples containing 4.8–16.7 mole% Fe^{3+} ion [(e)–(g)] revealed the presence of well-crystallized bayerite alone. Moreover, as the diffraction lines of both bayerites containing Cr^{3+} and Fe^{3+} ions had no shift, it is considered that the added Cr^{3+} and Fe^{3+} ions were not incorporated in the lattice of bayerite. In particular, the reason that Cr^{3+} ion was not incorporated in bayerite lattice and inhibited the crystallization of bayerite will be explained according to the previous studies as follows. In general, it is known that bayerite is obtained by ageing pseudoboehmite and the formation of bayerite proceeds by a dissolution–reprecipitation mechanism with a dissolved tetrahedrally coordinated $Al(OH)_4^-$ intermediate [14,15]. On the other hand, Cr^{3+} ion, which has a strong octahedral site preference, might prefer to redissolve than to adopt a tetrahedral coordination as $Al(OH)_4^-$ intermediate, which will be responsible for the inhibition of the formation process of bayerite. Therefore, the added Cr^{3+} ion may be adsorbed on the surface of the amorphous aluminum hydroxide shown in Fig. 5.

In the DTA curve of pure bayerite (Fig. 5a), an endothermic peak at 283°C and an exothermic peak at 1281°C correspond to the dehydration of bayerite and the α-transformation of the resultant alumina, respectively. With increasing Cr^{3+} ion content, the endothermic peak corresponding to the dehydration diminishes progressively and, on the contrary, a broad endothermic peak at around 150°C increases. This broad peak corresponds to the dehydration of amorphous aluminum hydroxide which is shown in X-ray diffraction patterns (b)–(d). The peak temperature of α-transformation shifted to lower temperatures with an increase in Cr^{3+} ion content [although the exothermic peak was not observed in (d)]. These facts contrast

TABLE 2

The influence of Cr^{3+} and Fe^{3+} ion content on the DTA peak temperatures of dehydration and α-transformation of aluminum hydroxides, shown in Figs. 1, 2 and 5

	Dehydration temp. (°C)		α-Transformation temp. (°C)	
	Cr^{3+}	Fe^{3+}	Cr^{3+}	Fe^{3+}
Pseudoboehmite	395		1172	
+4.8 mole%	422	404	1219	1084
+9.1 mole%	424	410	1219	1019
+16.7 mole%	464	400	1244	975
Boehmite	519		1254	
+4.8 mole%	513	517	1297	1092
+9.1 mole%	512	517	1310	1048
+16.7 mole%	509	519	1312	1037
Bayerite	283		1281	
+4.8 mole%	277	282	1234	1141
+9.1 mole%	275	282	1176	1077
+16.7 mole%	260	278		1059

with the results in the systems of pseudoboehmite and boehmite containing Cr^{3+} ion shown in Figs. 1 and 2. On the other hand, in the bayerite samples containing Fe^{3+} ion [(e)–(g)], the peak temperature of the dehydration at 280°C was almost unchanged, but the peak temperature of α-transformation shifted remarkably to lower temperatures with increasing Fe^{3+} ion content.

Table 2 summarizes the influence of Cr^{3+} and Fe^{3+} ions added by coprecipitation on the DTA peak temperatures of dehydration and α-transformation of the respective aluminum hydroxides (Figs. 1, 2 and 5). In the case of aluminum hydroxides containing Cr^{3+} ion, the peak temperature of dehydration varied from sample to sample depending on whether or not Cr^{3+} ion was incorporated. On the contrary, in the case of samples containing Fe^{3+} ion, the peak temperature of dehydration remained almost constant because Fe^{3+} ion was not incorporated in any of the aluminum hydroxides. Moreover, it is observed that Cr^{3+} and Fe^{3+} ions influence strongly the peak temperature of α-transformation rather than dehydration; the Cr^{3+} ion inhibited α-transformation in the pseudoboehmite and boehmite systems, but accelerated it in the bayerite system, while the Fe^{3+} ion accelerated remarkably α-transformation in all systems. These tendencies were enhanced by an increase in Cr^{3+} and Fe^{3+} ion content. The inhibiting or accelerating mechanism of the metal ions to α-transformation is examined below in connection with the state of existence of the ions.

The effect of Cr^{3+} and Fe^{3+} ions on the transformation of aluminum hydroxides to α-Al_2O_3

The results of isothermal experiments in the pseudoboehmite and boehmite systems are first described. Table 3 represents the forms of aluminas which were obtained by heating pure pseudoboehmite and boehmite and those containing 16.7 mole% Cr^{3+} ion at various temperatures in air or in vacuum (10^{-3} mm Hg). The forms were identified by X-ray diffraction. When plural aluminas were formed at a given temperature, they were noted in decreasing order of the amount present. The position of the diffraction lines of aluminas obtained from aluminum hydroxides containing Cr^{3+} ion was observed to shift to lower 2θ angles, which indicates the formation of Al_2O_3–Cr_2O_3 solid solution. As can be seen from Table 3, all the pseudoboehmite and boehmite with and without the addition of Cr^{3+} ion transform to α-Al_2O_3 via a similar sequence, i.e. pseudoboehmite or boehmite $\rightarrow \eta$(or γ) $\rightarrow \delta \rightarrow \theta \rightarrow \alpha$-$Al_2O_3$. However, the principal difference observed between the systems with and without the addition of Cr^{3+} ion is that in the systems containing Cr^{3+} ion, θ-Al_2O_3 was formed at lower temperatures and was stabilized up to higher temperatures, and the α-transformation was inhibited. This result agrees with that reported by Okada and Kuwazima [9] and Bye and Simpkin [7]. On the other hand, the forms of aluminas obtained by heating boehmite containing 16.7 mole% Cr^{3+} ion in vacuum, which are shown in the parentheses in Table 3, are similar to those obtained from pure boehmite, and the stabilization of θ-Al_2O_3 was not observed. As already

TABLE 3

Forms of alumina obtained by heating pseudoboehmite and boehmite containing 16.7 mole% Cr^{3+} ion at various temperatures in air and in vacuum

Calcination conditions	Pseudoboehmite	Pseudoboehmite + 16.7 mole% Cr^{3+}	Boehmite	Boehmite + 16.7 mole% Cr^{3+}
600°C [a]	η	η	γ	η
800°C, 3 h		η		
900°C, 3 h	η	δ, θ α-Cr_2O_3	δ	δ
1000°C, 3 h	θ, δ, α	θ, δ α-Cr_2O_3	δ, θ	θ (θ, δ) [b]
1100°C, 2 h	α	θ, α	θ, δ, α	θ (θ, α) [b]
1200°C, 2 h		α		α, θ
1300°C [a]	α	α	α	α

[a] Heated in the DTA apparatus.

[b] The aluminas in parentheses were obtained by heating in vacuum ($\sim 10^{-3}$ mm Hg).

TABLE 4

Forms of alumina obtained by heating the respective bayerites containing 4.8, 9.1 and 16.7 mole% Cr^{3+} ion at various temperatures in air

Calcination conditions	Bayerite	Bayerite +4.8 mole% Cr^{3+}	Bayerite +9.1 mole% Cr^{3+}	Bayerite +16.7 mole% Cr^{3+}
600°C [a]	η			amorphous
800°C, 3 h	η	η	η	α-Cr_2O_3 η
900°C, 3 h	θ	θ, η	η	α-Cr_2O_3 α
1000°C, 3 h	θ	θ	θ, η α-Cr_2O_3	α α-Cr_2O_3
1100°C, 2 h	θ	θ, α	α, θ	α
1200°C, 2 h	α, θ	α	α	α
1300°C [a]	α			α

[a] Heated in the DTA apparatus.

shown in Fig. 4, in θ-Al_2O_3 obtained by heating boehmite containing 16.7 mole% Cr^{3+} ion to 1100°C in air, Cr^{6+} ion existed in addition to Cr^{3+} ion, while Cr^{6+} ion did not exist in aluminas (a mixture of θ- and δ-Al_2O_3) obtained by heating in vacuum at 1000°C for 3 h. Therefore, from the above results it can be concluded that the θ-Al_2O_3 structure is stabilized by dispersion of Cr^{6+} ion in it, so α-transformation is inhibited. Bye and Simpkin [7] have deduced the same conclusion. They explained the inhibiting mechanism of Cr^{6+} ion for α-transformation according to the synchro-shear mechanism which was proposed for the transformation of γ-Fe_2O_3 to α-Fe_2O_3 by Kachi et al. [16]. If Al^{3+} ions in the tetrahedral cation site of θ-Al_2O_3 were substituted by Cr^{6+} ions and the covalent nature in the Cr^{6+}–O^{2-} bond increased, on α-transformation the conversion of cubic to hexagonal close packing of O^{2-} ions by the shear process, which occurs between O^{2-} ion layers which sandwich cations in the tetrahedral sites, could be expected to be inhibited.

Table 4 shows the X-ray diffraction results for aluminas obtained by calcining bayerites containing 0–16.7 mole% Cr^{3+} ion. It was found that α-transformation was accelerated by the addition of Cr^{3+} ion. The position of the diffraction lines of aluminas shifted to lower angles due to the incorporation of Cr^{3+} ion, while that of α-Cr_2O_3 shifted to higher angles due to the incorporation of Al^{3+} ion, indicating the formation of Al_2O_3–Cr_2O_3 solid solutions respectively. The disappearance of α-Cr_2O_3 above 1100°C is ascribed to the fact that the Al_2O_3–Cr_2O_3 system forms a continuous series of solid solution [17]. It is also observed in Table 4 that $\eta \rightarrow \theta \rightarrow \alpha$ transformation occurs in the case of pure bayerite, while amorphous $\rightarrow \eta \rightarrow \alpha$ transformation proceeds in the case of bayerite containing 16.7 mole% Cr^{3+} ion, in which α-transformation is remarkably accelerated. The α-transformation process of bayerites containing 4.8 and 9.1 mole% Cr^{3+} ion seems to be complex. As can be seen from Fig. 5, X-ray diffractions of samples containing 4.8 and 9.1 mole% Cr^{3+} ion revealed the presence of bayerite and pseudoboehmite, and bayerite and amorphous aluminum hydroxides, respectively. Therefore, the complexity of the transformation process of these bayerite samples will result from the overlapping of transformation processes of the respective aluminum hydroxides contained in them. So, on the basis of the results obtained in bayerite containing 16.7 mole% Cr^{3+} ion, the accelerating mechanism of Cr^{3+} ion can be considered as follows. It has already been shown in Fig. 5 that bayerite containing 16.7 mole% Cr^{3+} ion is in an amorphous state and the added Cr^{3+} ion is not incorporated in the bayerite structure, but may be adsorbed on the surface of amorphous aluminum hydroxide. On heating, this sample was converted to amorphous alumina at 600°C, to η-Al_2O_3 at 800°C accompanying separation and crystallization of α-Cr_2O_3, and then to α-Al_2O_3 and α-Cr_2O_3 at 900°C. From these results, the accelerating effect of Cr^{3+} ion on α-transformation can be explained on the basis of an assumption that a nascent α-Cr_2O_3 particle crystallized at 800°C (which has a corundum structure like α-Al_2O_3) acts as an active nucleus to the crystallization (i.e. α-transformation) of η-Al_2O_3 to α-Al_2O_3. This model will also explain why the $\eta \rightarrow \alpha$ transformation in the bayerite system containing Cr^{3+} ion proceeds directly, while the α-transformation in the pseudoboehmite and boehmite systems containing Cr^{3+} ion proceeds via δ- and θ-Al_2O_3.

From the results in Tables 3 and 4 it is apparent that the effect of Cr^{3+} ion on α-transformation varies, depending on the state of the ions existing in or on aluminum hydroxides. So, for a comparison with the effect of the coprecipitated Cr^{3+} ion, the effect of α-Cr_2O_3 mixed mechanically with η-, γ- and δ-Al_2O_3 on α-transformation was investigated.

Figure 6 shows the DTA curves of α-transformation of η-, γ- and δ-Al_2O_3 mixed mechanically with α-Cr_2O_3 in different molar ratios. The peak temperature of the exotherm due to α-transformation varies with the concentration of α-Cr_2O_3. In the η- and γ-Al_2O_3 systems, the peak temperature shifted to lower temperatures on the addition of α-Cr_2O_3 than that in the pure system, but the shift seems to be suppressed somewhat at 9.1 mole% α-Cr_2O_3. On the other hand, in the δ-Al_2O_3 system, the peak temperature shifted to lower temperatures at 4.8 and 50.9 mole% α-Cr_2O_3, and at 10.2–33.3 mole% α-Cr_2O_3 to higher temperatures than that in pure δ-Al_2O_3. Wakao and Hibino [8] have reported that α-transformation of γ-Al_2O_3 obtained by thermal decomposition of aluminum sulfate was accelerated by the addition of 1 wt.% α-Cr_2O_3. This seems to be consistent with the result in Fig. 6 for the γ-Al_2O_3 system. The fact that the effect of α-Cr_2O_3 mixed mechanically on α-transformation varies with its concentration can be explained in conjunction with the results obtained in the system containing Cr^{3+} ion added by coprecipitation, i.e. the effect may be determined by the balance between the inhibiting action of Cr^{6+} ion, which is formed from α-Cr_2O_3 and

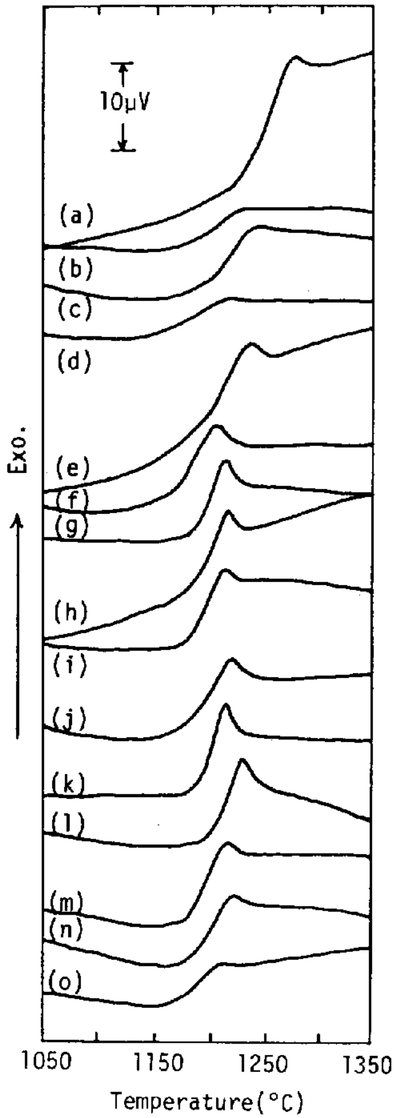

Fig. 6. DTA curves of α-transformation of η-, γ- and δ-Al_2O_3 mixed mechanically with α-Cr_2O_3 in different molar ratios. (a) η-Al_2O_3; (b) η-Al_2O_3 + 4.8 mole% Cr_2O_3; (c) η-Al_2O_3 + 9.1 mole% Cr_2O_3; (d) η-Al_2O_3 + 16.7 mole% Cr_2O_3; (e) γ-Al_2O_3; (f) γ-Al_2O_3 + 3 mole% Cr_2O_3; (g) γ-Al_2O_3 + 4.8 mole% Cr_2O_3; (h) γ-Al_2O_3 + 9.1 mole% Cr_2O_3; (i) γ-Al_2O_3 + 16.7 mole% Cr_2O_3; (j) δ-Al_2O_3; (k) δ-Al_2O_3 + 4.8 mole% Cr_2O_3; (l) δ-Al_2O_3 + 10.2 mole% Cr_2O_3; (m) δ-Al_2O_3 + 24.1 mole% Cr_2O_3; (n) δ-Al_2O_3 + 33.3 mole% Cr_2O_3; (o) δ-Al_2O_3 + 50.9 mole% Cr_2O_3.

TABLE 5

Forms of alumina obtained by heating pseudoboehmite, boehmite and bayerite containing 16.7 mole% Fe^{3+} ion at various temperatures in air

Calcination conditions	Psuedoboboehmite + 16.7 mole% Fe^{3+}	Boehmite + 16.7 mole% Fe^{3+}	Bayerite + 16.7 mole% Fe^{3+}
600°C [a]	amorphous	α-Fe_2O_3	η
800°C, 3 h	η δ	γ	δ, α α-Fe_2O_3
900°C, 3 h	α α-Fe_2O_3	α-Fe_2O_3 δ, α	α α-Fe_2O_3
1000°C, 3 h	α α-Fe_2O_3	α α-Fe_2O_3	α α-Fe_2O_3
1300°C [a]	α α-Fe_2O_3	α α-Fe_2O_3	α α-Fe_2O_3

[a] Heated in the DTA apparatus.

is incorporated in alumina structure, and the accelerating action of α-Cr_2O_3, which acts as an active nucleus for α-transformation.

Table 5 shows the results of X-ray diffraction for aluminas obtained by heating pseudoboehmite, boehmite and bayerite containing 16.7 mole% Fe^{3+} ion added by coprecipitation at various temperatures in air. The position of the diffraction lines of aluminas shifted to lower angles due to the incorporation of Fe^{3+} ion, while that of α-Fe_2O_3 shifted to higher angles due to the incorporation of Al^{3+} ion, indicating the formation of Al_2O_3–Fe_2O_3 solid solution. Table 5 shows that, even when heated to 1300°C, the coexistence of α-Fe_2O_3 with α-Al_2O_3 occurs. This is due to the solubility limit of α-Fe_2O_3 into α-Al_2O_3 (about 10 mole% [18]), which is different from the Al_2O_3–Cr_2O_3 system which forms a continuous solid solution series [17]. It is found from Tables 3–5 that the temperature of α-transformation in aluminum hydroxide systems containing 16.7 mole% Fe^{3+} ion (Table 5) is lower by 100–400°C than that in the corresponding pure aluminum hydroxide systems (Tables 3 and 4). This result agrees with that of DTA experiments shown in Figs. 1, 2 and 5. Moreover, in all systems containing Fe^{3+} ion shown in Table 5, it is observed that the transformation from poorly-crystallized δ-Al_2O_3 to α-Al_2O_3 occurs directly at a very low temperature, such as 800–900°C, without forming θ-Al_2O_3 as the intermediate. Since in the pseudoboehmite and bayerite systems containing Fe^{3+} ion the formation temperature of α-Al_2O_3 corresponds to the crystallization temperature of α-Fe_2O_3, the accelerating mechanism of α-transformation in the system containing Fe^{3+} ion can be explained on the basis of the same model as in the system of bayerite containing Cr^{3+} ion, i.e. α-Fe_2O_3 having a corundum structure acts as an active nucleus for α-transformation. Besides, Table 5 shows that α-transformation in the boehmite system is less promoted than in the bayerite and pseudoboehmite systems. This result can be ascribed to the difference in reactivity of α-Fe_2O_3 which acts as a nucleus. It is resonable to assume that the nascent α-Fe_2O_3, which was separated from alumina and was crystallized on heating (in the bayerite and pseudoboehmite systems), is more active than the oxide originally existing in a starting material (boehmite).

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