

EFFECT OF GRINDING OF MIXTURES OF GOETHITE AND HYDRATED ALUMINA ON THE FORMATION OF Fe_2O_3 – Al_2O_3 SOLID SOLUTIONS

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ABSTRACT

Equimolar mixtures of goethite and hydrated alumina (gibbsite, bayerite and boehmite) were ground for 1 h and 4 h in a planetary ball mill and heated to various temperatures in TG–DTA runs. It was confirmed by X-ray diffraction that the resulting oxides, Fe_2O_3 and Al_2O_3 , were partially soluble in each other. On grinding, the formation of α - Fe_2O_3 solid solutions was observed at 500 °C in the goethite–gibbsite and goethite–bayerite mixtures and at 900 °C in the goethite–boehmite mixture, in contrast to 1100 °C or above in the unground mixtures. On the other hand, the formation of α - Al_2O_3 solid solutions was also accelerated by grinding. The possible accelerating effect of grinding on the formation of solid solutions was discussed on the basis of the formation of disordered and/or amorphous phases and the improvement of the contact conditions between the reaction particles.

INTRODUCTION

The Fe_2O_3 – Al_2O_3 system has been a typical subject of the study of the formation of solid solutions. The similarity of the ionic radii of Fe^{3+} (0.69 Å) and Al^{3+} (0.67 Å) [1] and the hexagonal crystal structures of α - Fe_2O_3 and α - Al_2O_3 are favourable for the formation of solid solutions between their oxides. The results for the solubility limits of Al_2O_3 in α - Fe_2O_3 and Fe_2O_3 in α - Al_2O_3 , however, are still contradictory [2–4]. In addition, kinetic and thermoanalytical study of the formation of solid solutions in the Fe_2O_3 – Al_2O_3 system is particularly interesting with respect to the reactivity of solids. The reactivity of solids is influenced by mechanochemical treatments. Mechanical activation for the dehydration and α -transformation of hydrated aluminas such as gibbsite, bayerite and boehmite has already been reported [5].

The purpose of the present study is to elucidate the effect of the dry grinding of starting materials on the formation of Fe_2O_3 – Al_2O_3 solid solutions which result from the thermal treatment of mixtures of goethite and hydrated alumina.

EXPERIMENTAL

Preparation procedures for gibbsite ($\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), bayerite ($\beta\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) and boehmite ($\alpha\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) were described in the previous paper [5]. Goethite ($\alpha\text{-FeOOH}$) was purchased from Rare Metallic Co. Ltd. Equimolar mixtures of goethite and the various hydrated aluminas were mixed in an agate mortar for 30 min and then ground in air for 1 h and 4 h in a P-7 type of planetary ball mill (Fritsch). The ground samples were kept in a silica gel desiccator. The samples were heated to 500, 750, 900, 1100 and 1300 °C in the TG-DTA apparatus, quenched to room temperature and then subjected to X-ray diffraction. In order to confirm the formation of $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ solid solutions, the diffraction angles of the (104) lines of $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ which resulted from the thermal treatment of the goethite-hydrated alumina mixtures were precisely measured by using an internal standard of 9N silicon.

Simultaneous TG-DTA measurements were carried out with a model 8085 thermoanalyser (Rigaku Denki Co.) at a heating rate of $10^\circ\text{C min}^{-1}$ in air.

Powder X-ray diffraction (XRD) patterns were obtained with a Geigerflex 2001 (Rigaku Denki Co.) using iron-filtered $\text{Co } K\alpha$ radiation (35 kV, 10 mA).

Scanning electron microscopy (SEM) was carried out with a JSM-35CF apparatus (JEOL Ltd.) at an accelerating voltage of 25 kV.

RESULTS AND DISCUSSION

Figure 1 shows the effect of grinding time on XRD patterns of goethite. On grinding for 1 h and 4 h, a broadening and a decrease in intensity of the

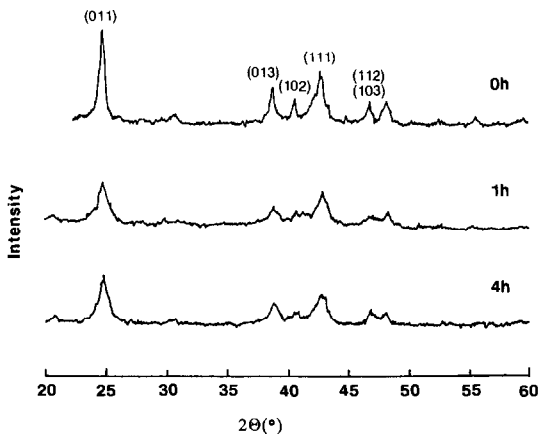


Fig. 1. Variation of XRD patterns of goethite with grinding time.

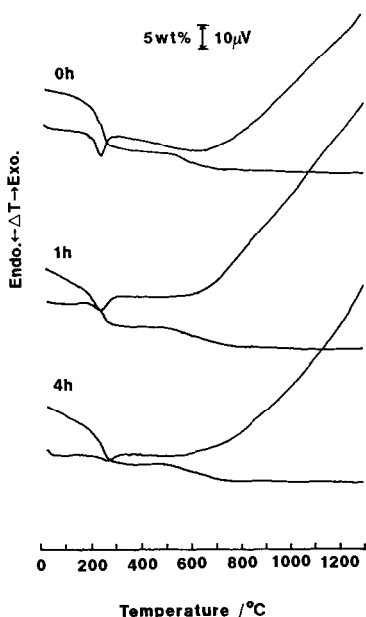


Fig. 2. TG and DTA curves of goethites that were ground for 0 h, 1 h and 4 h.

diffraction lines can be observed. In contrast, the effect of grinding time on the X-ray diffraction patterns of hydrated aluminas was more drastic, and gibbsite and bayerite that were ground for 4 h and boehmite that was ground for 8 h changed to amorphous hydrated aluminas [5].

Figure 2 shows TG and DTA curves of goethites that were ground for 0 h (unground), 1 h and 4 h. The unground goethite shows an endotherm at 255 °C which corresponds to the dehydration $2\alpha\text{-FeOOH} \rightarrow \alpha\text{-Fe}_2\text{O}_3 + \text{H}_2\text{O}$. On grinding for 1 h and 4 h, this endotherm became broad and small. The weight loss was ca. 12 wt.% on heating all goethite samples to 500 °C, which was somewhat larger than the stoichiometric weight loss of 10.13 wt.% owing to the dehydration. Another small weight loss (ca. 4 wt.%) is observed in the temperature range 500–800 °C. This is probably due to desulphurisation. In fact, the goethite sample showed an IR absorption band assigned to the SO_4^{2-} ion near 1140 cm^{-1} . Incomplete washing during the preparation of goethite seems to have caused residual sulphate ions [6].

Figure 3 shows the effect of grinding time on XRD patterns for the goethite–gibbsite, goethite–bayerite and goethite–boehmite mixtures. As the grinding time increases, the intensities of the diffraction lines of goethite and hydrated aluminas decrease at different rates. The rate of decrease caused by grinding for goethite and boehmite in the mixtures are relatively low and are approximately the same as those in goethite (Fig. 1) and boehmite alone [5] respectively. In contrast, gibbsite and bayerite in the mixtures changed immediately to amorphous phases after grinding for 1 h, although for 4 h in

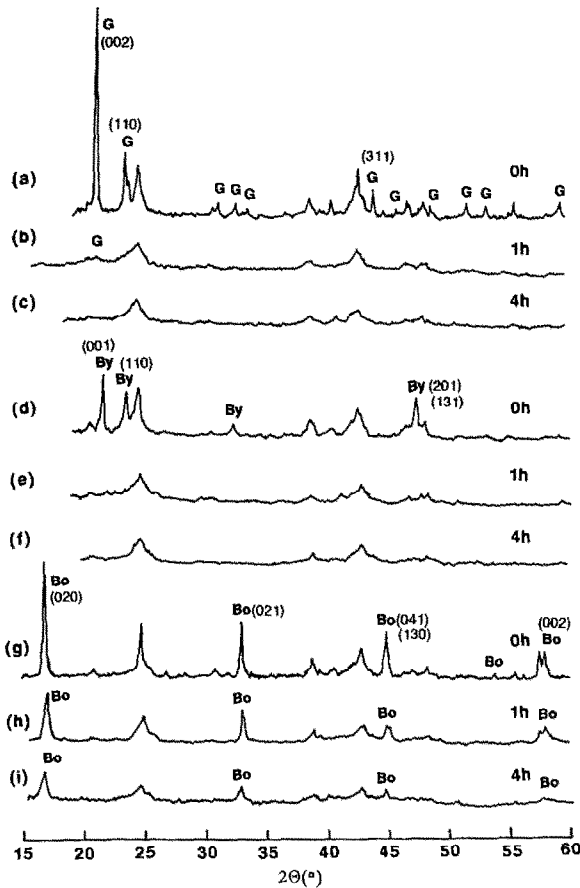


Fig. 3. Variation of XRD patterns of goethite-hydrated alumina mixtures with grinding time: a-c, goethite-gibbsite mixtures; d-f, goethite-bayerite mixtures; g-i, goethite-boehmite mixtures. G, Gibbsite; By, bayerite; Bo, boehmite; no mark, goethite.

the case of hydrated alumina alone [5]. The different effect of grinding on these behaviours is probably attributable to Mohs' hardness, i.e. 2.5–3.5 for gibbsite, 3.5–4 for boehmite and 5–5.5 for goethite, and to the layered structures of gibbsite and bayerite which readily break under grinding [5].

Figure 4 shows scanning electron micrographs for goethites and goethite-gibbsite mixtures that were ground for 0 h and 4 h. The unground goethite shows aggregated particles of different sizes, which are composed of primary particles of size less than 0.1 μm . On grinding for 4 h, they segregated into smaller particles. The unground mixture in Fig. 4c shows a poor contact condition between smaller goethite particles and larger gibbsite crystals having smooth surfaces. However, by grinding for 4 h (Fig. 4d), the crystals of gibbsite were finely ground and then mixed thoroughly with goethite particles.

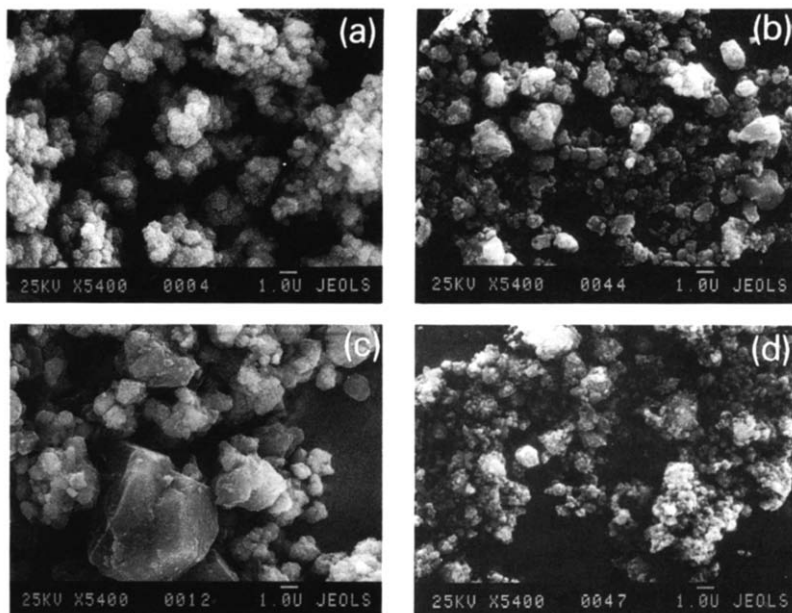


Fig. 4. SEM micrographs of (a) unground and (b) 4 h ground goethites, and (c) unground and (d) 4 h ground goethite-gibbsite mixtures.

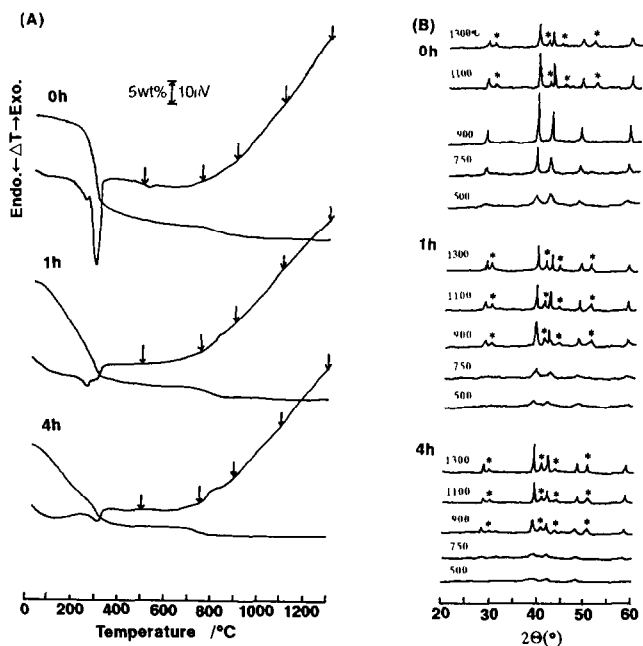


Fig. 5. TG and DTA curves (A) of goethite-gibbsite mixtures ground for 0 h, 1 h and 4 h, and XRD patterns (B) of the mixtures calcined at various temperatures in TG-DTA runs: no mark, α - Fe_2O_3 ; *, α - Al_2O_3 .

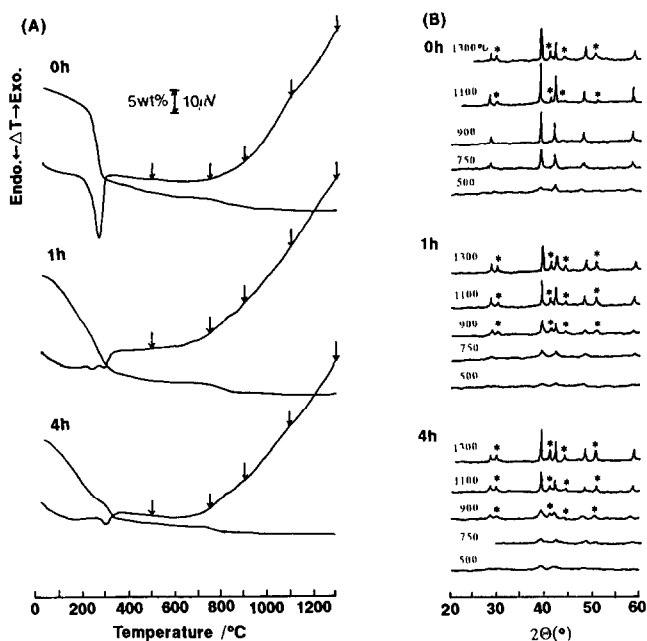


Fig. 6. TG and DTA curves (A) of goethite-bayerite mixtures ground for 0 h, 1 h and 4 h, and XRD patterns (B) of the mixtures calcined at various temperatures in TG-DTA runs: no mark, α - Fe_2O_3 ; *, α - Al_2O_3 .

Figures 5A, 6A and 7A show TG and DTA curves of the goethite-gibbsite, goethite-bayerite and goethite-boehmite mixtures that were ground for 0 h, 1 h and 4 h respectively. The mixtures were heated to various temperatures shown by the arrows on DTA curves, quenched to room temperature and then subjected to X-ray diffraction. The results of X-ray diffraction are shown in Figs. 5B, 6B and 7B.

The unground goethite-gibbsite mixture (Fig. 5A) shows an endotherm at 300°C , which corresponds to the dehydration of gibbsite to χ - Al_2O_3 [5]. A shoulder peak at 255°C is due to the dehydration of goethite to α - Fe_2O_3 as shown in Fig. 2. The weight loss corresponding to both dehydrations is observed as a single stage in TG. A small endotherm at 520°C is due to the dehydration of boehmite to γ - Al_2O_3 ; the former resulted from the partial decomposition of gibbsite [5]. χ - and γ - Al_2O_3 phases, however, were not detected by XRD because of their lower crystallinity and high backgrounds that result from the fluorescence of secondary X-rays. The weight loss between 700 and 900°C is due to the desulphurisation from goethite as shown in Fig. 2. In Fig. 5B, the formation of α - Fe_2O_3 and α - Al_2O_3 was detected to occur at 500 and 1100°C . The latter oxide formed at 1300°C from the gibbsite in the absence of goethite [5]. The formation of α - Al_2O_3 seemed to be accelerated by the mechanism in which α - Fe_2O_3 particles act as an active nucleus for the crystallization of α - Al_2O_3 [7]. On grinding for 1

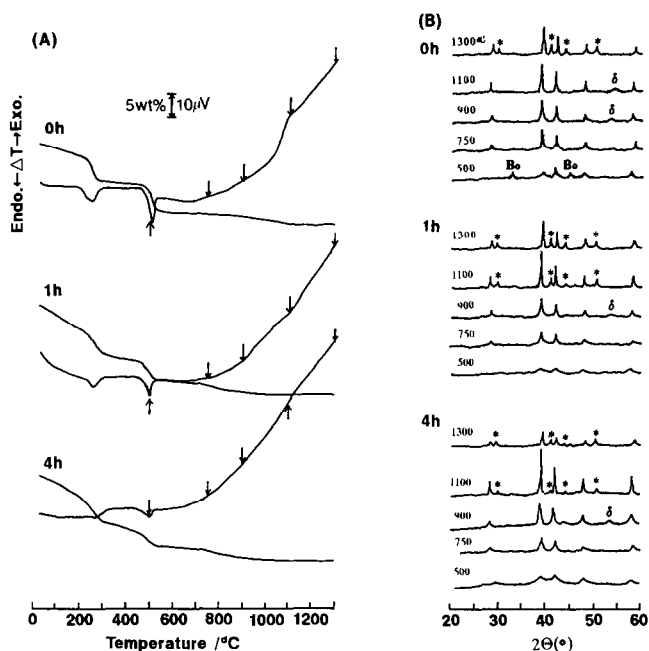


Fig. 7. TG and DTA curves (A) of goethite-boehmite mixtures ground for 0 h, 1 h and 4 h, and XRD patterns (B) of the mixtures calcined at various temperatures in TG-DTA runs: no mark, α - Fe_2O_3 ; *, α - Al_2O_3 ; δ , δ - Al_2O_3 ; Bo, boehmite.

and 4 h, the DTA endotherm for the dehydration of gibbsite became remarkably small. It corresponds to the formation of amorphous hydrated alumina from gibbsite as shown in Fig. 3 and ref. 5. However, the weight loss in the range from room temperature to 700°C was nearly equivalent to the sum of the weight losses corresponding to the dehydration of goethite and gibbsite. This result suggests that the mechanochemical dehydration has not occurred on grinding. On the contrary, the formation temperature of α - Al_2O_3 was lowered to 900°C by grinding. A small exotherm near 800°C may be responsible for the formation of α - Al_2O_3 .

In the unground goethite-bayerite mixture (Fig. 6A), a single endotherm is observed at 276°C as a result of the overlapping of dehydration peaks of both hydroxides. On grinding, the endotherm became remarkably small. The formation temperatures of α - Al_2O_3 and the occurrence of a small exotherm at around 800°C are very similar to those in the goethite-gibbsite mixtures.

The unground goethite-boehmite mixture (Fig. 7A) shows two endotherms at 254 and 510°C , which correspond to the dehydration of goethite to α - Fe_2O_3 and boehmite to γ - Al_2O_3 , respectively. Each corresponding weight loss appears in TG curve. On grinding, these endotherms became smaller and the latter peak shifted slightly to lower temperatures, i.e. $510^\circ\text{C} \rightarrow 505^\circ\text{C} \rightarrow 500^\circ\text{C}$. On heating unground mixture to 500°C (Fig. 7B), a small amount of undecomposed boehmite still remained and, on

further heating to 900 °C or 1100 °C, a small and broad peak appeared at about $2\Theta = 53.5^\circ\text{C}$. This peak was identified to be $\delta\text{-Al}_2\text{O}_3$ on the basis of a previous study [7]. The formation temperature of $\alpha\text{-Al}_2\text{O}_3$ decreased to 1100 °C in the ground mixtures from 1300 °C in the unground mixture.

The results shown in Figs. 5–7 are summarized as follows. $\alpha\text{-Fe}_2\text{O}_3$ formed in the goethite–hydrated alumina mixtures below 500 °C regardless of grinding. On the contrary, transition aluminas which were formed by the thermal decomposition of hydrated aluminas in the mixtures could not be detected by X-rays because of their lower crystallinity and high backgrounds. On further heating, $\alpha\text{-Al}_2\text{O}_3$ formed. The formation temperature of $\alpha\text{-Al}_2\text{O}_3$ decreased to 1100 °C in the unground mixtures from 1300 °C in the hydrated aluminas not containing goethite [5], and then decreased by a further 200 °C in the ground mixtures; that is, it decreased finally to 900 °C in the ground goethite–gibbsite and goethite–bayerite mixtures and to 1100 °C in the ground goethite–boehmite mixture. The remarkable accelerating effect of grinding on $\alpha\text{-Al}_2\text{O}_3$ formation appeared in the first two of these mixtures. The reason for this will be discussed later. Furthermore, in Figs. 5–7 the diffraction angles of $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ that formed in the mixtures were observed to be shifted to high or low angles. This indicates the formation of solid solutions between them.

Figure 8 shows the variation with the calcination temperature of the diffraction angle of the (104) line of $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ which were obtained by calcining various mixtures in TG–DTA runs (Figs. 5–7). The (110) line of $\alpha\text{-Fe}_2\text{O}_3$ also showed a similar variation to the (104) line. In Fig. 8A, the diffraction line of $\alpha\text{-Fe}_2\text{O}_3$ which was obtained from the goethite alone shows a slight shift to higher angles with calcination temperature because of the development of crystallinity. In this case, the angles of the (104) line of $\alpha\text{-Fe}_2\text{O}_3$ obtained from the goethites ground for 0 h, 1 h and 4 h were nearly constant and thus the average value is shown in this figure. In contrast, a large shift to higher angles for $\alpha\text{-Fe}_2\text{O}_3$ which was obtained in the goethite–hydrated alumina mixtures is, in general, observed. This is attributable to the formation of solid solutions of Al_2O_3 in $\alpha\text{-Fe}_2\text{O}_3$. Compared with $\alpha\text{-Fe}_2\text{O}_3$ obtained from the goethite, those from the unground goethite–hydrated alumina mixtures showed the shift to higher angles at 1100 °C or 1300 °C. On grinding for 1 h and 4 h, although there was no difference in their grinding effect, a large shift was observed at 500 °C in the goethite–gibbsite and goethite–bayerite mixtures and at 900 °C in the goethite–boehmite mixture, and it then increased with increasing calcination temperature. The accelerating effect of grinding on the formation of $\alpha\text{-Fe}_2\text{O}_3$ solid solutions was more pronounced than expected.

On the contrary, the formation of solid solutions of Fe_2O_3 in $\alpha\text{-Al}_2\text{O}_3$ can be observed in Fig. 8B. The solid solutions of Fe_2O_3 in transition aluminas formed by the thermal decomposition of hydrated aluminas could not be detected by X-rays because of their low crystallinity and high backgrounds.

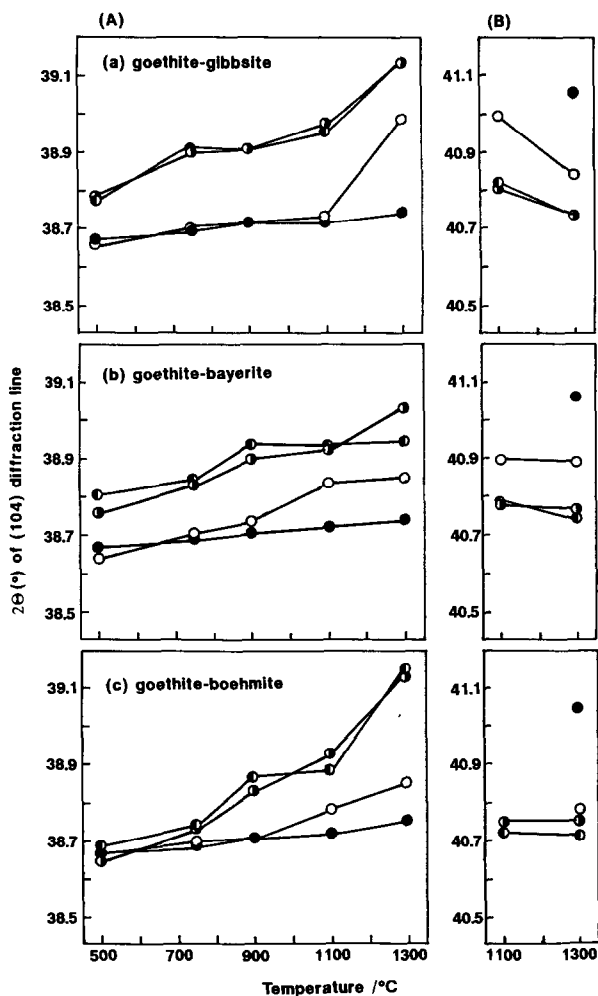


Fig. 8. Variation with calcination temperature of the diffraction angle of the (104) line of (A) $\alpha\text{-Fe}_2\text{O}_3$ and (B) $\alpha\text{-Al}_2\text{O}_3$ which were obtained by the calcination of goethite-gibbsite (curves a), goethite-bayerite (curves b), and goethite-boehmite (curves c) mixtures: ●, $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ obtained from goethite and hydrated aluminas respectively; ○, $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ obtained from the unground mixtures; ◐, $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ obtained from the mixtures ground for 1 h; ◑, $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ obtained from the mixtures ground for 4 h.

Compared with the diffraction angle of the (104) line of $\alpha\text{-Al}_2\text{O}_3$ which was obtained from the hydrated aluminas at 1300°C, those obtained in the unground goethite-hydrated alumina mixtures at 1100 and 1300°C shifted to lower angles. The grinding led to a shift to further lower angles.

From the above results, it has been found that the formation of solid solutions in the $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ system which resulted from thermal treatments of the goethite-hydrated alumina mixtures was remarkably accelerated by grinding the starting mixtures. On grinding for 1 h and 4 h, the

formation of α - Fe_2O_3 solid solutions was observed at 500°C in the goethite–gibbsite and goethite–bayerite mixtures and at 900°C in the goethite–boehmite mixture, in contrast to 1100°C or above in the unground mixtures. In addition, the amount of Al_2O_3 soluble in α - Fe_2O_3 increased with increasing calcination temperature. The possible accelerating effect of grinding on the formation of solid solutions between Fe_2O_3 and Al_2O_3 can be explained by the occurrence of disordered and/or amorphous phases having high reactivity, which is assumed from the decrease in the intensity and the increase in the broadening of diffraction lines of goethite and hydrated aluminas as shown in Fig. 3, and by the improvement of the contact conditions between goethite and hydrated alumina particles as shown in Fig. 4. Moreover, the effect of grinding was much more pronounced in the goethite–gibbsite and goethite–bayerite mixtures than in the goethite–boehmite mixture. Because gibbsite and bayerite have a layered structure and smaller Mohs' hardness, the adjacent layers linked by hydrogen bonds readily slip over each other under grinding [5]. Actually, they changed to amorphous phases after grinding for 1 h and 4 h. The amorphous gibbsite and bayerite particles decomposed at around 300°C and formed amorphous aluminas. Consequently, these amorphous aluminas react readily with the reactive α - Fe_2O_3 which formed from goethite at 250°C , and form the Fe_2O_3 – Al_2O_3 solid solutions during heating above 300°C . On the contrary, boehmite had not completely changed to an amorphous phase on grinding for 1 h and 4 h (Fig. 3) and decomposed to γ - Al_2O_3 at a higher temperature (ca. 500°C) than that for gibbsite and bayerite. These differences seem to have led to the difference in the reactivity for the formation of solid solutions.

In contrast, as shown in Fig. 5–7, the formation temperature of α - Al_2O_3 decreased in the presence of α - Fe_2O_3 , and was further lowered by grinding to 900°C in the goethite–gibbsite and goethite–bayerite mixtures and to 1100°C in goethite–boehmite mixture. As a result, as shown in Fig. 8B, the formation of α - Al_2O_3 solid solutions was accelerated by a similar mechanism to the formation of α - Fe_2O_3 solid solutions.

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