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Note

ETA–DTA study of mechanically ground gibbsite

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Abstract

Simultaneous emanation thermal analysis (ETA), DTA and TG measurements show that upon mechanical grinding the structure of gibbsite changes from well-crystallized to amorphous, with a small proportion undergoing mechanochemical dehydration to form amorphous alumina, a precursor of η-Al_2O_3, which then transforms to α-alumina by, it is proposed, a diffusion mechanism.

In a previous paper [1], the effect of mechanical grinding on the textural and structural changes, and thermal behavior such as the dehydration and α-transformation of hydrated aluminas was studied. In order to get further information about the amorphous phase obtained by the grinding of gibbsite for more than 4 h, emanation thermal analysis (ETA) and DTA experiments have been carried out. ETA is based on the measurement of the release rate of a radioactive inert gas from solids previously labelled by the inert gases. Inert gas atoms are used as trace indicators of the solid state and its changes. ETA is used in the study of various solid state processes such as ageing of precipitates, recrystallization, annealing of structure defects, sintering, phase changes, and so on [2].

Gibbsite (α-$Al_2O_3 \cdot 3H_2O$), BHP39 high-purity aluminum hydroxide supplied from Nippon Light Metal Co, was ground in air for 0.5 and 20 h in an P-7 type planetary ball mill (Fritsch). One gram of the sample, four alumina balls of 12 mm diameter and a 12 ml alumina jar were used. For ETA experiments, the ground gibbsites were labelled by a surface impregnation method using an aqueous ^{226}Ra solution ($\approx$3 μCi ml^{-1}). The impregnated samples were dried under an infrared lamp and stored for about one month in a desiccator until a radioactive equilibrium state was reached. During this period, the inert gas atoms ^{222}Rn are formed by alpha-decay of the parent nuclide ^{226}Ra and introduced into the surface layer to a depth of about 50 nm by the recoil energy. In ETA experiments, the release rate of inert ^{222}Rn gas from the surface layer is recorded as a function of the heating temperature. The simultaneous ETA–DTA–TG

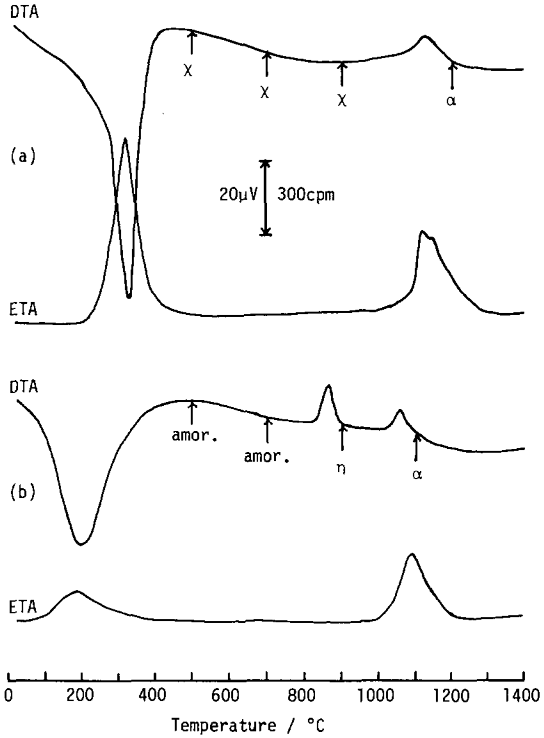

Fig. 1. ETA and DTA curves of gibbsites ground for the periods of (a) 0.5 h and (b) 20 h. Heating rate, 10°C $\min^{-1}$; N_2 flow rate, 50 ml $\min^{-1}$. Sample mass: (a) 100 mg; (b) 111.2 mg.

measurements were carried out with a Netzsch ETA 403-STA 409 apparatus under the conditions of heating rate of 10°C $\min^{-1}$, flow rate of nitrogen carrier gas of 50 ml $\min^{-1}$, threshold of 2 MeV and time constant of 100 s.

Figure 1 shows the ETA–DTA curves of gibbsites ground for periods of 0.5 and 20 h. Powder X-ray diffraction patterns (XRD) of these samples have been shown in a previous paper [1]. Gibbsite ground for 0.5 h still showed the presence of relatively well-crystallized gibbsite, though compared with unground gibbsite, a decrease in intensity and an increase in half-maximum line breadth were observed. In contrast, gibbsite ground for 20 h changed entirely to an amorphous phase. From TG–DTA runs, ^{27}Al MASNMR and XPS spectra [3], it was found that most of this amorphous phase consisted of amorphous hydrated alumina with the same stoichiometric composition as gibbsite, but a small part underwent mechanochemical dehydration to form amorphous alumina. In addition, the amorphous alumina thus resulting was considered to be a precursor of η-Al_2O_3, because of the appearance of tetrahedral coordinate Al in ^{27}Al MASNMR spectra and the similarity of binding energies of O1s, Al2s and Al2p in XPS spectra to those of η-Al_2O_3.

In the DTA curve of gibbsite ground for 0.5 h shown in Fig. 1, a large endothermic peak and a small exothermic peak appear at 325 and 1130°C. From the XRD results of the samples heated up to various temperatures marked on DTA curves by the arrows, it can be seen that they correspond to the dehydration of gibbsite to χ-Al_2O_3 and the formation of α-Al_2O_3, i.e. α-transformation, respectively. The ETA peaks for the corresponding reactions are also observed in the same temperature ranges. Gibbsite ground for 20 h shows a broad DTA endothermic peak at 200°C and two exothermic peaks at 865 and 1060°C. the former peak corresponds to the dehydration of amorphous hydrated alumina to amorphous alumina, and the latter two peaks to the crystallization of amorphous alumina to η-Al_2O_3 and the transformation of η-Al_2O_3 to α-Al_2O_3. These DTA peaks due to the dehydration and α-transformation appear at lower temperatures compared with gibbsite ground for 0.5 h, indicating the higher reacativity of the amorphous phase. The ETA peaks of gibbsite ground for 20 h also appear in the temperature ranges corresponding to the DTA peaks, but strangely the ETA peak due to the crystallization of amorphous alumina to η-Al_2O_3 was not observed. Although the reason for this is not completely understood, it should be remembered that the amorphous alumina formed by the mechanochemical dehydration is a precursor of η-Al_2O_3 [3]. Thus, the structural similarity between them may mean that only a very little displacement of atoms is needed for the crystallization process. This must be reflected by the lower activity in ETA experiments. In contrast to this, the α-transformation proceeds by a diffusion mechanism involving much longer-range displacement of atoms and then causes the higher ETA activity.

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