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STUDIES ON THE THERMAL REACTIONS OF ALUMINIUM OXIDES AND HYDROXIDES

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The gibbsite →χ-alumina decomposition (in air) and the χ-alumina →boehmite transformation (under hydrothermal conditions) were investigated isothermally. Reaction products were characterized by TG and X-ray diffraction.

The rate of the gibbsite →χ-alumina reaction below 250 °C appears to be nucleation and growth controlled. That of the hydrothermal transformation of χ-alumina to boehmite depends on the time of grinding and the particle size of the gibbsite from which the χ-oxide has been prepared. During this reaction, partial re-formation of gibbsite was observed at lower temperatures, but the final product was always boehmite.

In the thermal decomposition of gibbsite, $Al(OH)_3$ two products are obtained: boehmite, AlO(OH) and χ-Al_2O_3. Their relative amounts depend on the origin and the grain size of the starting substance, the pressure, etc. Under hydrothermal circumstances, boehmite is the only product up to about 300°; it is, most likely, the thermodynamically stable form in the system [1]. The formation of boehmite from gibbsite, when heated in air, was explained by hydrothermal conditions inside the particles, while the gibbsite alumina transformation is a surface reaction [2–4]. If the latter process is carried out at a constant decomposition rate, it can be divided into two sections, the first proceeding at constant temperature and pressure [4–6]. Previously we studied the effect of water vapour pressure on the kinetics of the gibbsite →χ-alumina transformation [7], now some new data on the same process and on the hydrothermal reactions of χ-alumina are reported.

Experimental

Synthetic aluminium hydroxide was wet ground in a ball mill for 6 or 30 hours. The samples for the gibbsite → χ-oxide transformation were taken from different

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microsieve fractions of the ground material. Layers of uniform thickness 1 mm were formed of these materials and treated isothermally in flowing air.

For the study of the hydrothermal reaction of χ-alumina, samples prepared of gibbsite at 255° were processed isothermally in stainless steel vessels under water and saturated water vapour.

The reaction products were characterized by TG measurements carried out on a DuPont 951 thermobalance. Phase analysis was confirmed by X-ray patterns recorded on a Zeiss HZG–4 diffractometer.

Results and discussion

Decomposition of gibbsite to χ-alumina

A conversion curve of a gibbsite sieve fraction is presented in Fig. 1, the amount of gibbsite is related to the initial value. The curve consists of an acceleratory and a deceleratory part. At lower temperatures, a quite long induction period is also visible. The shape of all curves pointed to a nucleation and growth control of the rate. Under the given circumstances, grinding time and particle size slightly influenced the transformation.

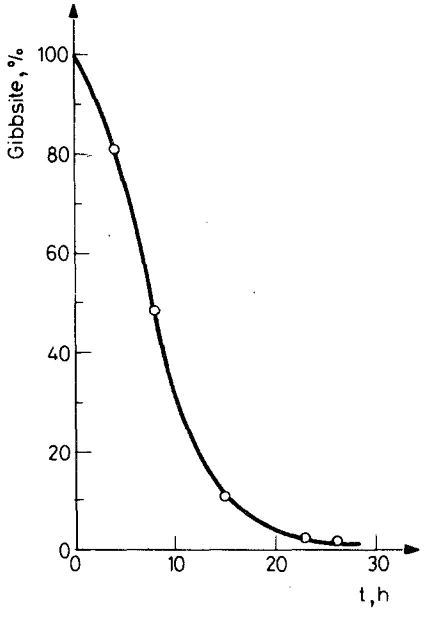

Fig. 1 The decomposition of gibbsite to χ-alumina in air. Sample: after 30 h of wet grinding, particle size 10–20 μm

Hydrothermal reaction of χ-alumina

The amount of boehmite in the reacted samples was calculated from the mass change in the 350–550° range (recorded by TG). The degree of transformation to boehmite is shown in Fig. 2 as a function of time for two sieve fractions and two temperatures. Visibly, the rate of reaction depends on the particle size. Moreover, in other experiments the time and (dry or wet) way of grinding were also found to have a considerable effect.

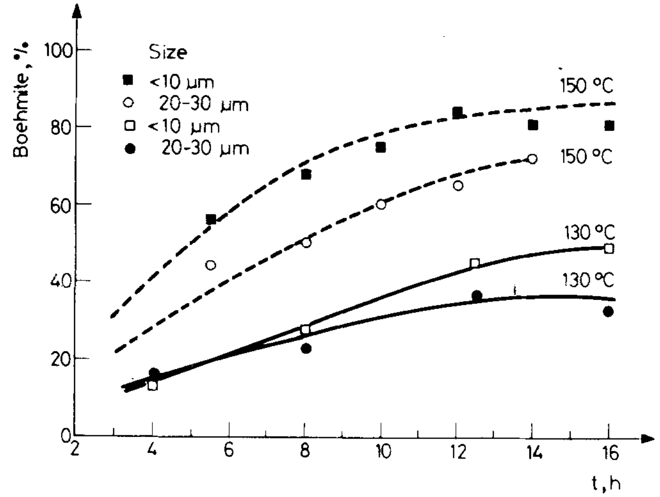

Fig. 2 The formation of boehmite in the hydrothermal treatment of χ-alumina prepared from different size fractions of gibbsite wet ground for 6 h.

Quite far from total conversion, the transformation to boehmite became very slow (Fig. 2), which can be attributed to the increasing role of diffusion in the control of the rate.

In the TG curves of several χ-alumina samples after hydrothermal treatment below 150°, a decomposition step occurred between 200 and 350°, i.e., in the range of the gibbsite → χ-oxide reaction. X-ray diffraction proved the presence of gibbsite in these samples. Some data belonging to relatively short times of treatment are shown in Fig. 3. Later the reformed gibbsite also transformed to boehmite, being the only final product.

Gibbsite re-formation from χ-alumina was favoured by lower temperature of hydrothermal treatment. Besides, less gibbsite was obtained from χ-aluminas prepared of gibbsite that had been ground for a longer time prior to decomposition. This may be explained by the activating effect of grinding. The thermodynamically favourable reaction (boehmite formation) is facilitated by a more active (i.e.,

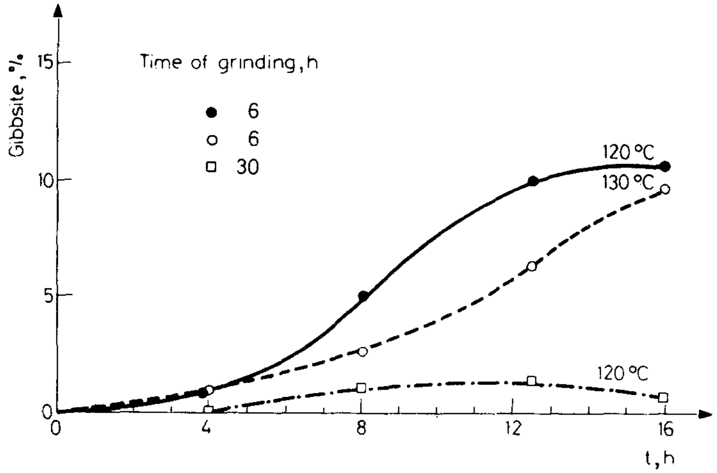

Fig. 3 The re-formation of gibbsite in the hydrothermal treatment of χ-alumina prepared of gibbsite (particle size below 10 μm) after 6 and 30 h of wet grinding.

unstable) starting material, while kinetic control may dominate in the case of a more stable oxide. A similar interpretation had been given by Lodding [8] for the difference between boehmite formation in the decomposition of natural and synthetic gibbsites.

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Zusammenfassung — Die Zersetzung von Hydrargillit zu χ-Aluminiumoxid in Luft und die Umwandlung von χ-Aluminiumoxid zu Böhmit unter hydrothermalen Bedingungen bei isothermer Versuchsführung wurden untersucht. Die Reaktionsprodukte wurden mittels Thermogravimetrie und Röntgenbeugung charakterisiert. Die Geschwindigkeit der Umsetzung von Hydrargillit zu χ-Aluminiumoxid unterhalb 250 C wird durch Keimbildung und Wachstum bestimmt. Die Geschwindigkeit der hydrothermalen Umsetzung χ-Al_2O_3→Böhmit hängt von der Mahldauer und der Teilchengrössen des Hydrargillits ab, aus dem das χ-Al_2O_3 präpariert worden war. Während letztere Reaktion wird bei tieferer Temperatur partiell Hydrargillit gebildet, das Endprodukt war stets Böhmit.

Резюме — Изотермически исследовано разложение гиббсита до χ-окиси алюминия в атмосфере воздуха и превращение его до боэмита в гидротермических условиях. Методом ТГ и рентгенофазового анализа охарактеризованы продукты реакции. Скорость реакции разложения гиббсита до χ-окиси алюминия ниже 250° соответствует механизму образования центров кристаллизации и их контролируемому росту. Гидротермическое превращение χ-окиси алюминия до боэмита зависит от времени измельчения и размера частиц гиббсита, из которых был получен χ-оксид алюминия. Во время этой реакции при более низкой температуре вновь наблюдалось образование гиббсита, но конечным продуктом реакции во всех случаях был боэмит.