Two Types of Water Contained in Transient Aluminas

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All the polymorphs of alumina except the well-crystallized alpha modification have only a little water. The behavior of the water has, however, hardly been clarified at all. The water remaining after being heated at temperatures of 100—120°C has been simply explained as being combined with the oxygen atoms on the surface or in the lattice of alumina. The amount of the water depends either on the type of alumina[1] or on the forming conditions. For example, in gamma alumina the amount of water and the degree of the splitting of the 400-reflection in the powder pattern vary in accordance with the conditions of preparation.

Through an investigation into thermal effects on the lattices of gamma and eta alumina, the present authors have previously pointed out there should exist a certain type of water within only the former, one which causes a change in the lattice dimensions.[2]

For the present work, the behavior of the water within transient aluminas was investigated quantitatively with the help of a precise thermobalance.

Gamma alumina was prepared from the dehydration of well-crystallized boehmite in air at 750°C, and the delta, from the dehydration of the same boehmite under a water vapor of 1 atm. at

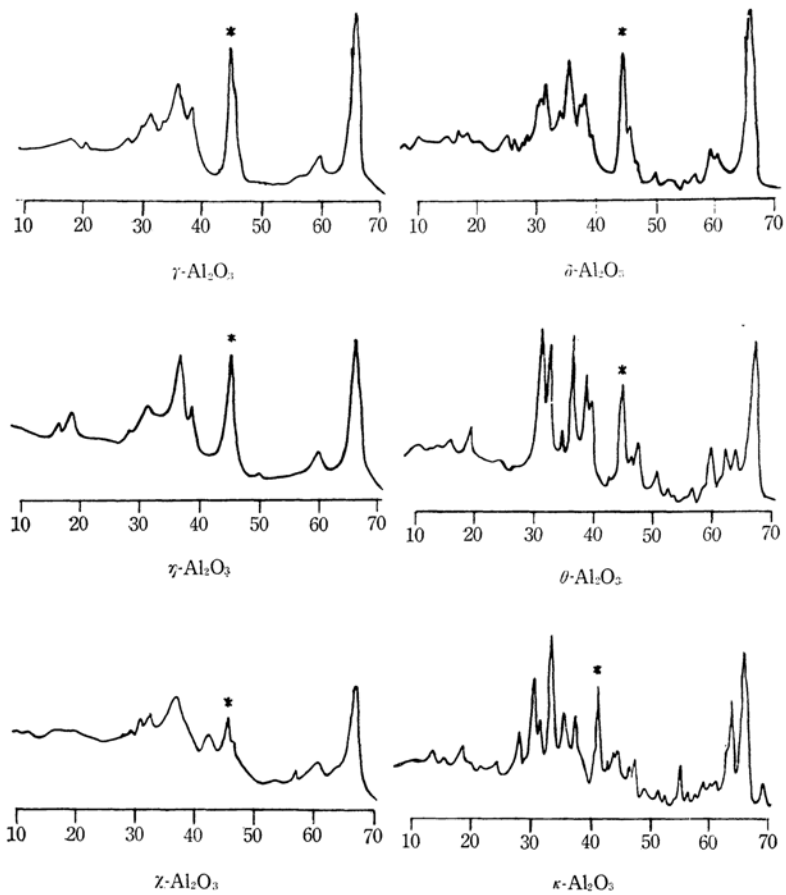

Fig. 1. X-Ray powder diffraction pattern of six transient aluminas using Cu$K\alpha$ radiation.

1) B. C. Lippens, Thesis, "Structure and Texture of Aluminas."

2) H. Yanagida and G. Yamaguchi, This Bulletin, **37**, 1229 (1964).

950°C. Eta and theta forms were obtained from the dehydration of bayerite in air, at 750°C and at 1100°C respectively. Chi and kappa forms were prepared from the dehydration of micro-crystalline gibbsite in air, at 750°C and at 1100°C respectively. The X-ray powder diagrams of these six aluminas are shown in Fig. 1.

The total amount of water (except that physisorbed (W_0 mg./g. Al_2O_3)) and the amount of water remaining in or on an alumina denoted as W_t (mg./g. Al_2O_3) at a temperature were determined as follows; after being heated at 120°C for 24 hr. in air in order to remove the physisorbed water, each alumina was held at each given temperature in air or under a water vapor pressure of 1 atm. until the loss in weight could no longer be observed at that temperature in determining an ignition loss under the quasi-equilibriumic conditions. The weighings were made with a model LB-Shimazu direct vision balance (sensitivity; 0.1 mg.).

The typical d-spacings of each alumina, marked in Fig. 1. by an asterisk are measured by the Cu-$K\alpha$ irradiation X-ray powder diffraction method, after heat treatments at 120°C, 400°C, and 600°C.

The total amount of water, W_0, on transient aluminas and their specific surface areas as measured by the nitrogen adsorption method are summarized in Table I. They seem considerably different from each other. However, after plotting the ratio of W_t to W_0, the present authors found the following rules.

Table I. The total amount of water except that physisorbed and specific surface area

Transient alumina	Water content W_0 mg./g. Al_2O_3	Specific surface area $m^2/g.$
γ-Al_2O_3	11.0	44.8
δ-Al_2O_3	5.6	32.7
η-Al_2O_3	34.0	183.7
θ-Al_2O_3	17.3	119.7
χ-Al_2O_3	25.2	126.3
κ-Al_2O_3	6.7	74.6

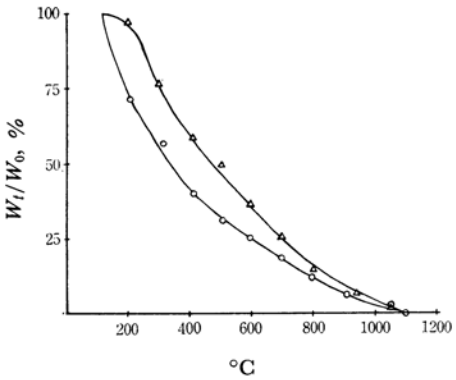

Fig. 2. Relation between heating temperature and ratio of remaining water to the total amount of water (W_t/W_0) on eta, ○; in air, △; in a water vapor of 1 atm.

Figure 2 shows the W_t/W_0 curve vs. the temperature for eta alumina in air and under a water vapor pressure of 1 atm. Theta, chi and kappa aluminas show curves approximately identical with that of eta when the W_t/W_0 ratios are plotted. As is shown in Table II, the typical d-spacings of these four aluminas are hardly changed at all by the thermal treatments. The present authors classify this type of water as the water not affecting the lattice dimensions and name it "non-lattice water."

Figure 3 shows the W_t/W_0 curve vs. the temperature for gamma alumina in air and under a water vapor pressure of 1 atm. Here the curve becomes quite different if the vapor pressure of the water is changed. The curve for delta alumina is identical with that for gamma. Table II shows that the removal of this type of water causes a change in the d-spacings. The present authors classify this as the water affecting the lattice dimensions and name it "lattice water."

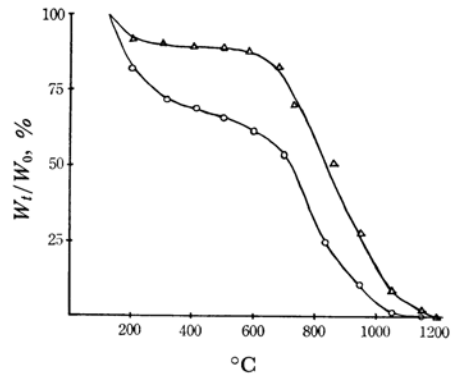

Fig. 3. Relation between heating temperature and ratio of remaining water to the total amount of water (W_t/W_0) on gamma, ○; in air, △; in a water vapor of 1 atm.

Table II. The change of the typical d-spacing of transient aluminas by thermal treatments measured at 25°C

Transient alumina	Heating temperature 120°C	400°C	600°C	$d_{120}-d_{600}$
γ-Al_2O_3	1.9867 Å	1.9835 Å	1.9810 Å	0.0057 Å
δ-Al_2O_3	1.9899	1.9879	1.9867	0.0032
η-Al_2O_3	1.9790	1.9787	1.9787	0.0003
θ-Al_2O_3	2.0183	2.0186	2.0183	0.0000
χ-Al_2O_3	1.9909	1.9909	1.9909	0.0000
κ-Al_2O_3	2.1195	2.1186	2.1186	0.0009

With the infrared absorption method, Peri showed that there are several types of water on the surface but not within the lattice of gamma-type

alumina.[3] The present results, however, show a certain type of water exists in the lattice of gamma and delta aluminas.

The present authors will report the results of further investigation into these types of water and the effects on the thermal conversions of transient aluminas in a later paper.

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3) J. B. Peri and R. B. Hannan, *J. Phys. Chem.*, **64**, 1526 (1960).