Thermal Effects on the Lattices of η- and γ-Aluminum Oxide

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In a previous paper,[1] the present authors found that the lattice dimensions and the tetragonal axial ratio of γ-aluminum oxide vary with hydrothermal and heat treatments and proposed that η-aluminum oxide may be an end-member of the γ-aluminum oxide series with little tetragonal deformation. In the present paper, the lattice dimensions of η- and γ-aluminum oxide will be measured with a high temperature X-ray diffraction apparatus at various temperatures and after various heat treatments in order to discuss further the relation between η- and γ-aluminum oxide.

1) G. Yamaguchi and H. Yanagida, This Bulletin, 35, 1896 (1962).

The γ-aluminum oxide examined had a tetragonal axial ratio of 1.0357 and was obtained from a hydrothermal treatment, at 500°C under 50 atm. for 20 hr., of γ-aluminum oxide which had been formed from the dehydration

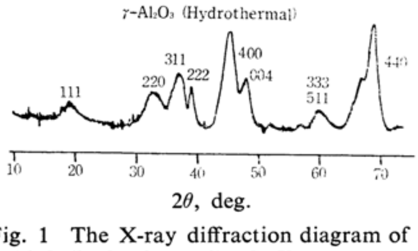

Fig. 1 The X-ray diffraction diagram of γ-Al_2O_3(hydrothermal), Cu$K\alpha$ ray.

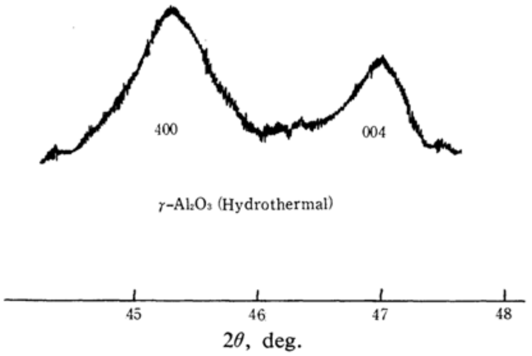

Fig. 2. The slow-scanning X-ray diffraction pattern of γ-Al_2O_3 about the (400) peak in the spinel indices; Cu$K\alpha$, 35kV., 12 amp. 1°1° 0.2 mm. slit system; rate meter 8; time constant 4 sec.; scanning speed 1°/4 min. Geigerflex.

of well-crystallized boehmite AlOOH in air at 700°C. The X-ray diffraction diagram is shown in Fig. 1, while the slow-scanning pattern about the (400) peak in the spinel indices is in Fig. 2. This specimen contained 7.5% water at 150°C. Another γ-aluminum oxide with the axial ratio of 1.0183 was also examined; it contained 3.5% water at 150°C.

The η-aluminum oxide with little tetragonal deformation was obtained from the dehydration, at 700°C in air, of bayerite $Al(OH)_3$ which had been formed by the neutralization of an aqueous solution of aluminum chloride by ammonia. The (400) peak of this specimen is hardly split at all. This had 3.8% water at 150°C.

Table I. The lattice dimensions of γ-Al_2O_3 measured with a high temperature X-ray diffraction apparatus Cu$K\alpha$, 35 kV., 15 mamp.; 1°1° 0.02 mm. slit system; rate meter 8; time constant 4 sec.; scanning speed 1°/4 min.; Geigerflex

No. of Heating procedure		d(400 and 040)* Å	d(004)* Å	Tetragonal** Axial ratio
1	Room temperature	2.0015	1.9325	1.0357
2	130°C	2.0043	1.9321	1.0374
3	270°C	2.0089	1.9340	1.0387
4	Room temperature	2.0005	1.9314	1.0358
5	400°C	2.0055	1.9331	1.0375
6	Room temperature	1.9984	1.9300	1.0354
7	600°C	1.9914	1.9300	1.0318
8	Room temperature	1.9856	1.9182	1.0351
9	800°C	1.9918	1.9298	1.0321
10	Room temperature	1.9799	1.9167	1.0330
11	900°C	1.9934	1.9329	1.0313
12	Room temperature	1.9799	1.9163	1.0332

* The d-values are ±0.0008 Å

** The axial ratios ±0.0006

Table II. The lattice dimensions of η-Al_2O_3 measured with a high temperature X-ray diffraction apparatus

Cu$K\alpha$, 35 kV., 15 mamp.; 1°1° 0.2 mm. slit system; rate meter 8; time constant 4 sec.; scanning speed 1°/2 min; Geigerflex

No. of Heating procedure		d(400, 040 and 004)* Å
1	Room temperature	1.9799
2	130°C	1.9819
3	270°C	1.9831
4	Room temperature	1.9815
5	400°C	1.9840
6	Room temperatnre	1.9815
7	600°C	1.9873
8	800°C	1.9918
9	Room temperature	1.9799

* The d-values are ±0.0012Å

The curves plotting the heating temperatures versus the lattice dimensions of η-aluminum oxide and γ-aluminum oxide are shown in Tables I and II and in Figs. 3 and 4. The curve for η-alumnum oxide is reversible whereas that for γ-aluminium oxide is not reversible. The lattice dimensions of γ-aluminum oxide decrease, and, at the same time, the degree of tetragonal deformation is lowered through the heat treatments numbered 5—9 in Table I and in Fig. 3. The axial ratios decreased 1.0357 to 1.0332 and 1.0183 to 1.0158. Curves plotting the heating temperatures versus the amount of water in or on the aluminas are shown in Fig. 5, in which the axial ratios of the starting γ-aluminum

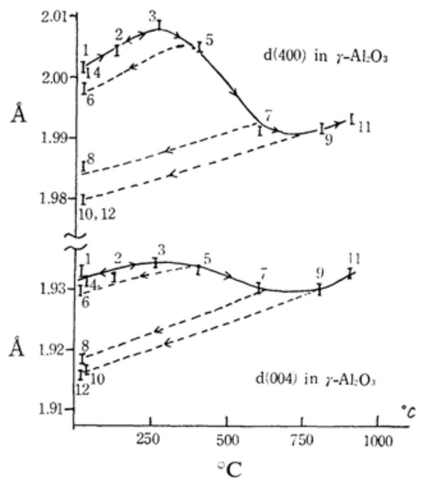

Fig. 3. The lattice dimension of γ-Al_2O_3 measured with a high temperature X-ray diffraction apparatus; Cu$K\alpha$, 35kV., 15 amp.; 1°1° 0.2 mm. slit system; rate meter 8; time constant 4 sec.; scanning speed 1°/4 min. Geigerflex.

oxide are also indicated. We can see the loss of water from the aluminas take place through the heat treatments. The changes in the lattice dimensions and the tetragonal axial ratio are accompanied by the loss of water from the γ-aluminum oxide, while the loss of water from the η-aluminum oxide does not cause those changes.

These results lead us to consider that a certain type of water should be present in the lattice of γ-aluminum oxide with considerable tetragonal deformation, especially in such a hydrothermal substance,[1] but the water of this type is not there in the lattice of η-aluminum oxide as an end-member of the γ-aluminum oxide series with little tetragonal deformation. Unfortunately, we cannot discuss the type of water and the relation between the amount of this water and the axial ratio in the present work. We will try to clarify the relation in a later paper.

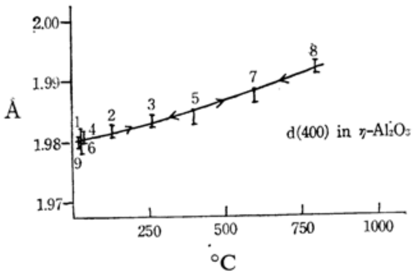

Fig. 4. The lattice dimension of η-Al_2O_3 measured with a high temperature X-ray diffraction apparatus; Cu$K\alpha$, 35kV., 15 amp.; 1°1° 0.2 mm. slit system; rate meter 8; time constant 4 sec.; scanning speed 1°/2 min.; Geigerflex.

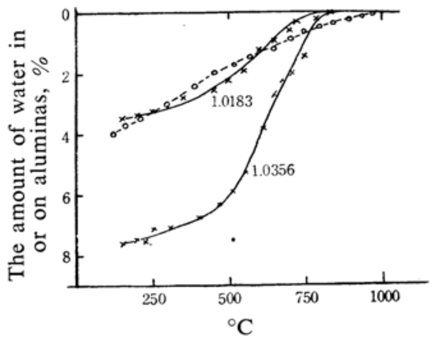

Fig. 5. The relation between the temperatures and the amount of water in or on η-Al_2O_3 (-○-) and γ-Al_2O_3 (-×-).

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