Delta- and Theta-Al_2O_3 under Hydrothermal Conditions

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In a previous paper,[1] Yamaguchi *et al.* reported that under hydrothermal conditions, γ-Al_2O_3 obtained from the dehydration of boehmite was deformed further, more tetragonally, but not inverted into δ-Al_2O_3. In this experiment the authors treated η- and γ-Al_2O_3, with various origins, under hydrothermal conditions.

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

Preparation of Standard Samples

In order to compare and discriminate the polymorphs, standard samples were prepared.

Preparation and Identification of η-Al_2O_3. Commercial fine gibbsite was heated in vacuum at 900°C for 30 min. The X-ray diffraction pattern of this product is given in Fig. 1a showing the character of η-Al_2O_3.

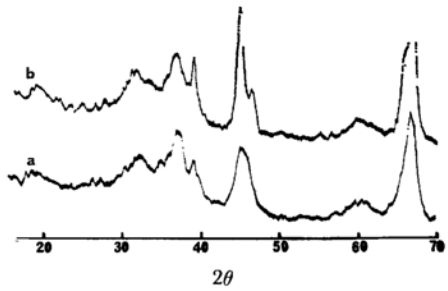

Fig. 1. X-ray diffraction patterns of η-Al_2O_3 (a) and γ-Al_2O_3 (b).

Preparation and Identification of γ-Al_2O_3. Well crystallized boehmite obtained hydrothermally from gibbsite was treated again under hydrothermal conditions (500°C, 50 atm) for 20 hr. The X-ray diffraction pattern of this product is given in Fig. 1b, showing the character of γ-Al_2O_3.

Preparation and Identification of δ-Al_2O_3. Well crystallized boehmite obtained hydrothermally from gibbsite was heated in air at a heating rate of 5°C/min, up to 1000°C, and kept there for 1 hr. The X-ray diffraction pattern of this product is given in Fig. 2a, showing the character of δ-Al_2O_3.

Preparation and Identification of θ-Al_2O_3. Bayerite, obtained by aging alumina gel[2] in conc. NH_3 aqueous solution, was heated in air at a heating rate 5°C/min, up to 1100°C, and kept there for 1 hr. The X-ray diffraction pattern of this product is given in Fig. 2b, showing the character of θ-Al_2O_3.

The characters of the X-ray diffraction pattern of these polymorphs are summarized in Table 1.

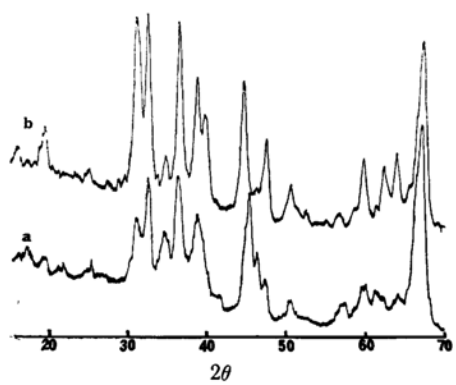

Fig. 2. X-ray diffraction patterns of δ-Al_2O_3 (a) and θ-Al_2O_3 (b).

Hydrothermal Treatment of η- and γ-Al_2O_3

Starting materials were as follows:

1. η-Al_2O_3 A. Bayerite, obtained by treating alumina gel with conc. NH_3 aqueous solution at room temperature for 3 days, was heated and dehydrated in air at 800°C for 1 hr.

2. η-Al_2O_3 B. Bayerite, obtained by hydrolyzing sodium aluminate aqueous solution (NaOH 3.5 mol/*l*, Na/Al=1.35) at 15°C for 3 days, was heated and dehydrated in air at 800°C for 1 hr.

3. η-Al_2O_3 C. Nordstrandite, obtained by treating alumina gel with a 5% ethylenediamine

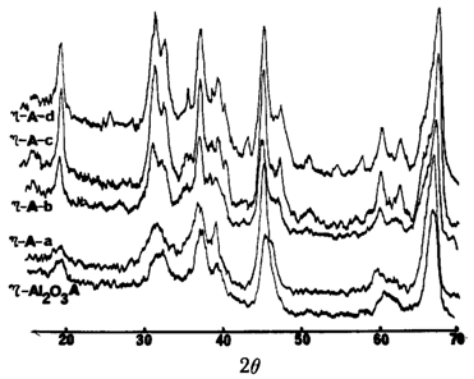

Fig. 3. X-ray diffraction patterns of products from η-Al_2O_3 A.

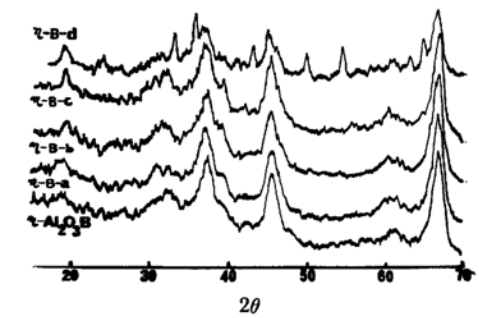

Fig. 4. X-ray diffraction patterns of products from η-Al_2O_3 B.

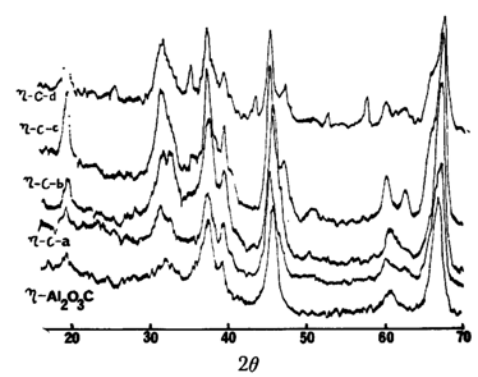

Fig. 5. X-ray diffraction patterns of products from η-Al_2O_3 C.

2) G. Yamaguchi and W. This Bulletin, Feb. (1968).

TABLE 1. CHARACTER OF DIFFRACTION PATTERN OF Al_2O_3 POLYMORPHS, ( ) SHOWS SPINEL INDEX

2θ range	η	γ	δ	θ
67—68	(440) singlet	(440) doublet	(440) doublet	doublet
59—64	(333) (511) broad	(333) (511) broad	two peaks	three peaks
45—48	(400) singlet	(400) doublet	(400) doublet and one more small peak	two or three peaks
ca. 39	(222) singlet	(222) singlet	(222) singlet	singlet
36—38	(311) broad	(311) broad	two peaks	two peaks
34—35	—	—	one peak	small one peak
31—32	(220) broad	(220) broad	two peaks	two peaks

TABLE 2. STARTING MATERIALS, HYDROTHERMAL CONDITIONS AND PRODUCTS

Starting material	Notation	Hydrothermal condition			Product
		Temp. °C	Pressure atm	Period hr	
η-Al_2O_3 A	η-A-a	450	50	20	γ
	η-A-b	450	110	20	δ or θ
	η-A-c	500	40	175	θ
	η-A-d	500	50	20	$\theta+(\alpha)$
η-Al_2O_3 B	η-B-a	400	50	20	γ
	η-B-b	450	30	20	γ
	η-B-c	500	30	20	γ
	η-B-d	500	50	20	$\gamma+(\alpha)$
η-Al_2O_3 C	η-C-a	400	50	20	γ
	η-C-b	450	70	45	γ
	η-C-c	500	50	20	γ
	η-C-d	500	130	20	δ or $\theta+(\alpha)$
η-Al_2O_3 D	η-D-a	400	50	20	γ
	η-D-b	450	90	20	γ
	η-D-c	500	70	20	γ
	η-D-d	500	90	20	$\gamma+(\alpha)$
η-Al_2O_3 E	η-E-a	450	70	20	η
	η-E-b	450	130	20	γ
	η-E-c	500	80	20	γ
	η-E-d	500	200	20	$\gamma+\alpha$
η-Al_2O_3 F	η-F-a	400	40	20	η
	η-F-b	450	70	45	η
	η-F-c	500	70	45	γ
	η-F-d	500	130	20	$\gamma+(\alpha)$
γ-Al_2O_3	γ-a	400	50	20	γ; $a=7.98$ $c=7.78$
$a=7.94$	γ-b	450	90	45	γ; $a=7.98$ $c=7.73$
$c=7.85$	γ-c	520	50	20	γ; $a=7.99$ $c=7.72$
	γ-d	520	70	20	$\gamma+(\alpha)$ $a=8.00$ $c=7.72$

α α-Al_2O_3, γ γ-Al_2O_3, δ δ-Al_2O_3, η η-Al_2O_3, θ θ-Al_2O_3, ( ) small amout

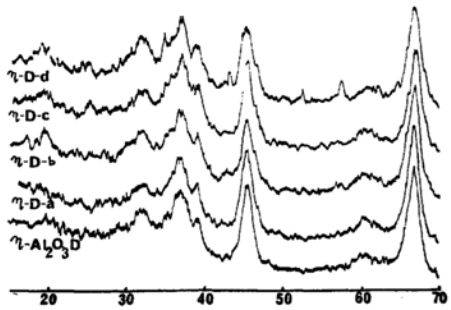

Fig. 6. X-ray diffraction patterns of products from η-Al_2O_3 D.

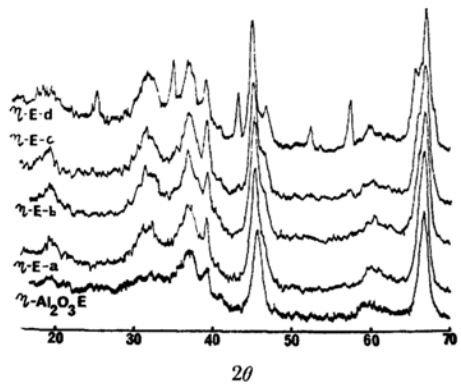

Fig. 7. X-ray diffraction patterns of products from η-Al_2O_3 E.

aqueous solution at 40°C for 2 days, was heated and dehydrated in air at 700°C for 1 hr.

4. η-Al_2O_3 D. Commercial gibbsite was heated and dehydrated in vacuum at 900°C for 0.5 hr.

5. η-Al_2O_3 E. Well crystallized boehmite was heated and dehydrated in vacuum at 900°C for 0.5 hr.

6. η-Al_2O_3 F. Bayerite, obtained by treating alumina gel with conc. NH_3 aqueous solution at room temperature for 3 days, was heated and dehydrated in vacuum at 800°C for 1 hr.

7. γ-Al_2O_3. Well crystallized boehmite was heated in air at 650°C for 0.5 hr.

These materials were treated under hydrothermal conditions and examined by an X-ray diffraction method. Results are given in Table 2, and Fig. 3 through Fig. 9.

Conclusion and Discussion

1. Similar to the previous paper, 1) γ-Al_2O_3, obtained from the dehydration of well crystallized boehmite was deformed further, more tetragonally, but not inverted into δ- or θ-Al_2O_3. As for η-Al_2O_3 however, some was only deformed into γ-Al_2O_3, while the rest was inverted into θ-Al_2O_3 before being finally inverted into α-Al_2O_3; η-Al_2O_3 A, and C belonged to the latter.

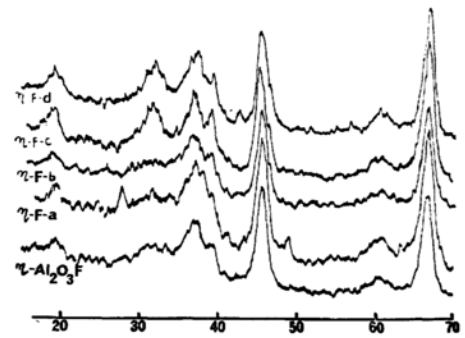

Fig. 8. X-ray diffraction patterns of products from η-Al_2O_3 F.

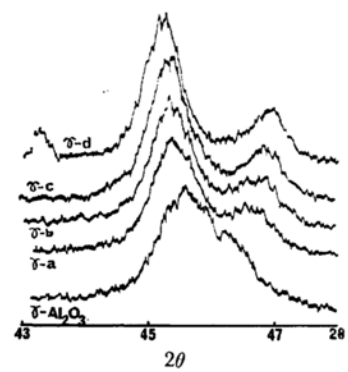

Fig. 9. X-ray diffraction peaks of (400) and (004) of γ-Al_2O_3 under hydrothermal condition.

2. Before the formation of θ-Al_2O_3, η-Al_2O_3 A, and C seemed to pass through an intermediate phase like δ-Al_2O_3 but the X-ray diffraction pattern of this intermediate phase was not correctly coincident with that of standard δ-Al_2O_3 (Fig. 2a). Interpretation of this phenomenon can not be accomplished before the structural problem of δ-Al_2O_3 and θ-Al_2O_3 is clarified. Whether or not δ-Al_2O_3 and θ-Al_2O_3 are considered to be of different phases is a problem which is now being investigated by the present authors.

3. Among η-Al_2O_3 specimens obtained from different origins, there were two types. One was hardly inverted into θ-Al_2O_3, and the other was easily inverted under hydrothermal conditions. This difference seems to be due to a delicate structural difference, but the explanation is left as a future problem.