THE REACTION SERIES, GIBBSITE→CHI ALUMINA →KAPPA ALUMINA→CORUNDUM. II*

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Since the experiments described in Part I (Brindley and Choe, 1961) were submitted for publication, an extensive study of the dehydration of gibbsite and of the crystallography of the transition aluminas has been published by Saalfeld (1960). Since the results of the two investigations agree in some respects and disagree in others, it will be worth while to make a brief comparison to see what general conclusions can be drawn.

In the first place, it should be emphasised that these studies are the first attempts to apply single crystal methods to obtain a better understanding of the reaction series, gibbsite→χ→κ→α-corundum. Saalfeld employed relatively large crystals of gibbsite which, under hydrothermal conditions, yielded the boehmite→γ→θ→α reaction series, and under atmospheric heating gave additionally the χ→κ→α series. In order to study the latter reaction series independently of the former, Brindley and Choe used <1 micron sized single crystals and electron diffraction technique.

Whether the crystal size of the gibbsite modifies the precise course of the χ→κ→α reactions is a question to be considered. The possible role of impurities, particularly alkali ions, has been mentioned by Saalfeld. The gibbsite sample used by Brindley and Choe contained Na_2O of the order of 0.3%.

FORMATION AND STRUCTURE OF χ-ALUMINA

The two investigations agree that χ-alumina is formed at about 270° C., that it is stable to about 850° C., that initially it contains considerable 'water' which is gradually lost at the higher temperatures, and that the structure is hexagonal with $a_H = 5.56$ (S) or 5.57 (B & C).†

There is difference of opinion regarding the c parameter, given as 13.44 Å (S) and 8.64 Å (B & C). If the structures are composed of close-packed oxygen layers, then these cells contain respectively 6 and 4 such layers, of the same thickness as that of the octahedrally coordinated layers in gibbsite, as the following data show:

$$13.44/6 = 2.24 \text{ Å}$$
$$8.64/4 = 2.16 \text{ Å}$$

Thickness of Al-OH layer in gibbsite = 2.12 Å.

† Here, and elsewhere, (S) signifies Saalfeld, (B & C) Brindley and Choe.

The reflections for χ-alumina listed by Brindley and Choe with one exception have *even* l indices and therefore could be indexed equally well with the larger cell given by Saalfeld; $l=2$ becomes $l=3$, $l=4$ becomes $l=6$, and so on. The exceptional reflection, (003), is a weak x-ray powder line which does not fit the larger cell. Saalfeld comments on the disorderly packing of the oxygen layers in χ-alumina which produces considerable diffuse scattering parallel to c^* and possibly gives rise to non-integral maxima. It is conceivable that different layer sequences can be obtained by using different starting materials and/or heat-treatments.

The pseudo-cubic character of χ-alumina is more readily interpreted by Saalfeld's cell. The question can be asked, however, whether Saalfeld's use of relatively large crystals of gibbsite predisposed his material to transform to a state nearer to the cubic γ-form. Although the x-ray powder data for χ-alumina given by different investigators are sparse and mainly ill-defined, there appear to be divergencies which perhaps can be attributed to differences in the stacking sequences of the various χ-aluminas.

FORMATION AND STRUCTURE OF κ-ALUMINA

The two investigations agree that this form is stable in the range 800–1200° C. (S) or about 900–1200° C. (B & C), and that the structure is hexagonal. It is agreed also that more than one structural form exists in this temperature range. Saalfeld records no data for forms other than the one he labels κ, while Brindley and Choe record the hexagonal a-parameters for four different cells, of which one agrees with that given by Saalfeld. In this respect the electron diffraction data have provided more information than the x-ray data.

For material heated to temperatures between 900 and 1200° C., Brindley and Choe found the following:

> 7 patterns of χ-alumina, with $a_H = 5.53$ Å
> 54 patterns of κ_1-alumina, with $a_H = 16.78$ Å
> 4 patterns of κ_2-alumina, with $a_H = 9.70$ Å
> 4 patterns of ν-alumina, with $a_H = 5.54$ Å
> 2 patterns of ξ'-alumina, with $a_H = 5.37$ Å.

The designations κ_1 and κ_2 are used here for the first time. Saalfeld records an hexagonal parameter $a_H = 9.71$ Å which agrees with the relatively rare κ_2 found by Brindley and Choe. There is no ambiguity nor uncertainty in the electron diffraction data as regards the κ_1 and κ_2 forms; the κ_1 type with the large a_H parameter is much the more common. Figure 1 shows that the κ_1 and κ_2 basal reciprocal nets are related in a simple way and that $hk0$ reflections of κ_2 can be indexed on the larger κ_1 cell; the converse is obviously not true. The indexing of the powder diagrams given by Saalfeld could be based equally well on the larger cell. The writer
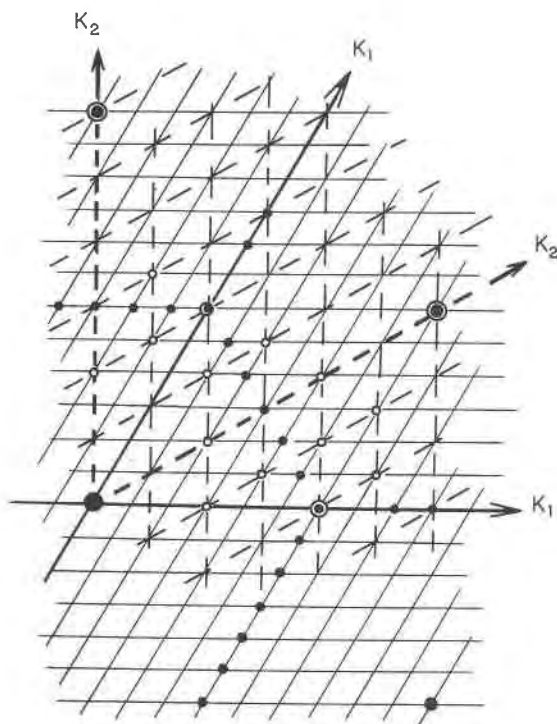
FIG. 1. Superposed single crystal, electron diffraction diagrams for κ_1—Al_2O_3 (hexagonal parameter $a_H = 16.78$ Å) and κ_2—Al_2O_3 (hexagonal parameter $a_H = 9.70$ Å). Solid circles show reflections from κ_1—Al_2O_3 and open circles from κ_2—Al_2O_3; continuous lines apply to κ_1 and dashed lines to κ_2. Observe that the κ_2 reflections can be indexed on the κ_1 axes, but the reverse is not valid.

does not question the correctness of the unit cell given by Saalfeld *for his material,* but at the same time it must be affirmed that the gibbsite studied by Brindley and Choe yielded predominantly a different unit cell for the same temperature of heat-treatment.

Saalfeld recognized that different structural forms occur in the temperature range 800–1200° C. and he named these "κ-like" structures. In the light of the two investigations, it can now be stated that several κ-type structures exist, and that, according to particular circumstances, *one or other of these may be dominant, but not always the same structure.*

CONCLUSIONS

It appears that the crystallography of the transition aluminas χ- and κ- can vary according to precise experimental conditions. χ-alumina is essentially hexagonal with $a_H = 5.56$ Å, with disorderly stacking in the c-

direction and a variable c-parameter corresponding to 6 or 4 layers. A number of κ-type forms are recognized and at least two hexagonal cells are recognized with a_H respectively 16.78 and 9.71 Å. These are now called κ_1 and κ_2. The forms ν- and ξ'-alumina, previously noted by Cowley (1953), have also been observed in the same temperature range in which the κ-aluminas are found.

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