been well outgassed, either speed can be obtained by a suitable electrode potential switching sequence. The duality of pumping speeds has been found to be a result of charging of the glass walls to either approximately cathode or anode potential.

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Evidence for a Variable Long-range Order in Nearly Anhydrous Gamma Alumina

THE nature of the cubic or nearly cubic alumina called γ- or η-Al_2O_3 has been the subject of much speculation. Its structural similarity to the spinels has been known for many years[1-3] and led to the view that γ-Al_2O_3 is a defect structure which can be written $Al_{21\frac{1}{3}}\square_{2\frac{2}{3}}O_{32}$ with $21\frac{1}{3}$ aluminium ions occupying statistically 24 cation sites in the spinel structure.

The recognition that γ-Al_2O_3 is frequently not a fully dehydrated alumina led de Boer and Houben[4] to suggest that 'water' may be an integral part of the structure and that an ideal formula may be $H\,Al_5O_8$ analogous to the spinels $Li\,Al_5O_8$ and $Li\,Fe_5O_8$ (see ref. 5). In these structures the lithium ions occupy particular positions in the lattice and therefore one might expect that if γ-Al_2O_3 is really $H\,Al_5O_8$, the hydrogen ions (or more likely the OH ions) likewise will occupy particular positions.

Saalfeld[6] has discussed the dehydration of gibbsite to boehmite and the subsequent formation of a nearly anhydrous alumina. The reactions are orderly in a crystallographic sense and the resulting γ-alumina is shown to be tetragonal with $a = b = 7{\cdot}95$ A. and $c = 7{\cdot}79$ A. We have found confirmation of this result in the course of studying the dehydration kinetics of a well-crystallized gibbsite. The nearly anhydrous alumina yielded a double peak in the position of the strong (400) spinel reflexion with components $d = 1{\cdot}98$ and $1{\cdot}95$ A. The longer spacing gives the more intense reflexion and corresponds to (400) and (040) with $a = b = 7{\cdot}96$ A. and the shorter spacing corresponds to (004) with $c = 7{\cdot}80$ A.

One may reasonably surmise that if dehydration occurs slowly from well-crystallized material, the ordered tetragonal structure is formed. This appears to be the γ-alumina of Stumpf[7] and Russell[8]. When dehydration takes place in a less orderly manner or from less favourable starting materials, then a statistically cubic material is formed which gives the spinel-type X-ray pattern.

We have obtained additional evidence for structural order in nearly anhydrous alumina prepared by slow dehydration of gibbsite. When the dehydration is carried beyond about 90 per cent of completion, a long spacing of the order of 30–90 A. is reproducibly formed and is fairly stable to atmospheric conditions. The peak occurs in the region of $2\theta = 1$–$2°$, with copper $K\alpha$ radiation. The peak is observed first at about 80 per cent of complete dehydration but at this stage some boehmite still remains. Fig. 1 shows plots of diffracted intensity against 2θ and it is obvious that, as dehydration goes to completion, the diffraction peak moves to smaller 2θ values and finally is lost in the direct beam. Usually only one peak is observed, occasionally two can be observed, so that the long-range order arising from the residual 'water' is of a statistical character. The well-defined peaks shown in Fig. 1 were obtained by 12-hr. heat-treatments at successively higher temperatures up to about 500° C. Dehydration carried out directly at 450–500° C. gave poorer peaks, though they still occurred.

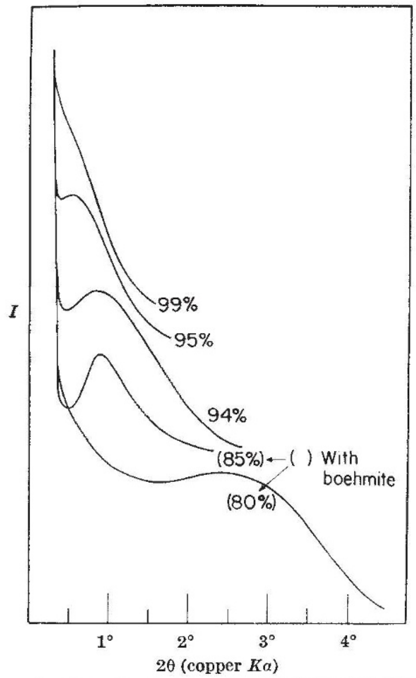

Fig. 1. Small-angle X-ray diffracted intensity from nearly anhydrous gamma-aluminas prepared from gibbsite. The percentage dehydration of the gibbsite is given for each curve. Note, however, that for 80 and 85 per cent dehydration, the remaining water is contained partly in residual boehmite

In terms of oxides, the ideal formula $H\,Al_5O_8$ is $Al_2O_3.\frac{1}{5}H_2O$ and corresponds to one-fifteenth of the initial 'water' content, that is, $6{\cdot}7$ or $93{\cdot}3$ per cent of complete dehydration, and the corresponding long spacing in Fig. 1 is about 65 A.

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