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# Thermal evolution of thin boehmite films

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Using transmission electron microscopy, electron diffraction and resistance change measurements, we studied the process of thermal evolution of thin boehmite ($\alpha$-$Al_2O_3 \cdot H_2O$) films. It has been shown that the crystal lattice of boehmite decomposes at a temperature of 670 K, with simultaneous partial dehydration. Above 875 K crystallization of $\gamma$-$Al_2O_3$ occurs and the morphology of the film changes from fibrous to granular. Annealing of $\gamma$-$Al_2O_3$ at 1300 K results in its transformation into $\delta$-$Al_2O_3$. At temperatures of 1475 to 1575 K the transformation of $\delta$-$Al_2O_3$ into $\alpha$-$Al_2O_3$ was observed. Depending on the temperature of annealing, thin $\alpha$-$Al_2O_3$ films were composed of fine crystals or of large (micrometre) corundum crystals. The method of producing of the various aluminas in the form of thin films presented in this report makes investigation of the structure transitions in aluminium oxides by means of transmission electron microscopy possible, and such films can be also used as supports for transmission electron microscopy studies of the model metal-oxide supported catalysts.

## 1. Introduction

In a previous paper [1] we presented a simple method of the preparation of thin boehmite films, suitable as supports for transmission electron microscopy (TEM) and electron diffraction (ED) studies. The method of preparation consists of hydration of aluminium oxide films, obtained by reactive evaporation of elemental aluminium in an oxidizing atmosphere, in hot distilled water. Transformation of aluminium oxide into boehmite greatly improves the mechanical strength of the films and such films can be used as a starting point for the preparation of various alumina films suitable as model catalyst's supports, important e.g. in studies on strong metal support interaction (SMSI) [2–4] or sintering and redispersion of the metal phase [4–6].

In the present work we report the results of TEM, ED and electrical resistance investigations of structure changes occurring in hydrated aluminium oxide (boehmite) during its thermal treatment in the temperature range from 300 to 1600 K. We believe that our results may be interesting in comparison with results of other studies on aluminium oxides obtained by dry methods, i.e. oxidation of aluminium foil [7, 8] or by reactive evaporation of aluminium in an oxidizing atmosphere [9].

## 2. Experimental details

Details of the procedure of preparation of thin boehmite films reported previously [1]. Here we present only the most important points. A piece of aluminium foil was evaporated in an atmosphere of laboratory air at $\sim 10^{-1}$ Pa pressure onto a freshly cleaved NaCl crystal placed ca. 15 cm from the aluminium source. When the evaporation was complete the NaCl crystal was immersed for a while into a large amount of hot distilled water ($\sim$ 360 K). Then the crystal was removed and floating aluminium oxide was left for $\sim$ 12 min. In these conditions hydration of aluminium oxide to boehmite ($\alpha$-$Al_2O_3 \cdot H_2O$) took place with a simultaneous change of the film structure from a very fine grain (nearly amorphous) into a polycrystalline one with pin-shaped crystals [1]. Pieces of the floating boehmite were picked up onto platinum microscope grids and then examined by TEM (Tesla BS 613) and/or underwent thermal treatment.

For measurements of changes of d.c. electrical resistance of the thin boehmite films during their dehydration we prepared also such films supported on fused silica plates. Geometry of the boehmite film and gold electrodes is shown schematically in Fig. 1. Electrical resistance of the boehmite film was determined by the method of measuring the voltage drop on a standard resistance. Thermal treatment of thin boehmite films in the temperature range 300 to 1100 K was performed in a furnace at room atmosphere, while at higher temperatures in vacuum of $\sim 10^{-4}$ Pa.

## 3. Results and discussion

### 3.1. Dehydration of boehmite

Typical thin ($\sim$ 30 nm) boehmite film obtained by hydration of aluminium oxide film in hot water is shown in Fig. 2. The most striking feature of the film is the presence of pin-shaped crystallites. Such films undergo dehydration upon heating, and to determine the onset of this process we measured changes in d.c. electrical resistance of the film during heating with constant rate to 680 K and then during annealing at this temperature. Results of the measurements are shown in Fig. 3. In the temperature range 520 to 660 K we observed a rapid exponential decrease of the resistance with the activation energy for electrical conductivity, determined from the relation $R \sim \exp(E_a/kT)$, where $R$ is the d.c. electrical

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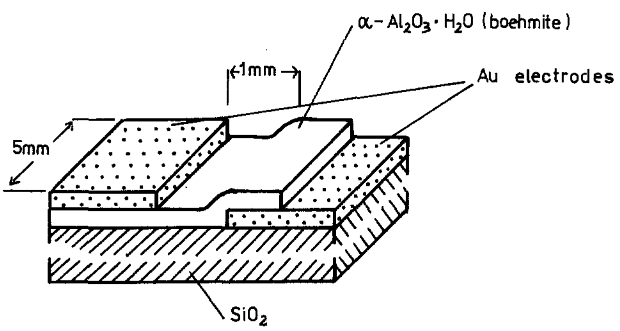


*Figure 1* Fused silica plate with deposited film of boehmite and with gold electrodes for electrical resistance measurements.

resistance, $T$ is the temperature, $k$ is the Boltzmann's constant and $E_a$ is the activation energy for electrical conductivity, equals to $E_a = 0.35\,\text{eV}$. At the temperature of 670 K, the resistance of the film achieved its minimal value and then started to grow. At this moment we stabilized the temperature of the film at 680 K and further resistance changes were measured at this temperature. From Fig. 3 it appears that annealing at 680 K results in significant increase of the film resistance most probably due to progressive dehydration of boehmite.

ED studies carried out parallel to resistance measurements revealed that the crystal lattice of boehmite starts to decompose at temperatures above 570 K. In Fig. 4, electron diffractograms of "fresh" boehmite dried at room temperature, (a) boehmite annealed at 520 K for 24 h (b) and annealed at 620 K for 24 h (c) are presented. Diffraction rings observed for boehmite annealed at the temperature 570 K or higher are broad (see Fig. 4c), and annealing at 680 K causes the complete disappearance of the boehmite diffraction pattern. Decomposition of boehmite at 680 K is accompanied by morphology changes in the film. In Fig. 5, a micrograph of boehmite annealed at 680 K for 24 h is shown. Areas between the pin-shaped crystallites have a granular structure, and some "pins" broke into smaller units. This process is even more pronounced at higher temperatures, as follows from Fig. 6, where boehmite film annealed at 875 K for 24 h is shown. The film exhibits granular structure with all "pins" divided into smaller parts.

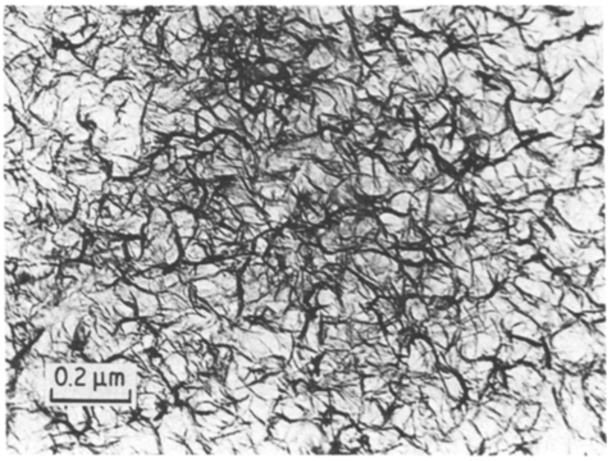


*Figure 2* Transmission electron micrograph of thin boehmite film prepared by the hydration of aluminium oxide film.

### 3.2. Transformation into $\gamma$-Al$_2$O$_3$

Slow transformation of thin aluminium oxide film into $\gamma$-Al$_2$O$_3$ occurs at 875 K, as can be concluded from electron diffractograms of the samples annealed at this temperature for 72 h, which contain several broad rings characteristic of $\gamma$-Al$_2$O$_3$. However, annealing at temperature of 975 K or higher is necessary to obtain well-crystallized $\gamma$-Al$_2$O$_3$, whose

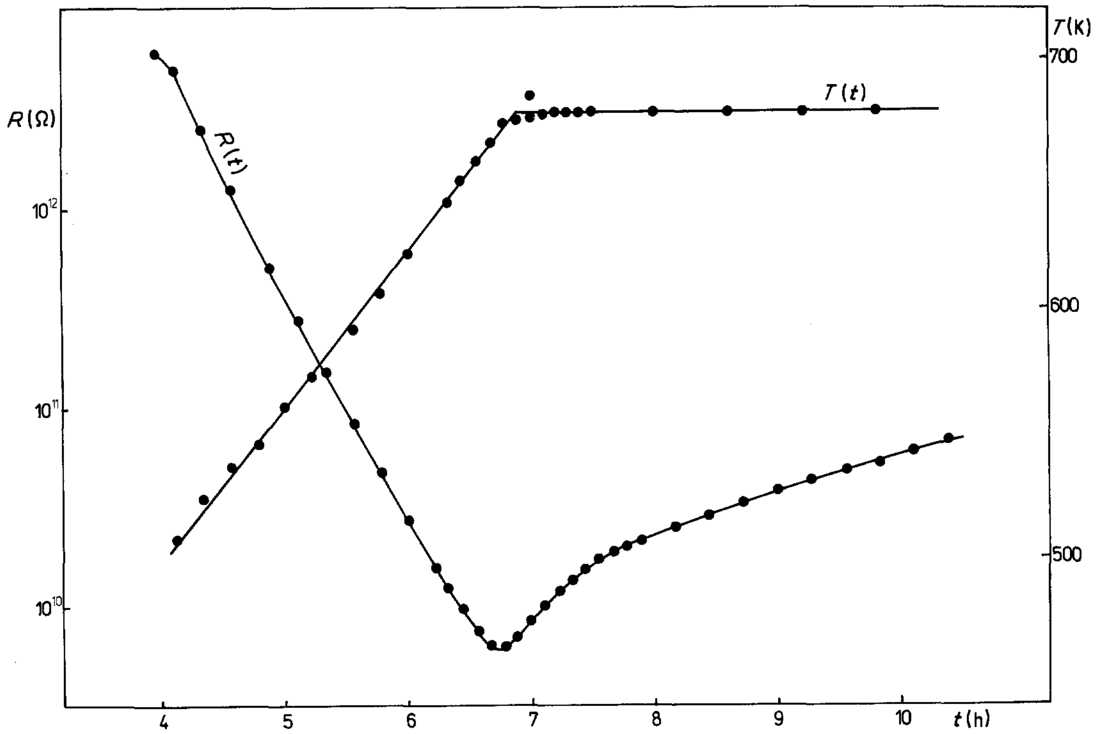
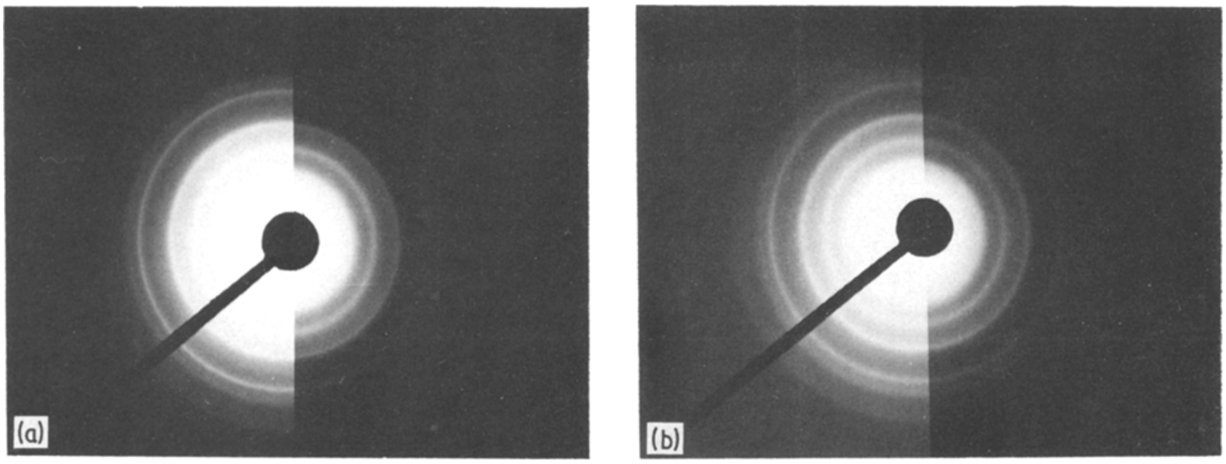


*Figure 3* Plot of electrical resistance changes against annealing time of the thin boehmite film. Temperature was increased linearly up to 680 K an then, when resistance of the film started to grow, temperature was stabilized at 680 K and annealing at this temperature was continued.



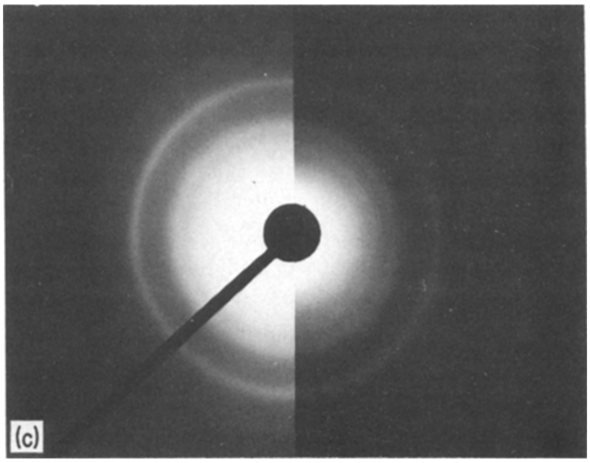


*Figure 4* Electron diffractograms of thin boehmite films (a) after hydration and drying at room temperature, (b) after annealing at 520 K for 24 h, (c) after annealing at 620 K for 24 h.

micrograph and electron diffractogram are shown in Fig. 7a and 7b, respectively.

When thin boehmite film dried at room temperature is heated directly to high temperature 1075 K, $\gamma$-$Al_2O_3$ presented in Fig. 8 is obtained. Morphology of this film is slightly different from that described previously (Fig. 7a), since now one can see many elongated crystallites, which have preserved their shape thanks to rapid heating to high temperature.

## 3.3. Transformation into $\delta$-$Al_2O_3$

Thin films of $\gamma$-$Al_2O_3$ described above, can be easily transformed into the $\delta$-form of aluminium oxide by annealing at temperatures of 1270 to 1320 K. A micrograph and an electron diffractogram of such $\delta$-$Al_2O_3$ film are shown in Fig. 9a and 9b, respectively. $\gamma$- into $\delta$-$Al_2O_3$ transformation is accompanied by growth of grains in the film with simultaneous "smoothing" of its surface (see Figs 7a, 8 and 9a).

Relatively "easy" transformation from $\gamma$-$Al_2O_3$ into $\delta$-$Al_2O_3$ has its origin in the similarity of the crystallographic structure of these phases. Both exhibit spinel structure and differ in distribution of $Al^{3+}$ cations in voids in the close packed, cubic lattice of $O^{2-}$ anions [12].

## 3.4. Transformation into $\alpha$-$Al_2O_3$

Annealing of aluminium oxide films at temperatures of 1475 K or higher enabled us to observe their transformation into corundum ($\alpha$-$Al_2O_3$). In Fig. 10 domains of $\alpha$-$Al_2O_3$ formed as the result of heating of the samples at 1475 K for 5 h are shown. Prolonged heating at this temperature causes the growth of corundum and eventually a film composed of small, randomly oriented $\alpha$-$Al_2O_3$ crystallites is formed, as it can be seen in the micrograph and electron

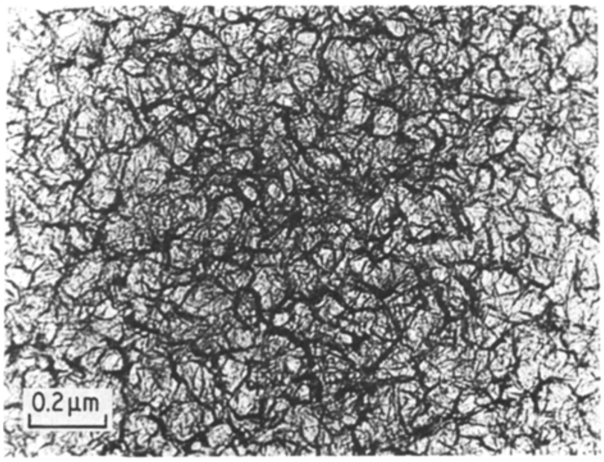


*Figure 5* Electron micrograph of thin boehmite film after annealing at 680 K for 24 h.

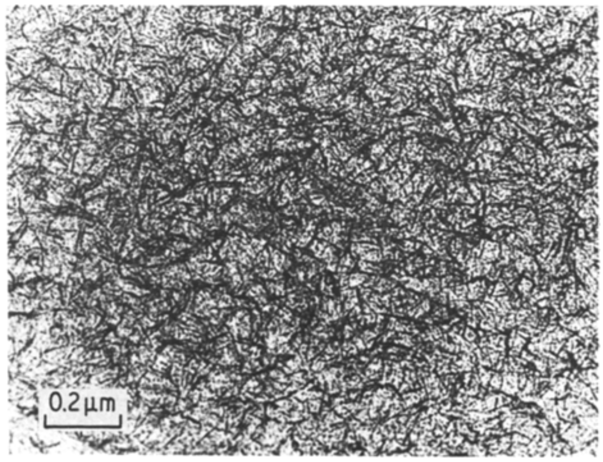


*Figure 6* Electron micrograph of thin boehmite film after additional annealing at 875 K for 72 h.

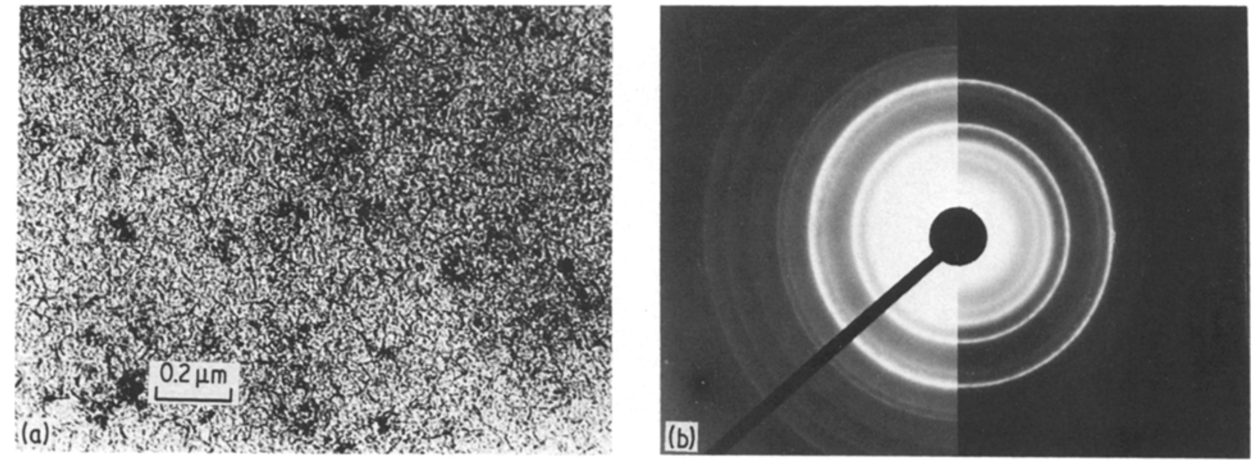


*Figure 7* (a) Electron micrograph and (b) electron diffractogram of thin $\gamma$-$Al_2O_3$ film obtained by annealing of boehmite at 975 K for 24 h. Interplanar distances corresponding to the diffraction rings in (b) agree well with those of $\gamma$-$Al_2O_3$ [10].

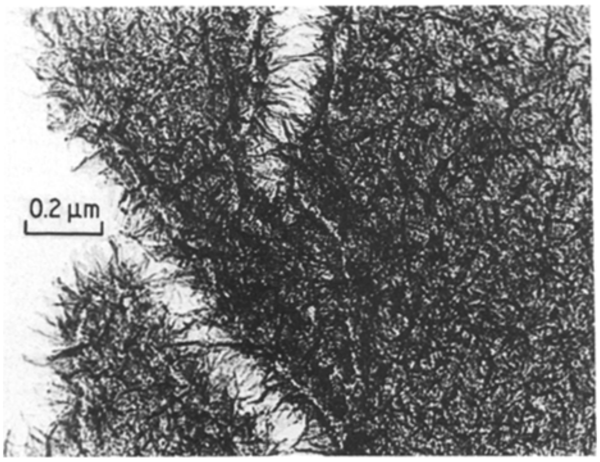


*Figure 8* Electron micrograph of thin $\gamma$-$Al_2O_3$ film prepared by rapid heating of boehmite to 1075 K and then annealing at this temperature for 24 h.

diffractogram of such film shown in Fig. 11a and b, respectively.

Annealing of $\delta$-$Al_2O_3$ films at higher temperature (1520 K) results in the formation of a two-phase system consisting of large grains of corundum embedded in the $\delta$-$Al_2O_3$ matrix (see Fig. 12). The fine crystalline $\delta$-$Al_2O_3$ seen in Fig. 12 is very stable, and does not transform into $\alpha$-$Al_2O_3$ even after additional, prolonged annealing at this temperature. Thin films containing large $\alpha$-$Al_2O_3$ crystals and free from $\delta$-$Al_2O_3$ inclusions could be produced only after prolonged annealing at a temperature of 1570 K. During such processing, severe losses in the film occur, probably due to the breaking of the film caused by growth of $\alpha$-$Al_2O_3$ in the form of elongated domains connected by narrow areas of $\delta$-$Al_2O_3$. An example of such a film, photographed in the intermediate stage of the phase transition, i.e. after 2.5 h annealing at 1570 K is shown in Fig. 13. Additional annealing of this film at 1570 K for 2.5 h caused complete transformation of $\delta$-$Al_2O_3$ into $\alpha$-$Al_2O_3$ and the resulting film is shown in Fig. 14.

Another similar $\alpha$-$Al_2O_3$ film with platinum particles evaporated on it is presented in Fig. 15. Deposited platinum "decorates" the substrate imaging grain boundaries in this way. We believe, that such a system can be used as a model for high temperature $Pt/\alpha$-$Al_2O_3$ catalysts.

## 4. Conclusions

(a) Heating of boehmite in the form of thin film to above 570 K results in slow decomposition of its crystal lattice. At the temperature of 670 K dehydration of

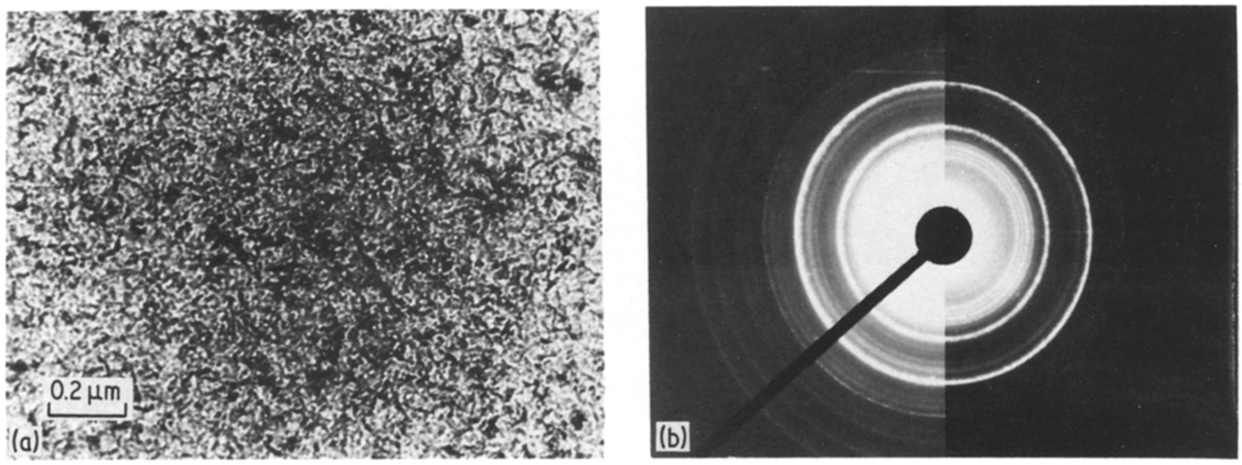


*Figure 9* (a) Electron micrograph and (b) electron diffractogram of thin $\delta$-$Al_2O_3$ film prepared by annealing of $\gamma$-$Al_2O_3$ at 1300 K for 24 h. Interplanar distances corresponding to the diffraction rings in (b) agree well with those of $\delta$-$Al_2O_3$ [11].

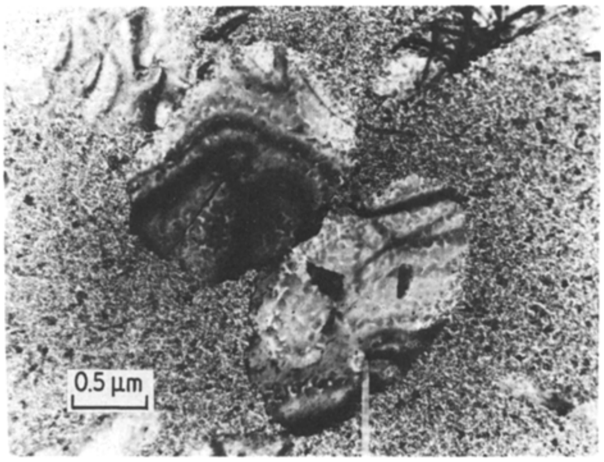


*Figure 10* Electron micrograph showing $\delta$-$Al_2O_3$ to $\alpha$-$Al_2O_3$ transformation. The film was annealed at 1475 K for 5 h.

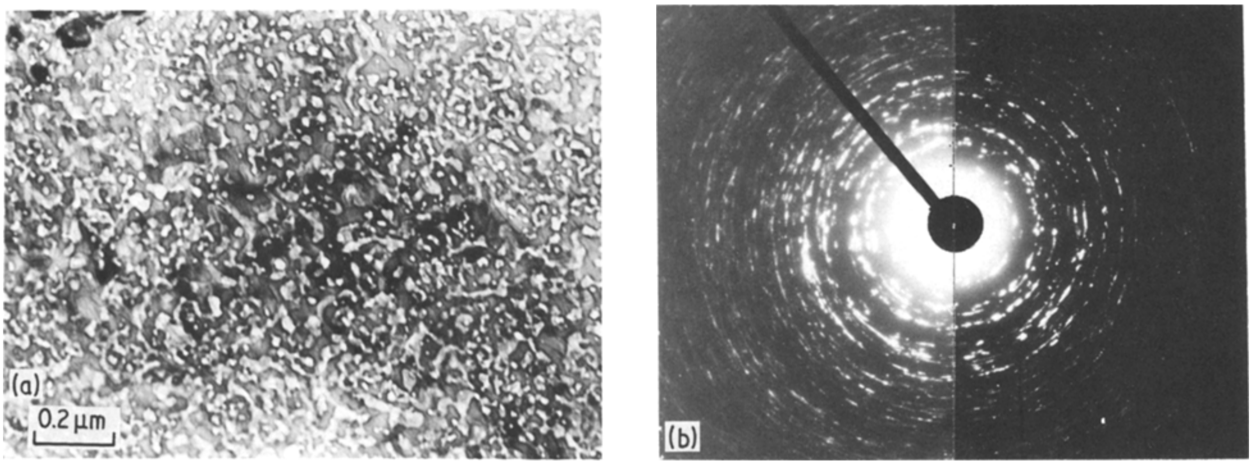


*Figure 11* (a) Electron micrograph and (b) electron diffraction of fine crystalline $\alpha$-$Al_2O_3$ film obtained by annealing of the film shown in Fig. 10 at 1475 K for 3 h. The quasi-continuous rings in (b) correspond to interplanar distances of $\alpha$-$Al_2O_3$ [13].

boehmite begins. This process is accompanied by structure changes in the film – large pin-shaped crystallites divide into smaller ones, and areas between them exhibit granular structure.

(b) Thin boehmite films can be transformed into $\gamma$-$Al_2O_3$ by heating in the temperature range from 875 to 1100 K. With increasing temperature the ordering of the $\gamma$-$Al_2O_3$ and the size of crystallites increase.

(c) At the annealing temperature above 1300 K, $\gamma$-phase transforms into $\delta$-$Al_2O_3$, without drastic change in the film appearance (only some increase in the size of the crystallites occurs).

(d) Thermal treatment at temperatures 1475 to 1570 K causes nucleation and growth of corundum ($\alpha$-$Al_2O_3$). Annealing at 1475 K results in the formation of fine crystalline corundum films. Increasing the temperature to 1520 to 1570 K however, leads to the

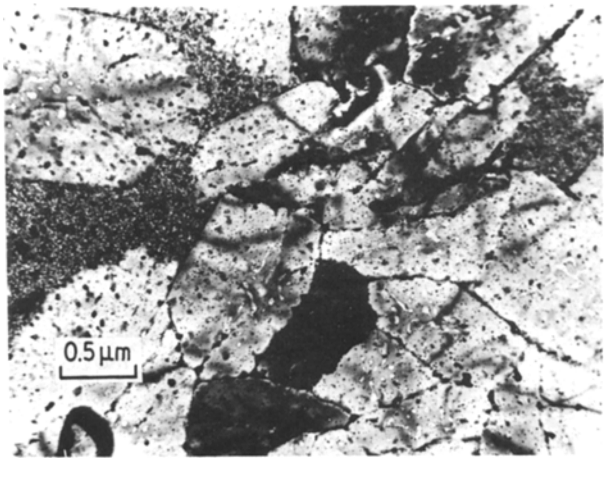


*Figure 12* Electron micrograph of the $\alpha$-$Al_2O_3$ film obtained by annealing at 1520 K for 5 h. In the picture areas of fine crystalline $\delta$-$Al_2O_3$ can be seen.

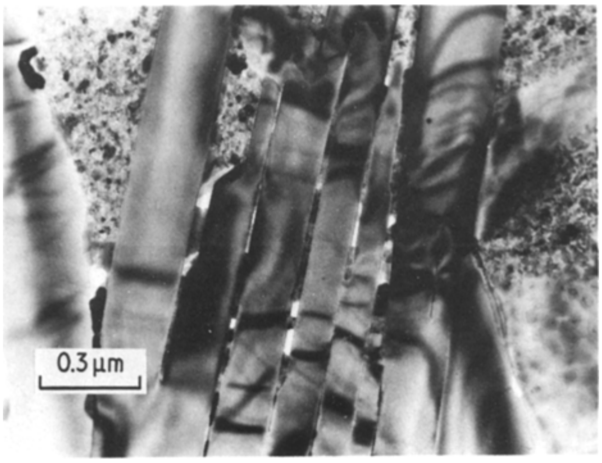


*Figure 13* Electron micrograph showing domains of single crystalline $\alpha$-$Al_2O_3$ formed during annealing at 1570 K for 2.5 h.

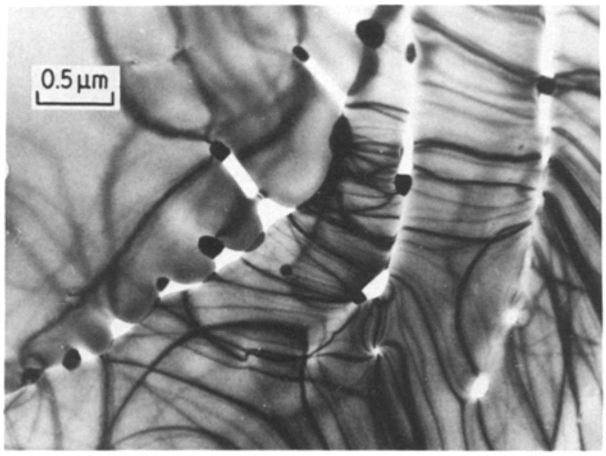


*Figure 14* Electron micrograph of thin $\alpha$-$Al_2O_3$ film after completion of $\delta$-$Al_2O_3$ to $\alpha$-$Al_2O_3$ transformation. The film was annealed at 1575 K for 4 h.

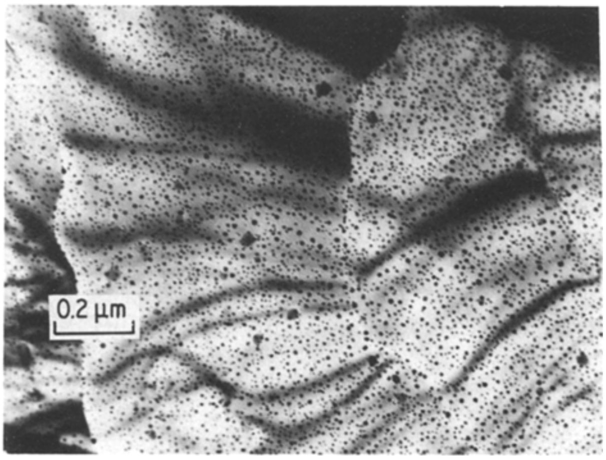


*Figure 15* Electron micrograph of thin $\alpha$-$Al_2O_3$ film with evaporated platinum particles – a model of the high temperature Pt/$\alpha$-$Al_2O_3$ catalyst.

growth of corundum in the form of large (few micrometres) grains coexisting with areas consisting of $\delta$-$Al_2O_3$. It is possible to obtain pieces of flat, pure corundum film supported on the microscope grid in such conditions, but most of the film is lost probably due to its breakage.

(e) The present method of preparation of various aluminas in the form of thin films seems to be useful in studies of model supported catalysts, where the support is in the form of thin films.

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