

Thermal stability of aluminium oxides prepared from gel

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This study deals with the thermal stability of the forms of aluminium oxide prepared by the sol-gel technique. The aluminium oxide gel was prepared using techniques described by Yoldas [1, 2]. Aluminium secondary butoxide ($\text{Al}(\text{OC}_4\text{H}_9)_3$), supplied by Aldrich Chemical Co. (97% pure) was used as the organometallic precursor.

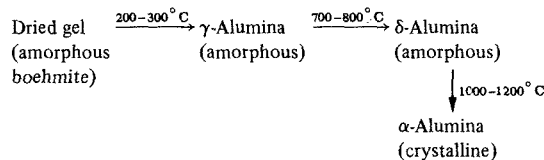
In order to prepare the gel, 0.041 moles of aluminium secondary butoxide were slowly introduced into 4.06 moles of vigorously stirred distilled water maintained at 85°C . Stirring was continued at 85 to 95°C for 30 min, after which 0.24 ml of concentrated hydrochloric acid was added as a peptizing agent while the slurry was continuously stirred. The slurry turned transparent 1 h after the addition of peptizing agent. The stirring at 85 to 95°C was continued for 3 h more after which the viscous transparent sol was poured into petri-dishes and allowed to gel and subsequently dried at room temperature for 48 h and at 60°C for 120 h.

The gels dried at 60°C for 120 h were subsequently heat treated at 120, 200, 300, 400, 500, 600, 700, 800, 900, 1000 and 1200°C . The samples were air-cooled after the heat treatment and analysed using X-ray diffraction. Figs. 1a and b show the diffraction patterns of the samples heat treated at various temperatures. It was noted that the samples heat treated at 120 and 200°C showed a diffused diffraction pattern with reflections corresponding to those of boehmite [3]. From the broadening of the intensity peaks the average crystallite size was estimated to be around 5 nm.

The sample heat treated at 300°C showed an amorphous structure with reduced presence of boehmite and increased presence of $\gamma\text{-Al}_2\text{O}_3^*$ [3]. The samples heat treated between 400 and 700°C showed the presence of only $\gamma\text{-Al}_2\text{O}_3$. The structure of the material remained highly amor-

phous with crystallite size increasing from about 4 nm at 400°C to about 11 nm at 700°C . The $\gamma\text{-Al}_2\text{O}_3$ changes to $\delta\text{-Al}_2\text{O}_3$ [4] between 700 to 800°C and its presence is indicated in the samples heat treated at 800, 900 and 1000°C . The X-ray diffraction pattern remained highly diffused. The X-ray diffraction patterns of the samples heat treated up to 900°C were fairly stable and did not change significantly even after heat treatment for 24 h. The sample heat treated at 1200°C showed presence of only α -alumina. In this case, the diffraction pattern was extremely sharp, indicating the presence of crystalline material.

From the aforementioned studies, it was inferred that the thermally activated structural changes in alumina gel can be represented as:



The dried gel prepared in this study transformed to amorphous γ -alumina between 200 to 300°C . This temperature range is lower than that reported for the transformation of crystalline boehmite to γ -alumina [5, 6]. Also, the amorphous γ -alumina to amorphous δ -alumina transformation takes place at temperatures lower than those reported by the earlier authors. Lower transformation temperatures may result from the lower activation energy required by the material because of its highly activated state.

Yoldas [7] prepared a form of alumina using a method very similar to that used in the present study. The material was found to give strong intensity peaks at 0.139, 0.199 and 0.240 nm when examined by X-ray diffraction. These reflections agree with those observed in the present study (0.140, 0.198 and 0.240). However, these

* γ -Alumina is referred to a group of transition aluminas.

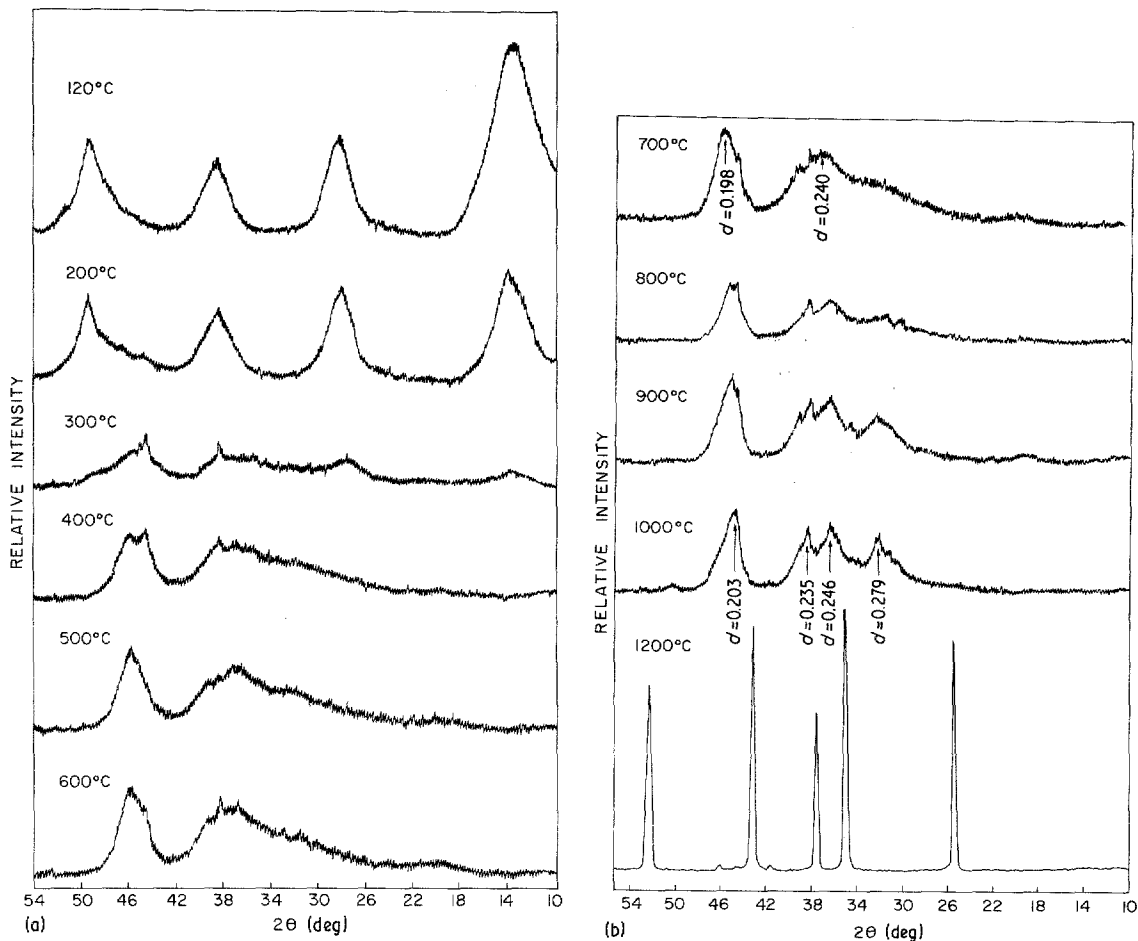


Figure 1 (a) X-ray diffraction patterns of aluminium oxide gels heat treated at 120, 200, 300, 400, 500 and 600°C for 1 h. The samples heat treated below 300°C showed an amorphous boehmite structure while those heat treated above 300°C showed an amorphous γ -alumina structure (CuK α radiation with nickel filter). (b) X-ray diffraction patterns of aluminium oxide gels heat treated at 700, 800, 900, 1000 and 1200°C for 1 h. The samples heat treated at 800 to 1000°C showed amorphous δ -alumina structure, while that heat treated at 1200°C showed the presence of crystalline α -alumina (CuK α radiation with nickel filter).

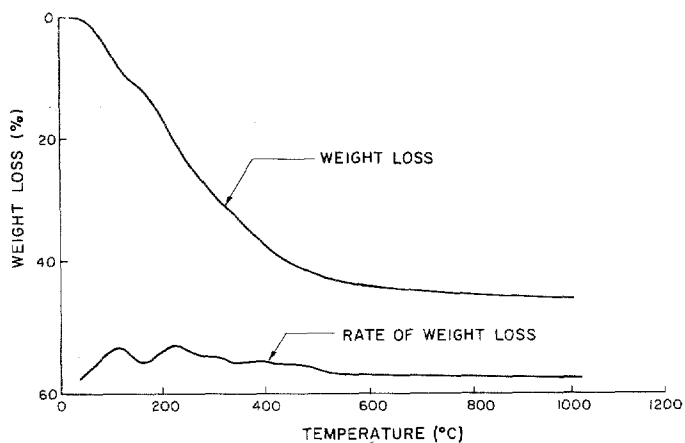


Figure 2 Weight loss on heat alumina gel sample (heating rate 10°C min⁻¹).

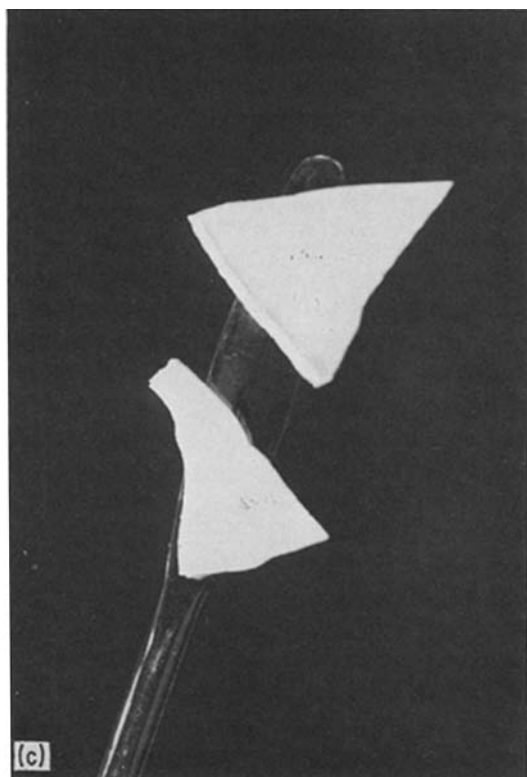
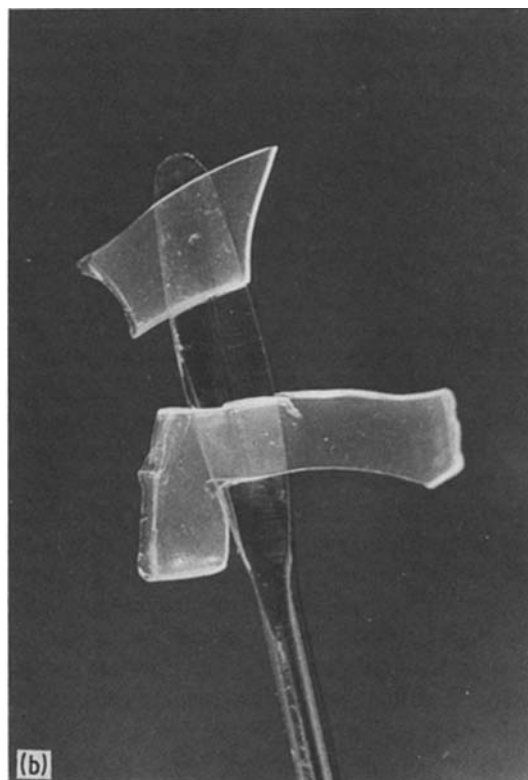
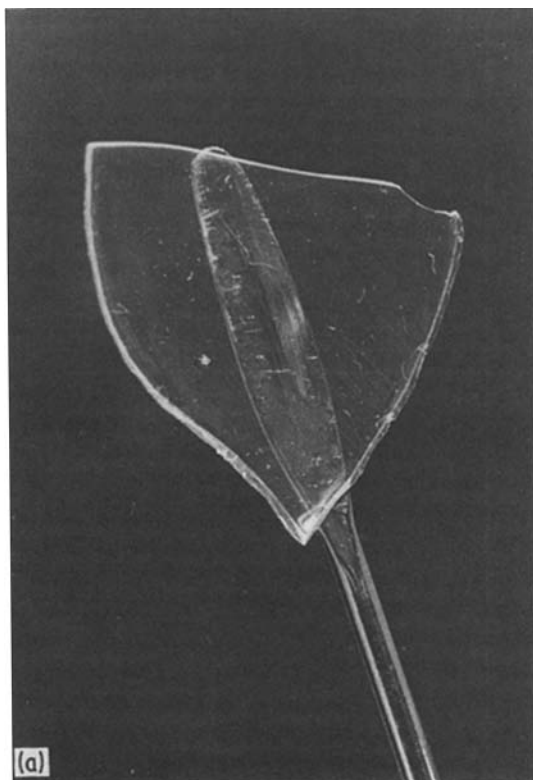


Figure 3 Alumina gel heat treated at (a) 120°C, (b) 500°C and (c) 1200°C.

reflections correspond to γ -alumina and not δ -alumina as asserted by Yoldas [7]. The reflections corresponding to δ -alumina (0.140, 0.201, 0.275, 0.230 and 0.245 nm) were observed in the samples heat treated between 700 and 1000°C. As can be seen from Fig. 1, these reflections are very different from those observed for samples heated between 400 to 700°C.

Fig. 2 shows the weight loss of dried gel sample (dried at 60°C). It is seen from this plot that the rate of loss of water is fairly uniform over the temperature range examined. Two separate regions in this plot are easily distinguishable. In the first stage, most of the unbonded water is lost by the time the sample reaches 150°C. This amounts to 10 to 12% of the original weight of the sample. In the second stage, from 150 to 500°C, the sample continuously loses water, presumably bonded water, at a uniform rate. The total loss amounted to about 35% of the original weight of the sample. The rate of water loss is different in the samples examined in the present study than

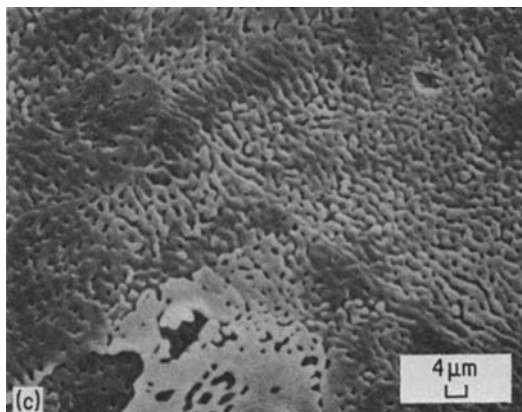
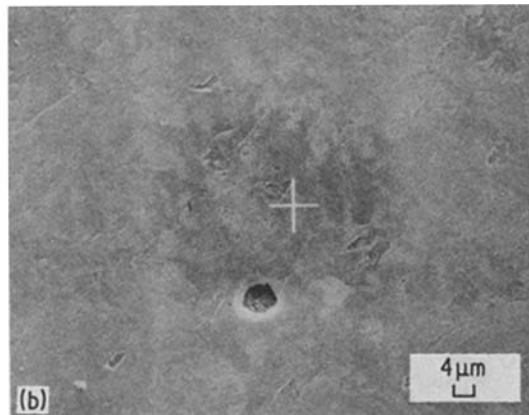
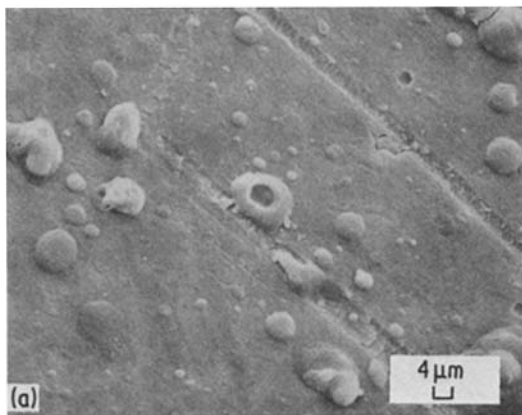


Figure 4 SEM micrographs of alumina gels heat treated at (a) 120°C, (b) 500°C and (c) 1200°C.

morphology of the material does not change significantly on heat treatment up to 500°C. It probably consists of gel containing varying amounts of water. The microstructure of the sample heat treated at 1200°C is very different from the samples heat treated at lower temperatures. This sample shows 0.3 to 0.4 μm thick strands of material separated by pores of smaller dimensions. The strand-like structure, presumably, results from the chain-structure of the polymer precursor.

those reported by Yoldas [1]. In the previous study [1] the rate of water loss was maximum at about 450°C whereas in the present case, rate of water loss was maximum at 120 and 250°C, decreasing steadily up to 550°C.

The visual appearance of the materials also changed with the heat treatment. The material remained transparent up to 500°C. Beyond this temperature the material steadily turned milky and finally white with fine china-like finish. Figs. 3a to c illustrate this effect. The samples of heat treated materials were also examined using scanning electron microscopy (SEM). Figs. 4a to c show the micrographs of the samples heat treated at 120, 500 and 1200°C. It is noted that the

References

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