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Preparation of pure boehmite, α–Al_2O_3 and their mixtures by hydrothermal oxidation of aluminium metal

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Hydrothermal oxidation is a well known route for the preparation of fine oxide ceramic powders such as Al_2O_3, ZrO_2, HfO_2, Cr_2O_3, etc., starting from their respective metal powders by their reactions with superheated or supercritical water at relatively low temperatures and pressures [1–3]. The method has the advantage that even very fine (submicron) oxide powders can be obtained in a single step at relatively low temperatures (300–700 °C).

Since the metal powders available in pure form are used, the product powders in turn could be obtained in pure form free of any other metallic contamination. The reaction is typically carried out by taking a small quantity of metal powder and water in sealed gold or platinum capsules which are in turn placed inside a thick walled hydrothermal reaction vessel. The sealed capsules are heated and pressurized externally in the reaction vessel by gas or supercritical water to pressures higher than that which would be generated inside the capsules. This process, though novel, for obtaining new materials, is also quite costly and is unsuitable to synthesize large quantities of materials.

To overcome this difficulty, we have carried out our experiments in an open container system so that the pressure is self-generated by the combination of the pressure of superheated or supercritical water and the pressure of hydrogen gas generated by the reaction of metal (e.g. Al) with water as per the equation given below.

$$2Al + 4H_2O \rightarrow 2AlOOH + 3H_2$$

The final pressure in the reactor vessel is a function of the percentage of volume of fill of the autoclave, the temperature of the reaction and the amount of reactants present. Use of metal powders leads to extremely fast reactions due to their large surface area and generates very high impulsive pressure due to the high rate of hydrogen gas evolution at the reaction temperatures. However, in the case of incomplete reactions, it is difficult to separate the unreacted metal powders from the products.

A novel patented and simple approach [4, 5] to counter the above difficulties and to slow down the reaction kinetics for conversion of aluminium to boehmite and alumina to controllable and desired levels is herein described. In this new approach, aluminium metal was taken in the form of rectangular metal pieces of typical dimensions 25 mm × 25 mm × 12 mm, weighing approximately 10 g. The pieces were cut from a commercially available 99% pure aluminium rod stock. The metal piece along with 25 ml water was placed in the hydrothermal reactor (autoclave). The total volume occupied in this case corresponds to 30% of the volume of fill of the autoclave. The autoclave was heated by an external heater and the temperature of the autoclave was measured by inserting a chromel–alumel thermocouple in its body which is located very close to the inside cavity of the reactor. The pressure inside the reactor was measured by a Bourdon gauge in direct contact with the autoclave through a hole in the lid of the autoclave. The autoclave was heated at a rate of 2–2.5 °C min^{-1} to a final temperature in the range of 300–550 °C and was soaked at temperature for 3 h in all cases. Pressures in the range of 10–120 MPa were generated in the autoclave depending upon the temperature and per cent volume fill of the autoclave. After the reaction, the autoclave was cooled to room temperature, and its residual pressure was released. The product powder was removed, washed, deagglomerated and dried at 110 °C to get a free flowing white powder. The same procedure was repeated for performing the reaction at 60% volume of fill of the autoclave by increasing the volume of water to 50 ml for the same weight of aluminium block (10 g).

The various product phases obtained under different experimental conditions were identified using a X-ray diffraction (XRD) technique with CuK radiation in a Philips PM-9002 X-Ray diffractometer (M/S Philips, Holland). The particle sizes and particle size distribution of the product powders were obtained on a sedigraph V-5100 (M/S Micromeritics, USA). The product powder morphologies were observed in a Jeol JSM-35 (M/S Jeol, Japan) scanning electron microscope (SEM).

The XRD spectra of products obtained for 30% and 60% volume of fill are presented in Figs 1 and 2, respectively. The different phases obtained are tabulated in Table I. The particle size and particle size distribution of some products are presented in Figs 3 and 4 for 30% and 60% volume of fill reactions, respectively. SEM pictures of some

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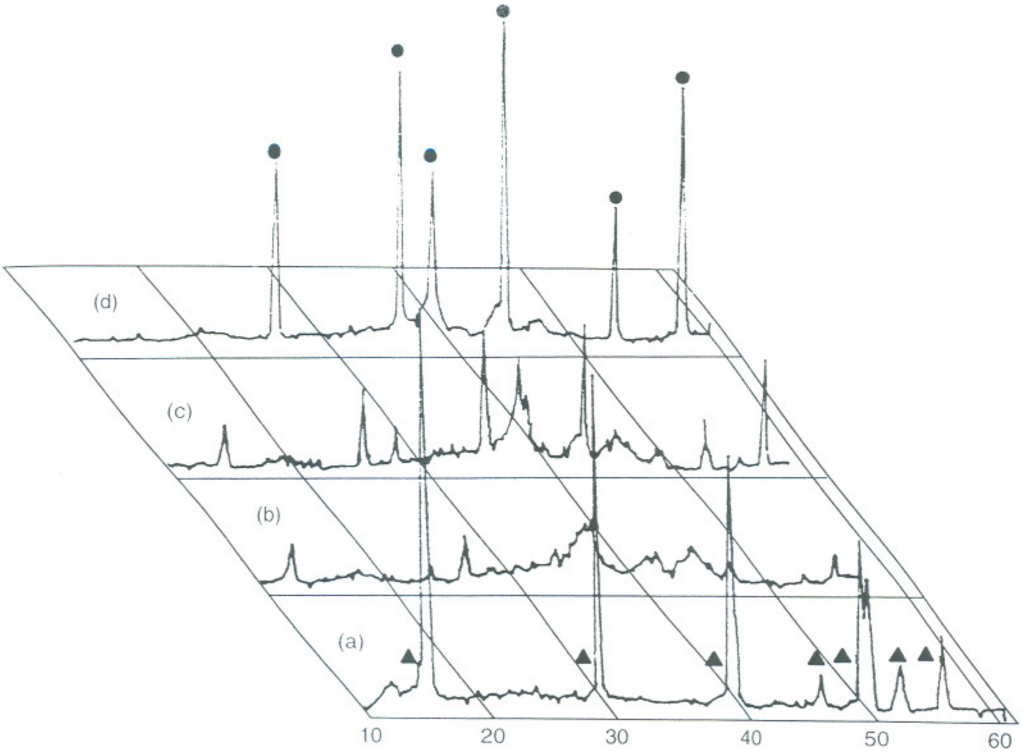
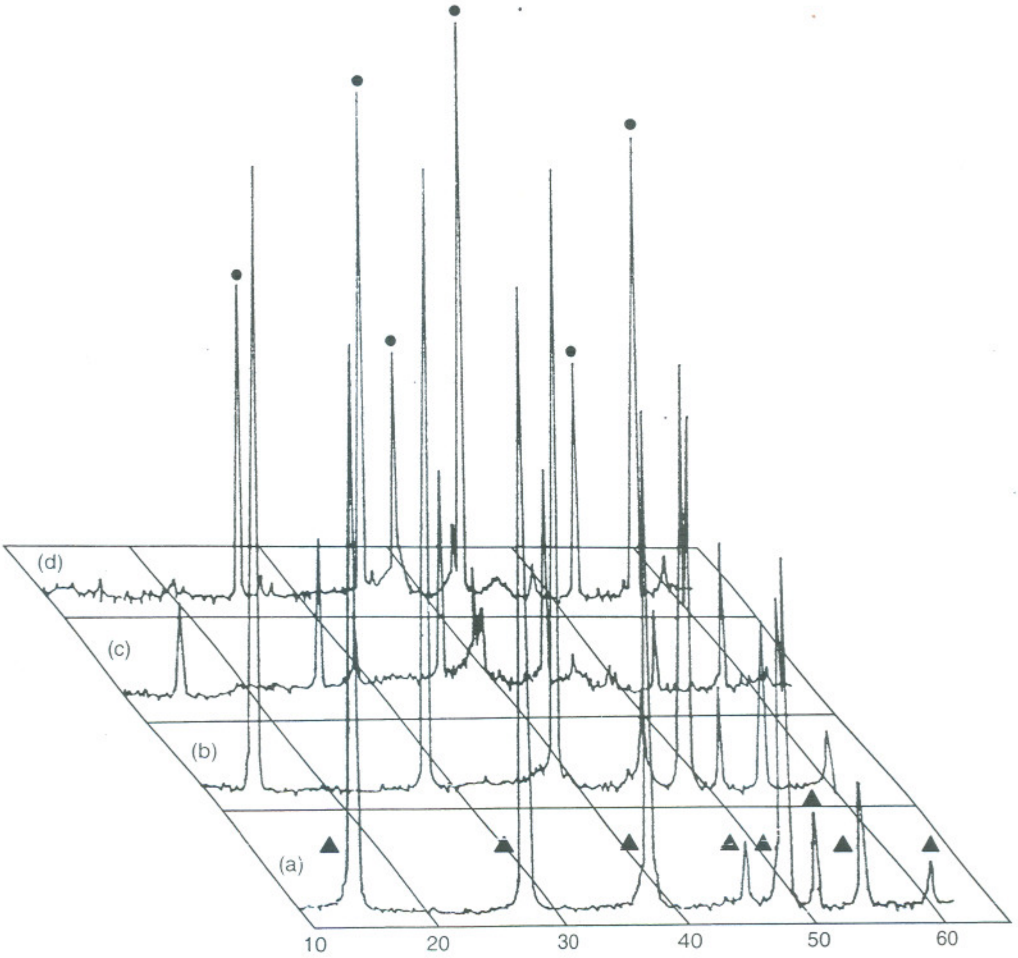


Figure 1 XRD patterns of the boehmite (▲) and α-Al_2O_3 (●) products obtained from the hydrothermal reaction of aluminium metal with 30% volume of fill of the autoclave at (a) 300 °C, (b) 350 °C, (c) 425 °C and (d) 550 °C.



gure 2 XRD patterns of the boehmite (▲) and α-Al_2O_3 (●) products obtained from the hydrothermal reaction of aluminium metal with 60% lume of fill of the autoclave at (a) 300 °C, (b) 350 °C, (c) 425 °C and (d) 550 °C.

TABLE I Product phases (major, minor) obtained at different temperatures and different percentage fills of autoclave

Temperature (°C)	Product phases present			
	30% volume fill		60% volume fill	
	Major	Minor	Major	Minor
300	AlOOH		AlOOH	
350	AlOOH	α-Al_2O_3	AlOOH	
375	AlOOH	α-Al_2O_3	AlOOH	
400	α-Al_2O_3	AlOOH	AlOOH	
425	α-Al_2O_3	AlOOH	AlOOH	α-Al_2O_3
450	α-Al_2O_3	AlOOH	α-Al_2O_3	AlOOH
550	α-Al_2O_3		α-Al_2O_3	AlOOH

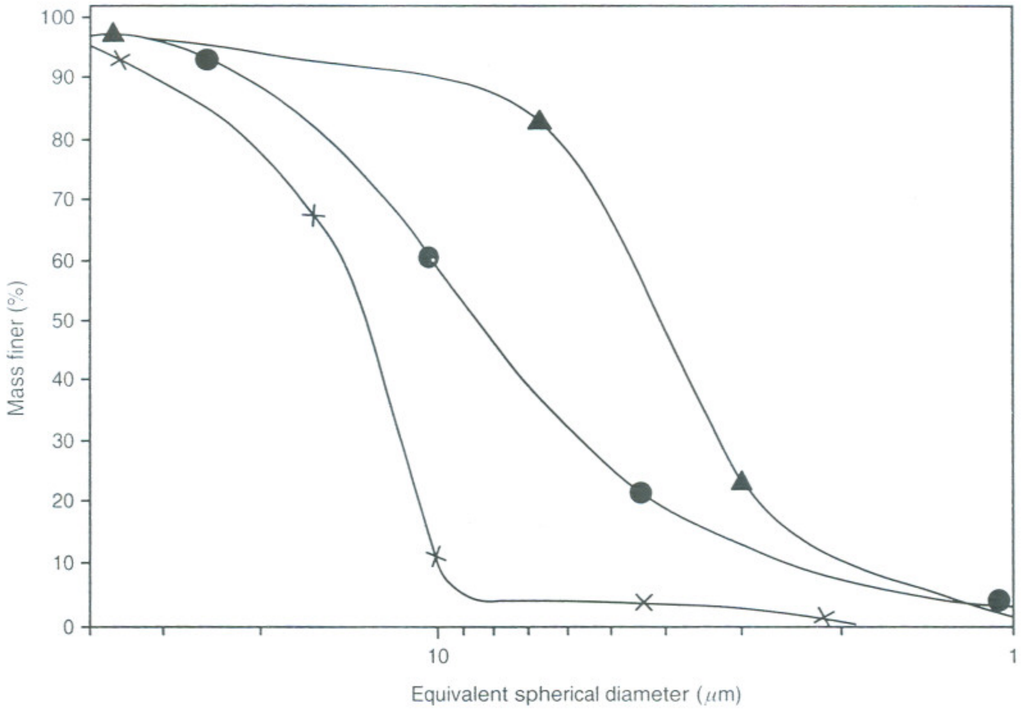


Figure 3 Cumulative particle size distribution graphs of products obtained from the hydrothermal reaction of aluminium metal with 30% volume of fill of the autoclave at 300 °C (×), 425 °C (▲) and 550 °C (●).

products are reproduced in Fig. 5. From Table I and Figs 1 and 2, it is evident that if per cent volume of fill of autoclave is more (60%), the decomposition to alumina is shifted to higher temperatures. Thus while the XRD peaks for Al_2O_3 were first seen at 350 °C for 30% volume fill of the autoclave, they were seen at 425 °C and above for 60% volume of fill. Further, it is noted that while the dehydration reaction of boehmite is complete at 550 °C in the case of 30% volume of fill of autoclave, minor quantities of boehmite are still present at 550 °C for 60% fill. The product, removed carefully from the autoclave, consisted of the unreacted aluminium block at the centre surrounded by white product layers on all sides. From this it could be inferred that water reacts with aluminium at the surface and penetrates layer by layer towards the core from the exterior. Once a layer is separated, a fresh surface is exposed for further reaction with superheated or supercritical water. The product is thus formed in successive layers. A typical layer-like structure of the product with the unreacted core material is shown in Fig. 6. Thus, in this case, contamination from unreacted raw materials was avoided in contrast to the cases where the raw materials are used in the form of fine powders or metal turnings [1–3].

Based on the XRD results, the following overall reaction mechanisms could be assigned for the formation of boehmite and α-alumina.

$$2Al + 4H_2O \xrightarrow{300\,^{\circ}C} 2AlOOH + 3H_2$$

$$2AlOOH \xrightarrow{350-425\,^{\circ}C} Al_2O_3 + H_2O$$

The median diameter (d_{50}), as calculated from the particle size distribution graphs (Fig. 3) of the products at 300, 425 and at 550 °C for 30% volume fill of the autoclave, was found to be 13.6, 4.4 and 8.8 μm, respectively. The higher d_{50} value at 300 °C indicates the agglomerated nature of the boehmite products. The products at 425 °C, which consist of alumina and boehmite, have a lower d_{50} value which

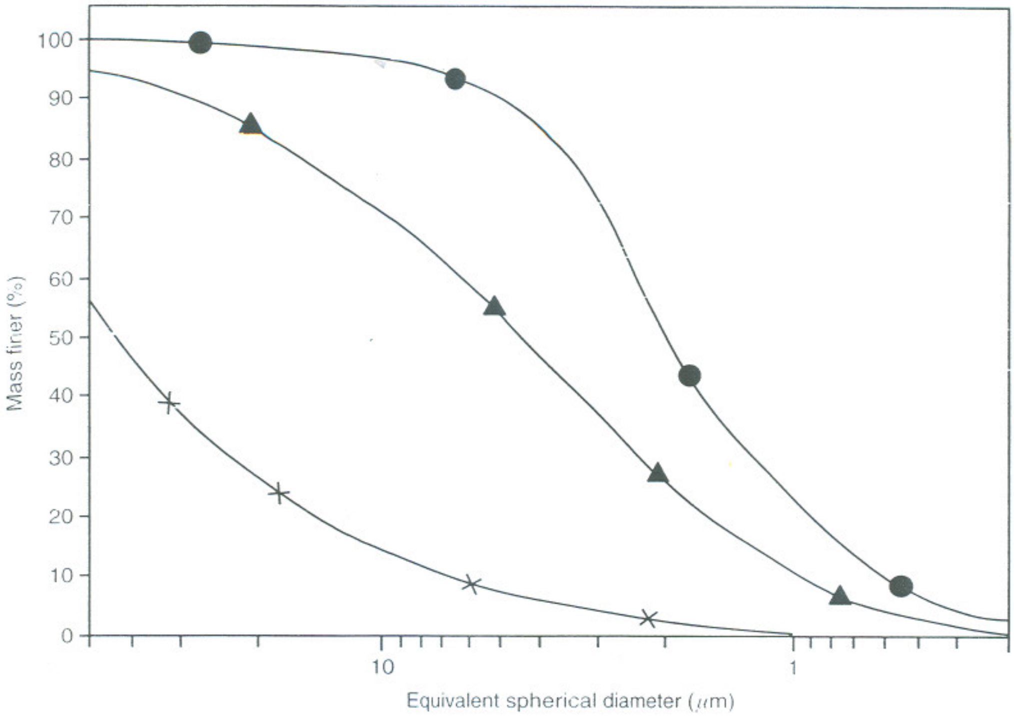


Figure 4 Cumulative particle size distribution graphs of products obtained from the hydrothermal reaction of aluminium metal with 60% volume of fill of the autoclave at 300 °C (×), 425 °C (▲) and 550 °C (●).

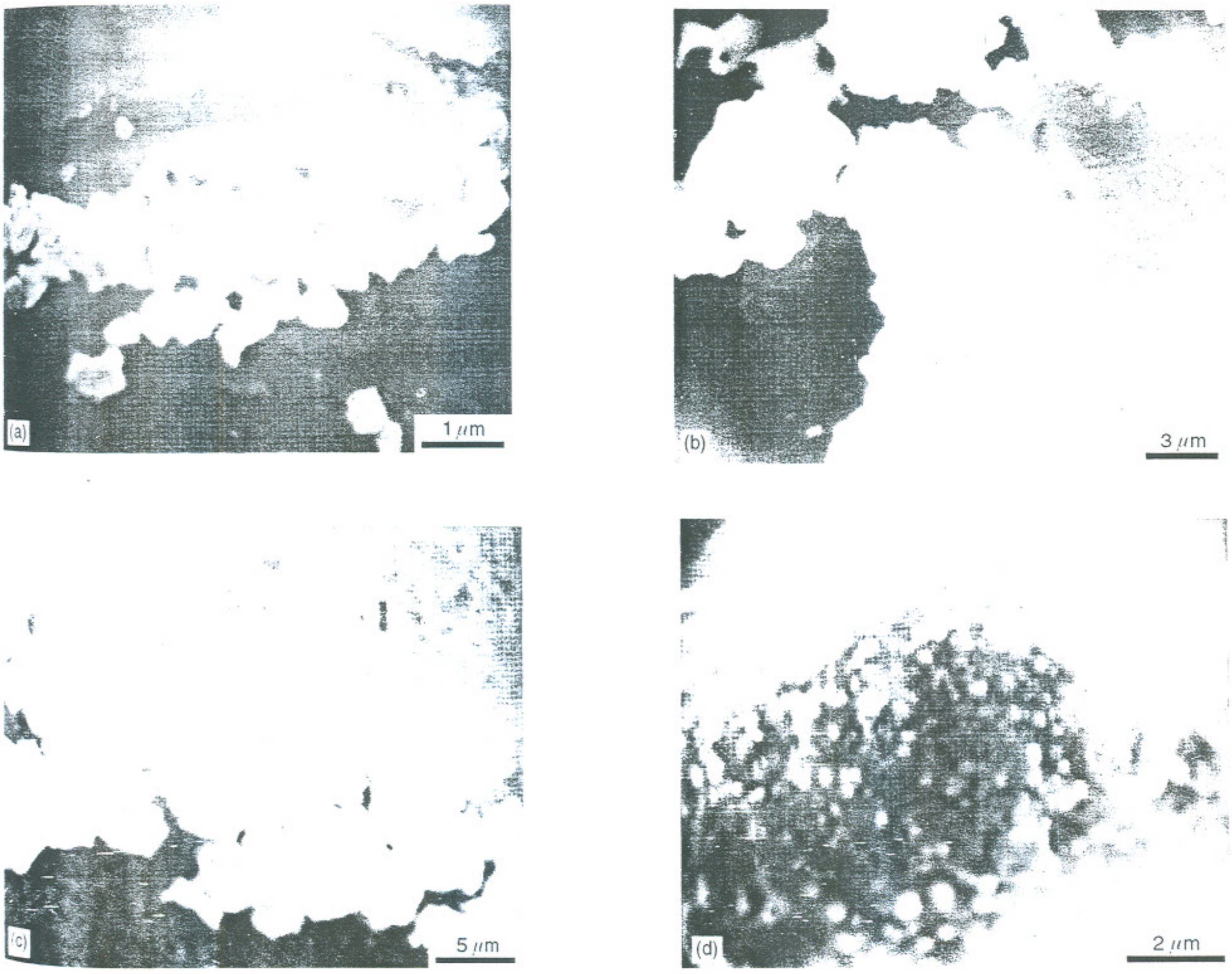


Figure 5 Typical SEM pictures of the products obtained from the hydrothermal reaction of aluminium metal with 30% volume of fill of the autoclave at (a) 300 °C, (b) 350 °C, (c) 425 °C and (d) 550 °C.

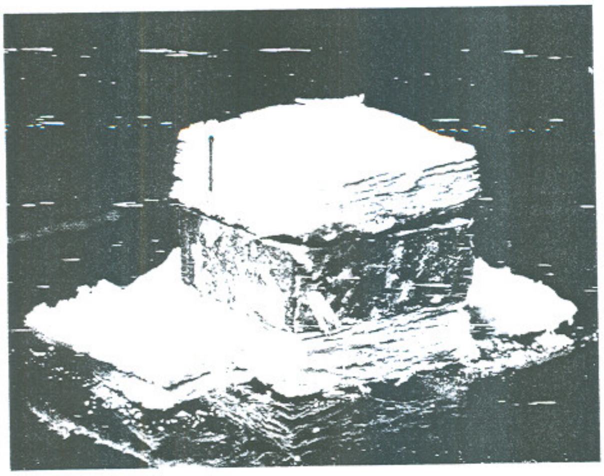


Figure 6 Typical layer-like structure of the boehmite product with the unreacted core material produced by hydrothermal reaction of the aluminium metal with water at 300 °C.

indicates that the dehydration of agglomerated boehmite produces smaller alumina particles. However, the increase in d_{50} value at 550 °C could be attributed to the coarsening of the alumina at high temperature.

The median diameter (d_{50}), as calculated from the particle size distribution graph (Fig. 4) of the products at 300, 425 and 550 °C for 60% volume of fill, was found to be 42, 4.2 and 2 μm, respectively. The d_{50} value decreases from 300 to 550 °C for the products unlike in the case of 30% volume of fill in which d_{50} increases from 425 to 550 °C. The continuous decrease in the size of the product indicates the continuous dehydration of the agglomerated boehmite which was still incomplete even at 550 °C (as seen from the XRD graph, Fig. 2). It is concluded that completion of the dehydration of the boehmite to alumina shifts to higher temperatures if the water used for the initial reaction is more. A higher water to aluminium ratio causes preferential stabilization of the boehmite phase vis-a-vis alumina formation.

The SEM pictures presented in Fig. 5 show the distinct morphology of the boehmite (a), boehmite + α-Al_2O_3 ((b) and (c)) and α-Al_2O_3 (d) phases. It can be seen that near spherical shapes of α-Al_2O_3 powder phases are obtained at 550 °C with 30% volume of fill experiments.

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