LETTER

Hydrothermal synthesis of boehmite and α-alumina from Bayer's alumina trihydrate

P. K. Panda · V. A. Jaleel · S. Usha Devi

α-Alumina (Al_2O_3) is a ceramic material used widely due to its versatile properties such as high temperature stability, high strength at high temperature, high hardness with higher wear resistance, good thermal shock resistance etc [1, 2]. In addition, it is available abundantly at relatively low cost, therefore, is a popular material for fabrication of structural components, electronic substrates etc. α-Al_2O_3 is generally prepared by Bayer's process [3], pyrolysis of suitable salts [4], freeze drying [5], plasma evaporation process [6], sol–gel processing [7–9], molten salt [10], hydrothermal [11–14] and solvothermal [15] techniques. Inoue et al. [16] obtained microcrystalline α-Al_2O_3 by glycol-thermal treatment of gibbsite under nitrogen blanket. Generally, the powder characteristics such as purity, particle size distribution, grain morphology, surface area etc. are influenced by the processing methods used for its preparation. For example, powders prepared by hydrothermal route are known to generate pure and crystalline oxide powders with relatively narrow size distribution. Hydrothermal reactions are carried out at low temperatures and the precursors in the form of metal powders [17] or metal salt solutions [18, 19] are used. The characteristics of the powders influence the sintering and grain growth process, thereby, influence the properties of the final products [20]. For examples, powders prepared by hydrothermal route are excellent for sintering to near theoretical density at relatively low temperature because of their fine and narrow size distribution,

highly crystalline nature, high reactivity due to their synthesis at low temperature. In our earlier studies, α-Al_2O_3 and boehmite were synthesised from Al metal blocks [21, 22]. Other groups have also been studied [23–27] mainly by using aluminium as the precursor. It is known that aluminium metal is the final product of Bayer's process, which uses cheap bauxite as the precursor. Alumina tri hydrate (ATH) is an intermediate product of the Bayer's process, which is much cheaper than aluminium metal. Therefore, in our present study, an attempt has been made to prepare α-Al_2O_3 from the cheap alumina tri-hydrate (ATH) by hydrothermal synthesis.

In this study, Bayer's alumina trihydrate (supplied by M/s. National Aluminium Company, Bhubaneswar, India) with median particle size distribution (d_{50}) of 80–100 μm and chemical composition: Al_2O_3-64.5%, Na_2O-0.3%, H_2O-35.2% was used as the chemical precursor. The coarse grained ATH was mechanically agitated for 20 min in a high speed blender, washed repeatedly and then subjected to attrition milling for 6 h using an attritor (M/s.Union Process,USA). The slurry was repeatedly washed with deionised water till neutral pH was obtained to remove adsorbed soda. The slurry was finally filtered and dried at 110 °C. The dried ATH powder was used as the precursor for the hydrothermal reactions. The particle size distribution of the dried alumina trihydrate is presented in Fig. 1. The median particle size distribution (d_{50}) of this processed powder was found to be nearly 2 μm.

Hydrothermal reactions were carried out in an indigenously built autoclave (EN-24 steel heat treated to 45 RC, internal volume 100 mL). The chemical precursors are kept in a sintered alumina container. The top half of the reactor is then tightly closed by

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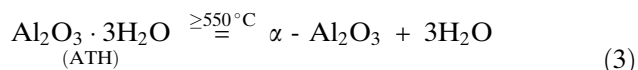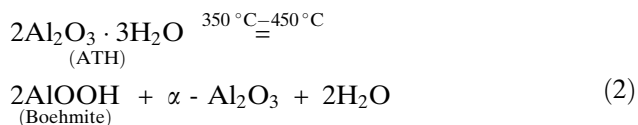e-mail: pkpanda@css.nal.res.in

suitable locking arrangements using a stainless steel gasket and bolts. The internal reaction zone is connected to a Bourden pressure gauge for measurement of hydrothermal pressure. The reactor is placed on a heater and its sides were covered with a suitable insulated jacket for prevention of heat loss. Temperature of the autoclave was monitored by a chromel–alumel thermocouple placed very close to the internal reaction zone. The hydrothermal pressure built up in the reactor was due to super heated steam generated in-situ by varying the water content inside the autoclave i.e. % volume fill of the autoclave.

From our earlier studies, boehmite and α-Al$_2$O$_3$ are the phases found at 400 °C and 550 °C respectively. It was thought that the ATH, which contains soda impurities could be effectively leached out by following two hydrothermal reactions successively i.e. one reaction at 400 °C (to convert the ATH to boehmite) followed by a second reaction at 550 °C. The first reaction leading to the formation of boehmite is believed to discard the most of the soda impurities. The second reaction was aimed at formation of the desired α-Al$_2$O$_3$ phase. In addition, the left over soda impurities, if any, are expected to eliminate during the second reaction due to further structural change from boehmite to α-Al$_2$O$_3$. Direct reaction at 550 °C was also considered for a comparative study on leaching of soda impurities. In addition, hydrothermal reactions were carried out at different temperatures between 300 and 550 °C at every 50 °C intervals to determine the evolution of phases.

In the direct reactions, alumina trihydrate with the required amount of water corresponding to either 30% or 60% volume fill were reacted in the autoclave at 550 °C. The rate of heating was 100 °C/h and was held at the maximum temperature for 4 hrs. The final

product was analysed by XRD analysis with CuKα radiation using an X-Ray Diffractometer (PW-1050, M/s Philips, Holland) and was found to be phase pure α-Al$_2$O$_3$. The phases present at different temperatures are presented in the Table 1. (Fig. 2).

Based on the Table 1, the following overall reactions are suggested.

$$\underset{(ATH)}{Al_2O_3.3H_2O} \overset{\leq 350\,°C}{\underset{15-55MPa}{=}} \underset{(Boehmite)}{2AlOOH} + 2H_2O \tag{1}$$

$$\underset{(ATH)}{2Al_2O_3 \cdot 3H_2O} \overset{350\,°C-450\,°C}{=}$$
$$\underset{(Boehmite)}{2AlOOH} + \alpha\text{-}Al_2O_3 + 2H_2O \tag{2}$$

$$\underset{(ATH)}{Al_2O_3 \cdot 3H_2O} \overset{\geq 550\,°C}{=} \alpha\text{-}Al_2O_3 + 3H_2O \tag{3}$$

It is clear from Table 1 that boehmite at lower temperatures (<400 °C) and α-alumina at higher temperatures (>450 °C) are the major phases formed during hydrothermal reaction. With higher % of fill, boehmite phase was more at a given temperature. For example, boehmite was found in traces even at 550 °C for higher % fill i.e. at 60% while it was completely absent with lower % fill (30%) at this temperature.
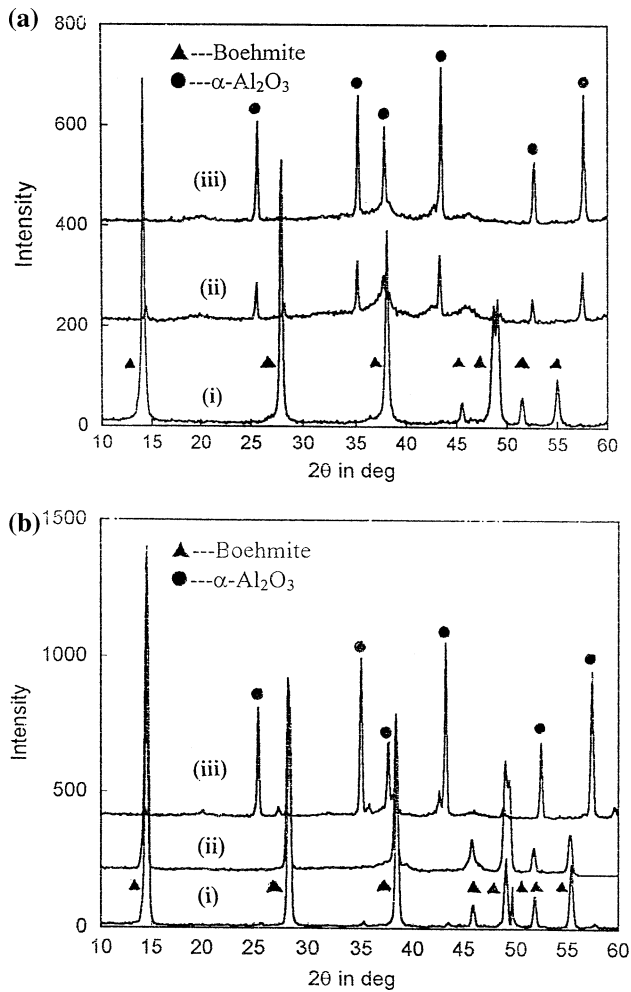
Absence of "transition aluminas" also can be noticed from the Table 1 and also from the XRD patterns (Fig. 1). This is in good agreement with the phase diagram of Al$_2$O$_3$-H$_2$O system (Fig. 3) indicating the absence of transition aluminas above hydrothermal pressure of 20MPa. Therefore, hydrothermal route is an important synthesis route for preparation of phase pure α-Al$_2$O$_3$. In contrast, other processing routes such as sol-gel or precipitation routes generate
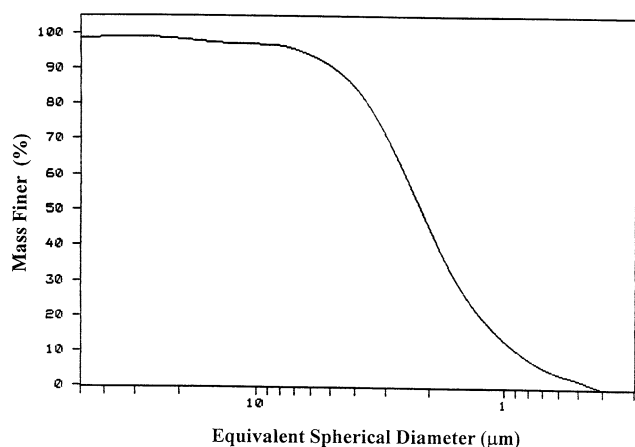
Fig. 1 Particle size distribution of alumina trihydrate used for hydrothermal reaction

Table 1 Product phases obtained at different hydrothermal reaction conditions

Temperature (°C)	Product phases present			
	30% volume fill		60% volume fill	
	Major	Minor	Major	Minor
300	AlOOH		AlOOH	
350	AlOOH	α-Al$_2$O$_3$	AlOOH	
375	AlOOH	α-Al$_2$O$_3$	AlOOH	
400	α-Al$_2$O$_3$	AlOOH	AlOOH	
425	α-Al$_2$O$_3$	AlOOH	AlOOH	α-Al$_2$O$_3$
450	α-Al$_2$O$_3$	AlOOH	α-Al$_2$O$_3$	AlOOH
550	α-Al$_2$O$_3$		α-Al$_2$O$_3$	AlOOH

(a)

(b)

Fig. 2 (a) Typical XRD patterns of hydrothermal reaction products of 30% volume fill and (b) Typical XRD patterns of hydrothermal reaction products of 60% volume fill

intermediate alumina phases such as gamma, delta, theta alumina at intermediate calcination temperatures although finally converting to pure α-Al_2O_3 at very
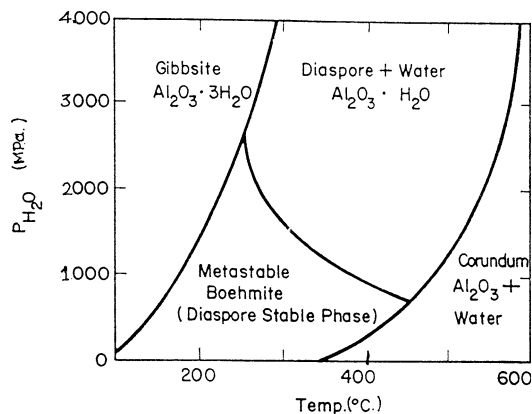
Fig. 3 Al_2O_3–H_2O phase diagram [Ref. G.C. Kennedy, Am. J. Sci, 257, 565 (1959)]

high temperatures. Also, Misra et al. [28] reported the conversion of aluminium hydroxide to pure α-Al_2O_3 above 370 °C and at a pressure above 20 MPa. It has been reported that the products at lower pressures are often associated with non-equilibrium alumina forms (transition alumina). J. Yang et al. [29] synthesized α-Al_2O_3 without transition alumina by hydrothermal treatment of aluminium hydroxide seeded with α-Al_2O_3. In our process, the "transition alumina" were absent could be due to higher hydrothermal pressure.

Hydrothermal reactions involving two successive reactions were preferred to increase the purity of α-Al_2O_3. Initially, a hydrothermal reaction was carried out at 400 °C/4 h with 60% volume fill. After the reaction, the pH of residual water was measured to be 10.5 suggesting the effective leaching of soda impurities. The product was identified as boehmite and was again subjected to a hydrothermal reaction at 550 °C for 4 h. The hydrothermal pressure of 14–40 MPa was recorded contributed by the water from the boehmite due to dehydration as well as from the additional water added to make up the % fill. The pH of the residual water after this reaction was found to be <10 suggesting further leaching of the alkali impurities. The final product was identified as α-Al_2O_3. To monitor the leaching of soda impurities, the ATH as well as the reaction products of both the above mentioned routes were analysed by Inductively Coupled Plasma (ICP) and are presented in Table 2.

According to the Table 2, the soda content of the processed ATH precursor was 0.34%. The soda content of α-alumina prepared by direct method was 0.078% while it was 0.015% (150 ppm) for α-alumina prepared by two sequential hydrothermal reactions. The above concludes that the two-reaction process followed was more effective in leaching impurities than the direct hydrothermal process.

The crystallite size of the powders was determined using the Scherer formula,

$$D = 0.9\lambda/(\beta \cos \theta)$$

where, λ = the wave length of the X-rays
θ = the diffraction angle
β = the corrected half width given by:

Table 2 Soda impurities analysed by ICP method

| Impurities (By % wt.)	Processed ATH precursor	α-Alumina (Direct reaction)	Boehmite (1st reaction at 400 °C)	α-Alumina (2nd reaction at 550 °C)
Na_2O	0.34	0.078	0.046	0.015

$$\beta^2 = \beta_m^2 - \beta_s^2$$

where, β_m is the measured half-width,

β_s is the instrumental half-width

The reflections (020), (120) and (031), (140) from boehmite at "d" values of 6.11, 3.161 and 2.345, respectively were used for the measurement. In the case of alumina, the reflections (012), (104) and (113) at "d" values of 3.479, 2.552 and 2.285 were selected. The diffraction experiments were made using a diffractometer and a Philips X-ray generator with a normal focus Cu tube. A graphite monochromator was used in the diffracted beam to improve the peak-to-background ratio. The data were collected by step scanning in the fixed time mode, the interval of 2θ being 0.02 and the counting time at each step 5 s. The instrumental width was determined using specimens of silicon, aluminium, copper and α-quartz, which were known to have no intrinsic broadening. The crystallite size measured by the above method was found to be 35–75 nm for boehmite and 75–130 nm for α-Al$_2$O$_3$.

From the SEM studies, it is observed that sword like boehmite particles (Fig. 4a) are present after first reaction at 400 °C. However, hexagonal plates of
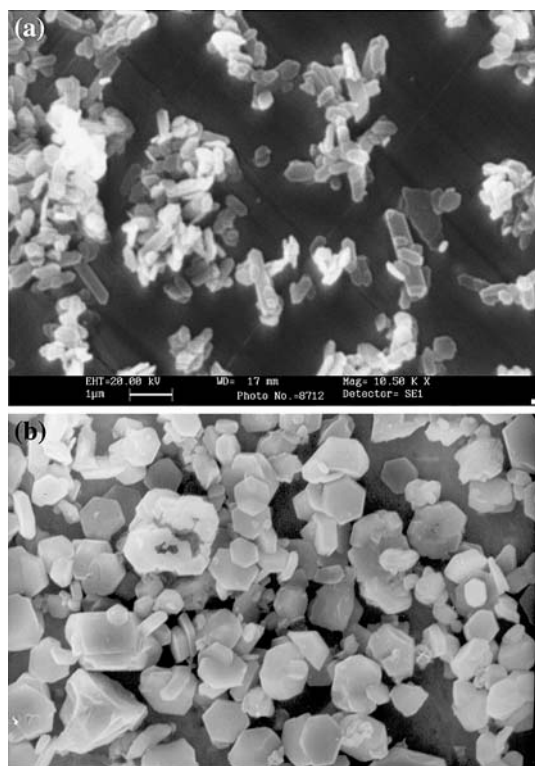
Fig. 4 (**a**) SEM pictures of boehmite from alumina trihydrate (**b**) SEM pictures of α-alumina by double step reaction from alumina trihydrate

α-alumina are found present after second reaction at 550 °C, similar to observations made by Adschiri et al. [25].

From the above studies, it is concluded that high purity α-alumina can be prepared by hydrothermal route using alumina trihydrate at relatively low temperature. In addition, transition aluminas are absent in the final product and the purity can be easily achievable up to 150 ppm level. Besides, the cost of alumina trihydrate is much less compared to pure aluminium metal, therefore, the process has high potential for commercialisation.

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