Advances in High Pressure Science & Technology
Edited by *A.K.Singh*
Tata McGraw-Hill, New Delhi

The Preparation of Boehmite and α-Alumina Powders by Hydrothermal Synthesis from Aluminium Metal

P.K.Panda, *V.A.Jaleel*, S.*Usha* Devi and *T.S.Kannan*
Materials Science Division, National Aerospace Laboratories, Bangalore - 560 017

Abstract

Hydrothermal oxidation of aluminium metal has been effected in the temperature and pressure ranges of 300-550^{0}C and 10-120 MPa respectively. While boehmite and a-alumina form at the extremities of these temperatures and pressures respectively, at intermediate temperatures their mixtures are obtained. The products which had average particle sizes in the range of 4-15 μm were further characterised by XRD, IR spectroscopy, and by SEM observations. The quantity of metal reacting with unit volume of water shows three regions having distinctly different slopes in the temperature ranges of **300**- 350^{0}C, 350-450^{0}C and 450-550^{0}C corresponding *to* the formation of fully crystalline forms of boehmite, boehmite + a-alumina and a-alumina respectively.

1 Introduction

Hydrothermal processing has generally been accepted to mean processing taking place in the presence of superheated steam or supercritical water (in the temperature and pressure ranges of 200-600^{0}C and of 10-100 MPa respectively). Hydrothermal synthesis when used for ceramic powder preparation gives fine, crystalline, hydrated or anhydrous ceramic powders. The hydrothermal processing is a single-step product formation process, and hence normally there is no need for high temperature calcination step. This, in turn, eliminates the need for milling used for breaking the large grain agglomerated products. By controlling these reactions, it is possible to produce anhydrous crystalline powders with controlled particle size, controlled stoichiometry and in some cases controlled morphology.

Hydrothermal synthesis of ceramic powders like ZrO_2,HfO_2, Al_2O_3 etc. from their salts was reported earlier [1,2]. Preparation of these powders from pure metals and alloys are also reported [3]. However, in these cases, the reactants are taken in small quantities inside sealed gold capsules, and the pressure is applied to the sealed tube externally. The temperature (500-700^{0}C) and pressure (100-300 MPa) used in such cases are quite high. The present paper deals with the formation of boehmite (300^{0}C) and a-alumina (450-550^{0}C) or their mixtures at relatively low temperatures (350-450^{0}C) and pressures (20-150 MPa) in an open container placed inside a pressure vessel, The pressure was self-generated by the pressure of the water vapor and by the hydrogen gas produced by the reaction of aluminium metal in direct contact with superheated steam or supercritical water (inside the pressure vessel) depending on the temperature of the reaction.

2 Experimental

The starting material was taken in the form of solid aluminium metal pieces of typical dimensions of 25x25x12mm^3 weighing approximately 10g each. The pieces were cut from a commercial aluminium rod stock. The metal piece along with 25ml water was taken in the autoclave. The total volume occupied corresponds to **30%** of volume of fill of the autoclave. The autoclave was heated by an external heater and the temperature of the autoclave was measured by a chromel-alumel thermocouple inserted into a 5mm horizontal hole drilled on one side of the autoclave. The pressure was measured with the help of a Bourdon gauge. The autoclave was heated to different temperatures in the range of 300-550^{0}C in intervals of 25^{0}C at the rate of 2-2.5^{0}C/min, and soaked at the highest temperature for a period of 3hr. The final pressure reached during the heating schedule was noted in each case. After the reaction, the autoclave was cooled to room temperature. The product was removed, washed, deagglomerated and dried to get a free flowing white powder.

The various phases present were identified by the X-ray powder diffraction analysis in a Philips Diffractometer using Cu-K, radiation. The product powders were subjected to particle size analysis in a sedigraph 5100. The infrared spectra of the powders were taken on a Perkin Elmer (Model 862) Infrared Spectrophotometer. Scanning Electron Micrographs were taken on a Jeol Electron Microscope.

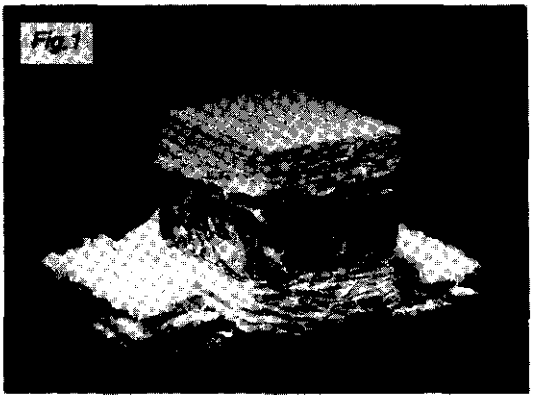
3 Results and discussion

The details of the experiments performed are shown in Table 1. In all cases the reaction of water starts from the external surface of the aluminium metal, and progresses towards interior to generate thin layers of oxidised product. Once a layer is separated after reaching a certain thickness, a fresh surface is exposed for ingress of superheated steam or supercritical water for reaction with further mass. The product is thus formed in successive layers. The unreacted mass, present at the core of the product is easily separable. **A** typical layer like structure of the product with the unreacted core material is shown in Fig.1. Thus, in this case, the contamination from unreacted raw materials is avoided in contrast to the cases where the raw materials are taken in the form of powders. In the latter case, the metal powder has to be separated from the product formed in the reaction using chemical procedures like leaching. The XRD spectra of three samples reacted respectively at 300^0C (H8) at 425^0C (H12) and at 550^0C (H7) all with 30% of volume of fill is shown in Fig.2. Sample H8 is rich in boehmite (AlOOH) while H7 is rich in a-alumina. Sample

Table 1: Particulars of typical conditions of hydrothermal oxidation reaction of aluminium stocks

Sample Code No.	Temperature of reaction T^0C taken	Weight of Aluminium taken (g)	Weight of Aluminium consumed (g)	Final pressure reached at T^0C (MPa)	Aluminium reacted per ml. of water (g)
8H	300	11.01	2.11	15	0.084
9H	350	10.65	7.12	35	0.285
11H	375	11.02	7.03	40	0.280
10H	400	11.02	7.86	45	0.315
12H	425	10.85	7.14	50	0.290
6H	450	9.91	8.10	55	0.324
7H	550	11.32	8.69	70	0.348

H12 is a mixture of both, as are the samples prepared at other temperatures in the interval of 350-450^0C. However, XRD also shows the formation **of** minor quantities of other forms of alumina perhaps as intermediate phases before total conversion to



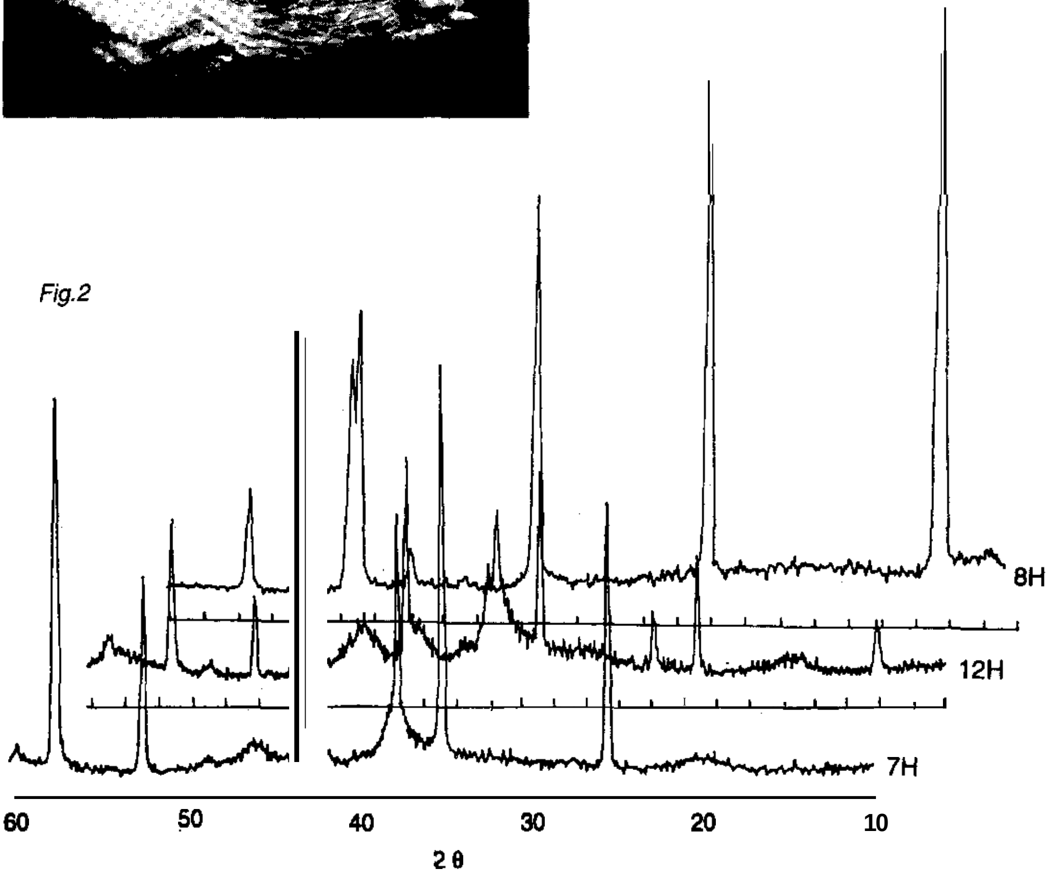


Figure 1: *Typical product and residual reactant block obtained after the reaction in the temperature range **of** 300- 550^0C.*

Figure 2: *XRD patterns **of** products **of** hydrothermal ozidation **of** aluminium at 300^0C (8H), 450^0C (12H) and 550^0C (7H).*

α- Al_2O_3 is reached at 550^0C. This is being investigated in detail presently, and will be reported subsequently elsewhere.

Based on the XRD patterns of the products the following overall reactions could be assigned for the formation of the products.

$$2Al + 4H_2O \xrightarrow{300-350^0C,\ 15-55\ MPa} Al_2O_3.H_2O \text{ or } 2AlOOH\ (Boehmite) + 3H_2 \quad (1)$$

$$Al_2O_3.H_2O \xrightarrow{450-500^0C,\ 55-70\ MPa} \alpha - Al_2O_3 + H_2O \quad (2)$$

The IR spectra of samples H7, H8 and H12 are shown in Fig.3. herein evidences to the presence of boehmite, *a*- alumina and their mixtures could be seen clearly.

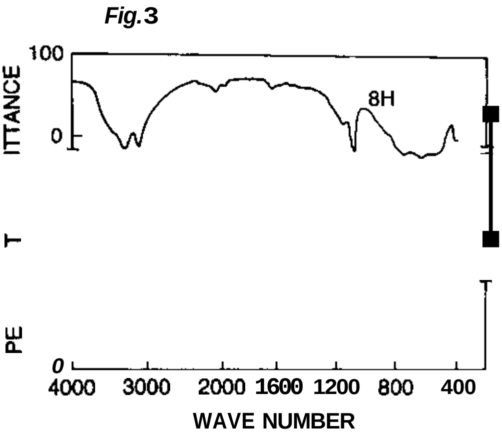
The SEM micrographs shown in Fig.4 reveal an agglomerated and lumpy morphology for the boehmite and alumina products with occasional spherical morphology for the case of a-alumina rich samples.

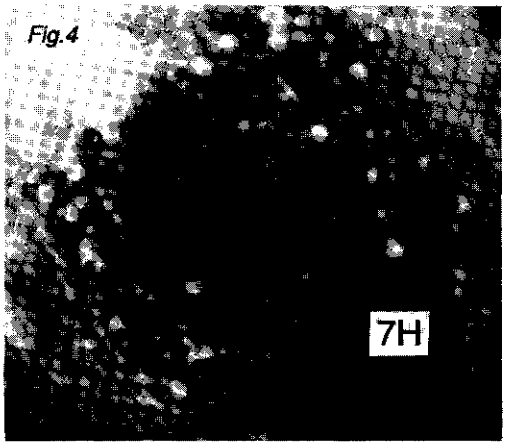
The product powders H7, H8, and H12 were found to have a wide distribution of particle sizes when subjected to sedigraphic analysis. Their cumulative size distribution curves reveal d_{50} values of 8.8 μm, 13.6μm and 4.4 μm for the above samples respectively. The cumulative size distribution curves are presented in Fig.5.

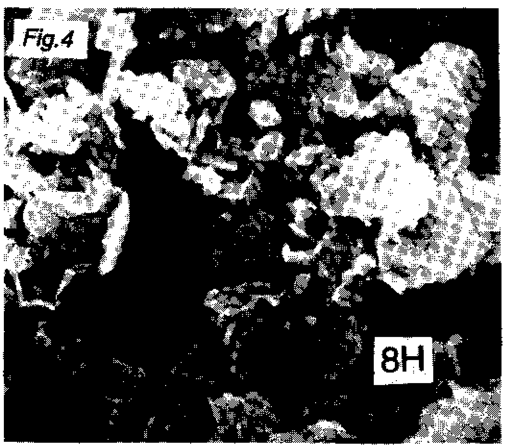
When the quantity of aluminium reacted upon by one milli liter ($1cm^3$) of water is plotted against the temperature of experiment, a typical graph shown in Fig.6. is obtained. The graph could be truncated into three regions with distinct slopes. The first between 300-350°C corresponding to the formation of boehmite, the second between 350-450°C corresponding to the overlaping region wherein a mixture of alumina and boehmite is formed and the last between 450- 550^0C, where a-alumina is predominantly obtained. This observation is endorsed by the XRD and IR spectral results. More detailed investigations are in progress.

4 Conclusion

Fine powders of boehmite, a-alumina and their mixtures have been synthesised by hydrothermal oxidation of solid aluminium between temperatures of $300\text{-}550^0C$ and pressures of 20-120 MPa in a open vessel hydrothermal system. The products were characterised by XRD, IR, SEM and particle size analysis. There exists 3 distinct







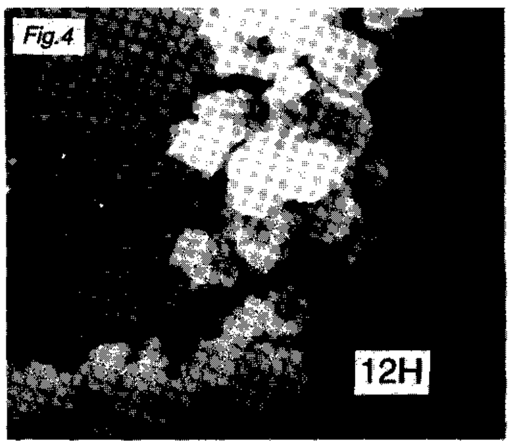
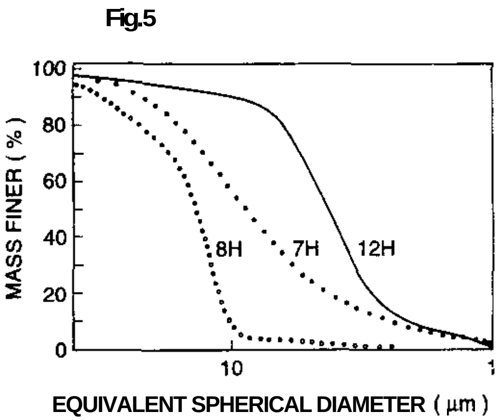


Figure 3: *IR spectra of products 7H, 8H and 12H.*

Figure 4: *SEM pictures of products* **7H** (x *6000), 8H (× 3000), 12H (× 2000).*



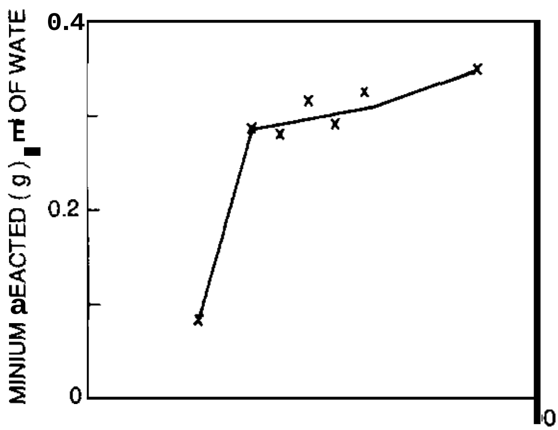


Figure 5: *Cummulative particle size distribution (mass population) graphs of products 7H. 8H and 12H.*

Figure **6:** *Plot of temperature Vs: quantity of metal reacted with unit volume (ml) of water.*

temperature ranges wherein boehmite (300-350^{0}C), a-alumina (450-550^{0}C) and their mixtures (350-450^{0}C) are obtained.

Acknowledgements

The authors thank Mr.Ravishankar (BHEL) and Mr.L.Mariappan for particle size analysis, Dr.T.A.Bhaskaran *for* SEM observations, Mr.P.S.L.Narasimhan for infrared spectra and Miss.H.N.Roopa for help in preparation of the manuscript.

References

1. D.H.H.Quon, S.S.B Wang, J.Aota, T.A.Wheat, A.K.Kuriakose and G.Torrie, *Inter-ceram*,**3**, *15 (1989).*
2. E.Tani, Yoshimura and Somiya, *J. Am. Cemm. Soc.*, **66**, 11 (1983).
3. N.Claussen, in *Advances in Cemmics - **Vo1.12,** Science and Technology **of** Zirconia*, N.Claussen, M.Ruhle and A.Heuer (eds.), American Ceramic Society, (1984),-P-806.