Bull. Mater. Sci., Vol. 33, No. 6, December 2010, pp. 737–740. © Indian Academy of Sciences.

Microwave assisted hydrolysis of aluminium metal and preparation of high surface area γ Al_2O_3 powder

A K SIVADASAN, I PACKIA SELVAM and SANKARA NARAYANAN POTTY*

Centre for Materials for Electronics Technology (C-MET), Department of Information Technology, Government of India, Athani PO, Thrissur 680 581, India

MS received 30 June 2009; revised 27 July 2009

Abstract. Phase pure boehmite particles were prepared by microwave assisted hydrolysis of aluminium sheets. These particles were calcined in air to produce γ Al_2O_3 particles with specific surface area of ~210 m^2/g. The alumina particles were characterized by studying X-ray diffraction, transmission electron microscopy and Fourier transform infrared spectroscopy. For comparison, the aluminium hydroxide particles were also prepared by normal hydrolysis of aluminium metal. Normal hydrolysis yielded a mixture of boehmite and bayerite particles whereas microwave assisted hydrolysis produced phase pure boehmite particles. The importance of using microwave radiation for the hydrolysis of aluminium metal is also manifested in a shorter reaction time.

Keywords. **Aluminum metal; γ Al_2O_3 powder; boehmite particles.**

1. Introduction

Recently, there has been an increasing interest in the synthesis of γ Al_2O_3 owing to its important applications in catalysis, miniature power supplies, space crafts etc (Xu *et al* 1994; Drost *et al* 1997; Prins 2001). There are several reports of physical and chemical processes for the synthesis of alumina particles in literature. In many chemical routes, boehmite and bayerite have been used as the starting materials for the preparation of alumina. Boehmite is prepared by various methods such as hydrothermal treatment of gibbsite (Inoue *et al* 1989), hydrolysis of alkoxides (Yoldas 1975) or aluminium nitrate solutions (Mani *et al* 1991), etc. Aluminium metal has also been used as a precursor for the synthesis of aluminium hydroxides and these hydroxides are used to prepare alumina particles (Kannan *et al* 1997; Mo and Yuan 1993; Thiruchitrambalam *et al* 2004). The use of microwave radiation has been widely accepted in many chemical reactions for different applications in the last few years (Michael *et al* 1991; Komarneni *et al* 1995). Microwave assisted hydrolysis of aluminium metal has been carried out in this study for the synthesis of boehmite powder. These particles were calcined in air to produce γ Al_2O_3 powder.

2. Experimental

Aluminium hydroxide particles were prepared by the hydrolysis of aluminium sheets in a domestic microwave oven working with a 2·45 GHz frequency. For this, aluminium metal sheets (analytical grade, 0·02 mm thickness and width about 300 mm) were used as starting material. In order to remove the alumina protective layer, the sheets were initially activated in an aqueous solution of 0·125% HgCl. The activated sheets were immersed in distilled water and kept in the microwave oven. The electron rich amalgam formed reduced water present in the solution to hydroxide, forming aluminium hydroxide, $Al(OH)_3$ and hydrogen gas (H_2). Three kinds of powders were prepared by varying the microwave power (20%, 40% and 80% of microwave power). In all the experiments, the hydrolysis duration was 10 min. The sols prepared by the above method were aged at room temperature in a glass beaker. The precipitate was separated and washed repeatedly by suspending them in distilled water and using an ultrasonic disintegrator. The precipitate was then dried at about 350 K. Based on the thermogravimetric analysis, the powders obtained were calcined at 873 K to prepare γ-alumina nanoparticles. For comparison, the hydrolysis was also carried out in water at room temperature, without using microwave energy. In this experiment, the hydrolysis was carried out for 40 min to get sufficient quantity of powder.

X-ray diffraction studies for the present investigation were performed using an AXS Bruker D5005 diffractometer (Germany) with a vertical goniometer. X-ray generator was operated at 40 kV and 30 mA. CuK_α (λ=1·54056Å) radiation was used with Ni filter. Thermogravimetric analysis was carried out in a simultaneous TGA/DSC instrument (TA Instruments, SDT Q600). Transmission

*Author for correspondence (snpotty@yahoo.com)

electron microscopy study was carried out using a Hitachi H600 (Japan) electron microscope to characterize the calcined alumina particles. Samples for the TEM were prepared by dispersing the powders ultrasonically in absolute alcohol and then placing a drop of the suspension onto a grid. The surface area analysis of the alumina particles has been carried out using a Quantachrome make NOVA 1200 BET surface area analyser. The surface area was calculated from the linear portion of the BET plot. FTIR spectra of the nanoparticles of γ Al_2O_3 were recorded using a Shimadzu FTIR spectrometer with KBr as the dielectric medium.

3. Results and discussion

Figure 1 (a,b,c) shows the XRD patterns of the precursor particles prepared by the hydrolysis of aluminium metal sheets in microwave oven by applying 20%, 40% and 80% microwave power. It is observed from the XRD patterns that the particles prepared with microwave power 20% and 40% contain boehmite phase (ICDD PDF No. 21-1307) predominantly. Bayerite peaks (ICDD PDF No. 20-0011) with very small intensity are also seen in these XRD patterns (figures 1a and b). Figure 1(c) shows the XRD pattern of the powder prepared using 80% microwave power. Comparison with the standard ICDD data revealed that the pattern contains only peaks corresponding to boehmite [AlO (OH)]. Figure 1(d) shows XRD patterns of the particles prepared by the normal hydrolysis at room temperature (300 K), without using microwave energy. XRD analysis showed that the powders contain both boehmite and bayerite phases with bayerite as the major phase. The sharp peaks of bayerite indicate the presence of highly crystalline and coarse particles.

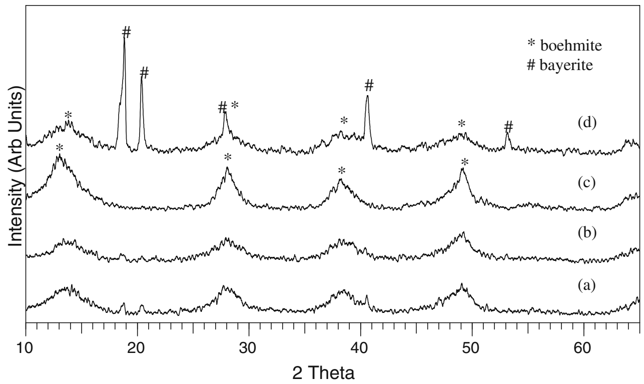

Figure 1. X-ray diffraction pattern of particles prepared in microwave oven with (a) 20%, (b) 40% and (c) 80% microwave power. (d) XRD pattern of the particles prepared by normal hydrolysis.

During the hydrolysis, aluminium foils were first reacted with water to form aluminium hydroxide gel. The gels were then dried to form a solid powder. In general, three different crystal phases have been reported to form after drying of the gel, viz. trihydroxide forms of AlO(OH). αH_2O, gibbsite and bayerite $Al(OH)_3$ (Park *et al* 2004). In the present work, the products formed were a mixture of bayerite and monohydroxide boehmite in the normal hydrolysis, through the following reactions.

$$2Al + 4H_2O \rightarrow 2AlO(OH) + 3H_2, \tag{1}$$
$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2. \tag{2}$$

In this study, it has been observed that the microwave assisted hydrolysis considerably suppressed the formation of bayerite. Preparation of pure boehmite from aluminium metal by hot water hydrolysis has been reported earlier (Thiruchitrambalam *et al* 2004). A similar effect has been observed in the present study when microwave energy was used for the hydrolysis. The formation of boehmite particles in the microwave process may be assisted by the heating of water and changed thermodynamic conditions

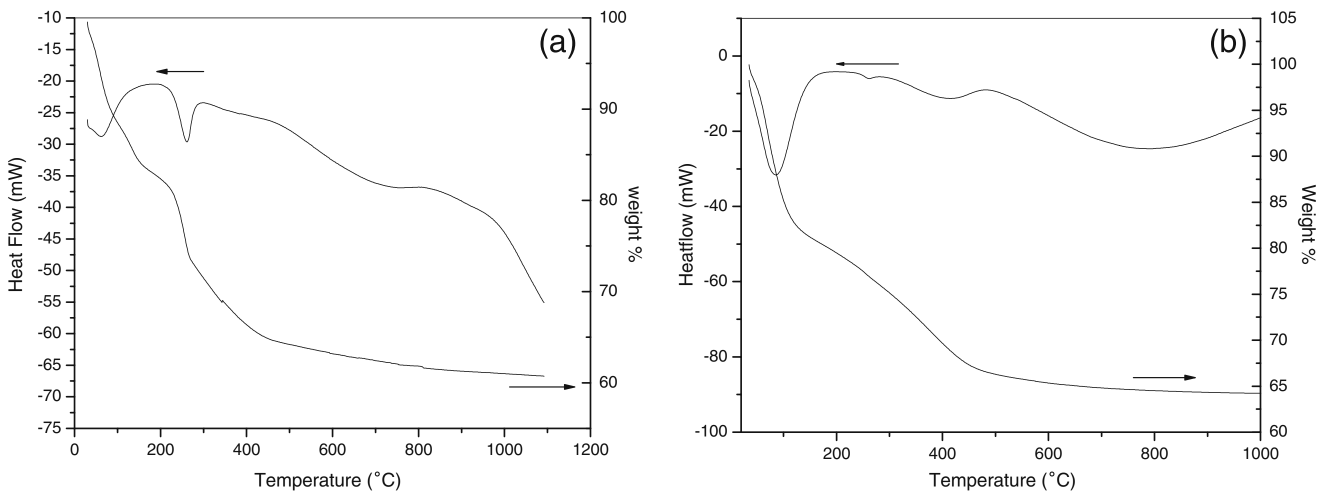

Figure 2. DSC–TGA patterns of the particles prepared by **(a)** normal hydrolysis and **(b)** microwave assisted hydrolysis.

lead to suppression of bayerite phase. Heating takes place by the interaction of the permanent dipole moment of the molecule with high frequency (2·45 GHz) electromagnetic radiation. In the case of normal hydrolysis, the duration of reaction was 40 min, while sufficient quantity of particles were produced in the microwave assisted hydrolysis in just 10 min. The importance of using microwave radiation is thus manifested in the shorter reaction time. Although, Al metal has been used for the synthesis of alumina by several authors (Mo and Yuan 1993; Kannan *et al* 1997; Thiruchitrambalam *et al* 2004), formation of boehmite through the microwave assisted hydrolysis has not been reported so far.

DSC–TGA patterns of the particles prepared by normal hydrolysis and microwave assisted hydrolysis (with 40% power) are shown in figures 2(a) and (b), respectively. In the case of room temperature hydrolysis, the small peak observed at ~260°C represent the dehydration of bayerite (Gasik 2003). In the microwave mediated powder, three peaks are observed. Very small peaks at 260°C and ~420°C represent the decomposition of small amount of bayerite that is present and decomposition of boehmite, respectively.

In the present study, the dehydration of bayerite in the room temperature process is expected to take place in two steps

$$2Al(OH)_3 \rightarrow 2AlOOH + 2H_2O \qquad (\sim 260°C),$$

$$2\ AlOOH \rightarrow \gamma Al_2O_3 + H_2O \qquad (\sim 410°C),$$

whereas in the microwave assisted process, the boehmite dehydration took place by a single reaction

$$2\ AlOOH \rightarrow Al_2O_3 + H_2O.$$

The peaks observed at ~780°C in the microwave processed particle probably represent the transformation to other phases of alumina (Levin and Brandon 1998; Gasik 2003).

XRD patterns of the nanoparticles of alumina obtained by the thermal decomposition of precursor particles obtained through normal and microwave assisted hydrolysis are shown in figures 3a and b, respectively. The ICDD-PDF data of γ Al_2O_3 is presented as vertical bars for comparison. The height of the bars represents the diffraction intensity. X-ray diffraction analysis clearly reveals that the particles prepared by both normal and microwave assisted process produced γ Al_2O_3 powders (ICDD PDF card No. 29-0063).

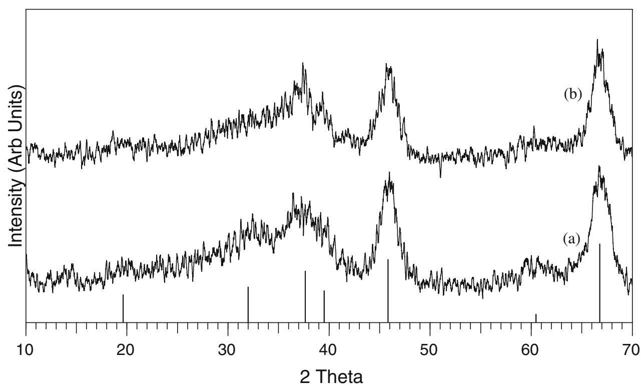

Figure 3. XRD patterns of the nanoparticles of alumina obtained by the thermal decomposition of precursor particles prepared through **(a)** microwave assisted hydrolysis and **(b)** normal hydrolysis. ICDD–PDF data of γ Al_2O_3 (29-0063) is also shown (vertical lines).

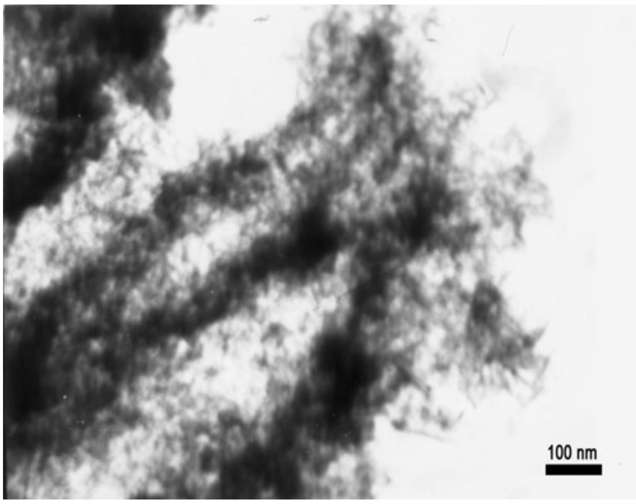

Figure 4. TEM image of nano alumina particles obtained by the thermal decomposition of the precursor particles.

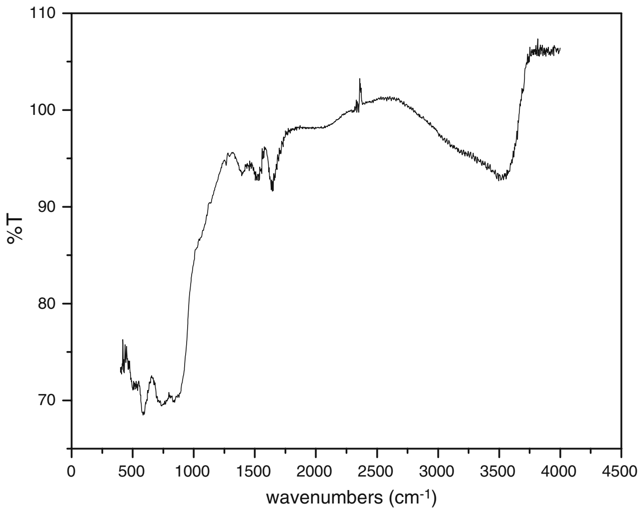

Figure 5. FTIR spectra of alumina particles prepared by microwave assisted hydrolysis of aluminium metal.

Surface area measurements using Brunauer–Emmett–Teller (BET) technique yielded a value of 211·6 m^2/g for the γ Al_2O_3 prepared using microwaves. Interestingly, the surface area of γ Al_2O_3 obtained through room temperature hydrolysis was also found to be 211 m^2/g. Figure 4 illustrates the transmission electron microscopic picture of the alumina particles processed with the help of microwave energy. The micrographs show agglomerates of nanoparticles.

Figure 5 shows the FTIR spectra of γ Al_2O_3 particles prepared through the microwave assisted hydrolysis of aluminium metal. γ Al_2O_3 belongs to the transition aluminas and generally obtained from the thermal treatment of boehmite, bayerite etc. The pathway for the synthesis of transition aluminas is complex and dependent on the precursor used for thermal decomposition (Wefers and Misra 1987; Levin and Brandon 1998; Souza Santos *et al* 2000). They often contain a residual content of hydroxyl groups depending on the precursor and pathway for the preparation of the samples. In the present study, the principal features of the FTIR spectra are identified in the regions (a) between 2800 and 3600 cm^{-1}, with a maximum around 3550 cm^{-1} due to the O–H stretching (Paglia *et al* 2004), (b) between 1500 and 1800 cm^{-1}, with a maximum around 1640 cm^{-1} due to the H–O–H scissor (Paglia *et al* 2004), (c) between 650 and 800 cm^{-1}, with a maximum around 750 cm^{-1} due to the AlO_4 symmetric stretching (Saniger 1995), (d) between 500 and 650 cm^{-1}, with a maximum near 580 cm^{-1} due to the AlO_6 asymmetric stretching (Saniger 1995) and (e) between 450 and 550 cm^{-1} with its maximum around 515 cm^{-1} due to the AlO_6 symmetric stretching (Saniger 1995).

4. Conclusions

Boehmite precursor particles have been successfully prepared through a microwave assisted process. Based on the thermogravimetric analysis, the precursor particles were calcined at 873 K to prepare γ alumina nanoparticles. The alumina particles were characterized using X-ray diffraction, Fourier transform infrared spectroscopy and Brunauer–Emmet–Teller (BET) surface area analyser. The γ Al_2O_3 particles exhibited a specific surface area of 211 m^2/g. In order to establish the effect of microwave energy, normal hydrolysis was also carried out, without using microwave oven. The importance of using microwave radiation for the processing of boehmite is manifested in a shorter reaction time.

Acknowledgements

The authors are grateful to Dr K R Dayas, Director, C-MET, Thrissur, for extending the facilities to carry out this study. The authors are also thankful to Dr R Ratheesh for helpful discussions. One of the authors (SNP) is grateful to the Department of Science and Technology, Government of India, for financial support received under the project SR/FTP/ETA-14/2004.

References

Drost M K, Call C J, Cuta J M and Wegeng R S 1997 *J. Microscale Thermophys. Eng.* **1** 321

Gasik M M 2003 *Handbook of aluminium* 2, *Alloy production and material manufacturing* (Boca Raton, FL: CRC Press) Ch. 2

Inoue M, Kazuhisa K, Hirokazu T, Hiroyuki N and Tomoyuki I 1989 *Clays and Clay Miner.* **37** 71

Kannan T S, Panda P K and Jaleel V A 1997 *J. Mater. Sci. Lett.* **16** 830

Komarneni S, Pidugu R, Li Q H and Roy R 1995 *J. Mater. Res.* **10** 1687

Levin I and Brandon D 1998 *J. Am. Ceram. Soc.* **81** 1995

Mani T V, Varma H K, Warrier K G K and Damodaran A D 1991 *J. Am. Ceram. Soc.* **74** 1807

Michael D, Mangos P and Baghurst D R 1991 *Chem. Soc. Rev.* **20** 1

Mo C and Yuan Z 1993 *Nanostruct. Mater.* **2** 47

Paglia G, Buckley C E, Udovic T J, Rohl A L, Jones F, Maitland C F and Connolly J 2004 *Chem. Mater.* **16** 1914

Park J H, Lee M K and Rhee C K 2004 *Mater. Sci. Eng.* **A375** 1263

Prins R 2001 *Adv. Catal.* **46** 399

Saniger J M 1995 *Mater. Lett.* **22** 109

Souza Santos P, Souza Santos H and Toledo S P 2000 *Mater. Res.* **3** 104

Thiruchitrambalam M, Palkar V R and Gopinathan V 2004 *Mater. Lett.* **58** 3063

Wefers K and Misra C 1987 *Alcoa Technical Paper* **19** 47

Xu Z, Xiao F S, Purnell S K, Alexeev O, Kawi S, Deutsch S E and Gates B C 1994 *Nature* **372** 346

Yoldas B E 1975 *Am. Ceram. Soc. Bull.* **54** 289