Conf-9308122--2

SOL-SPRAY PREPARATION, PARTICULATE CHARACTERISTICS, AND SINTERING OF ALUMINA POWDERS*

H. K. Varma, T. V. Mani, A. D. Damodaran, and K. G. K. Warrier
Regional Research Laboratory (CSIR)
Thiruvananthapuram 695 019, India

U. Balachandran
Energy Technology Division
Argonne National Laboratory
Argonne, IL 60439

July 1993

Paper submitted for publication in Proc. of the 3rd IUMRS International Conference on Advanced Materials, Tokyo, Japan, August 31-September 4, 1993.

*Work at Argonne National Laboratory is supported by the U.S. Department of Energy, under Contract W-31-109-Eng-38.

Sol–spray preparation, particulate characteristics, and sintering of alumina powders

H. K. Varma, T. V. Mani, A. D. Damodaran, and K. G. K. Warrier
Regional Research Laboratory (CSIR), Thiruvananthapuram 695 019, India

U. Balachandran
Energy Technology Division, Argonne National Laboratory, Argonne, IL 60439

Fine alumina powders of spherical morphology and narrow particle–size distribution have been synthesized by a technique that uses precipitation/peptization/spray drying of boehmite sol prepared from aluminum nitrate. The spray–dried powder was further washed with solvents of varying polarities, such as acetone, isopropanol, and tert-butanol. This post-spray-drying treatment changed the powder's particle-size distribution, morphology, density, and compaction characteristics. Microstructure, dielectric properties, and effect of post-treatment on the boehmite-sol-derived alumina powders in reducing agglomeration are discussed.

1. INTRODUCTION

Al_2O_3 is an advanced ceramic material with wide applications in the structural, electrical, automotive, and electronic fields. The properties of sintered Al_2O_3 products depend on the purity and particle characteristics of the starting powders. Many methods are in practice for preparation and processing to achieve desired properties. Attempts have been made to prepare alumina powders through a controlled precipitation/peptization–/decomposition of gels, starting from high–purity aluminum salts [1-4]. The precipitation medium was found to have profound influence on the particle size and surface charge of Al_2O_3 powders [5]. This paper discusses the preparation of micrometer–size spherical Al_2O_3 particles by the sol-spray technique, and the effect of post-treatment on spray-dried powders with respect to selected properties.

2. EXPERIMENTAL

Boehmite (Al-O-OH) was precipitated by addition of ammonium hydroxide to an aqueous solution of $Al(NO_3)_3$ at ≈90°C. Details of boehmite preparation have been described elsewhere [6,7]. The precipitate was washed free of nitrates and then peptized by addition of HNO_3. The clear sol thus obtained was aged for 48 h and then concentrated to 3 M/L by evaporation on a water bath. The concentrated sol was then spray dried to spherical microspheres in a Buch mini–spray dryer. The spray-dried powder was washed repeatedly with acetone, isopropanol, or tert-butanol. The resulting powders are designated as A (as-sprayed), B (acetone-washed), C (isopropanol-washed), and D (tert-butanol). After calcination at 500°C, the powders were heat treated at 1100°C. The spray-dried and calcined powders were characterized by thermogravimetric analysis (TGA), differential thermal analysis (DTA), X-ray diffraction (XRD), and scanning electron microscopy (SEM). Thin sheets (≈0.5 mm) were fabricated from powder C by tape casting and sintered in air at ≈1600°C. The dielectric constant of the sintered tapes was measured as a function of frequency.

3. RESULTS AND DISCUSSION

The XRD pattern of the powder immediately after spray drying (Fig. 1, curve a) shows the typical partially amorphous boehmite structure [2]. XRD analysis of powder heated at ≈1100°C exhibited peaks due only to the alpha-Al_2O_3 phase (curve b, Fig. 1). The TGA and DTA curves of spray-dried powders provided in Fig. 2 are similar to those of boehmite derived by the alkoxy route [2]. There is an initial weight loss of ≈12% up to 150°C due to loss of absorbed moisture, followed by a major weight loss of ≈55% between 150 and 450°C that is attributed to decomposition of the boehmite and the nitrate ions.

The spray-dried powder consists essentially of agglomerates of fine (≈30 nm) crystallites. Maintaining the nanocrystallites as loosely held agglomerates that can deform easily under compaction is possible through preferential washing treatments with solvents having different polarities. The extent of deagglomeration depends on the intensity of hydrogen-bonded OH groups on the oxide surface, as well as on the polarity of the solvents used for washing. The solvents used in the present study (acetone, isopropanol, and tert-butanol) have polarities of 3.5-5. The particle-size distribution of the washed powders is presented in Fig. 3. Acetone washing resulted in an increase of both average and maximum particle sizes up to 4.2 and 15 μm, respectively (Curve b), while isopropanol reduced the values to 2.4 and 7 μm. It is significant that the powder washed with isopropanol (Curve c) shows the minimum average particle size. Powder C, which was washed with isopropanol, had a green-body (as-compacted) density of ≈52% of theoretical value, compared to ≈47% for Powder A (as-sprayed) when compacted at 500 MPa. This clearly shows that agglomerate strength has been considerably influenced by the washing treatments. Further evidence is provided by the surface morphology of the powders: while Powder A has a wide range of sizes and clusters, Powder C has somewhat spherical morphology with less agglomeration and also contains more fine particles.

Thin sheets made from Powder C by tape casting were sintered at ≈1600°C in air after careful removal of organics through a low–temperature binder-burn–out procedure. The sheets were sintered to >98% of theoretical density, and there was no warpage or deformation. The sintered sample is α–alumina. A shrinkage of 20 vol.% was observed in the tape–cast samples upon sintering, and average grain size was ≈3 μm. Dielectric constant, measured as a function of frequency in the range of 50 to 10 MHz, was 9.5 at 50 Hz, and as expected, showed a very small drop with frequency.

4. CONCLUSIONS

The present work is related to preparation of Al_2O_3 by spray drying of boehmite sol obtained by controlled precipitation and peptization reaction, starting from an aqueous solution of $Al(NO_3)_3$. The spray-dried agglomerates contain ≈30–nm–size crystallites, and can be broken up by careful removal of the OH groups through washing with solvents of different polarities. The washed powders have good compaction characteristics. Fully dense thin sheets of Al_2O_3 with average grain size ≈3 μm have been obtained. These

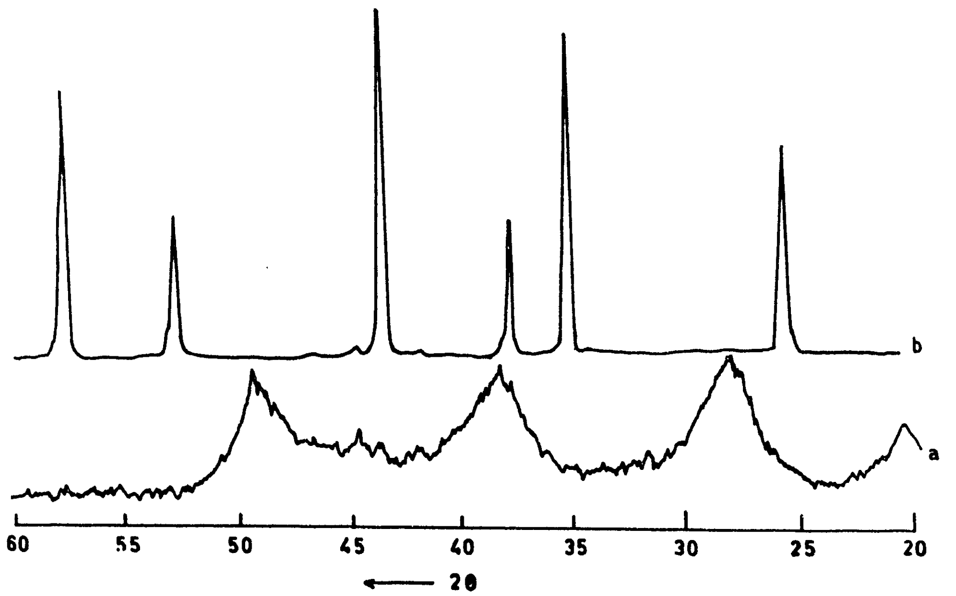

Figure 1. X–ray diffraction patterns of (A) spray–dried powder, and (B) powder heated at 1100°C for 1 h.

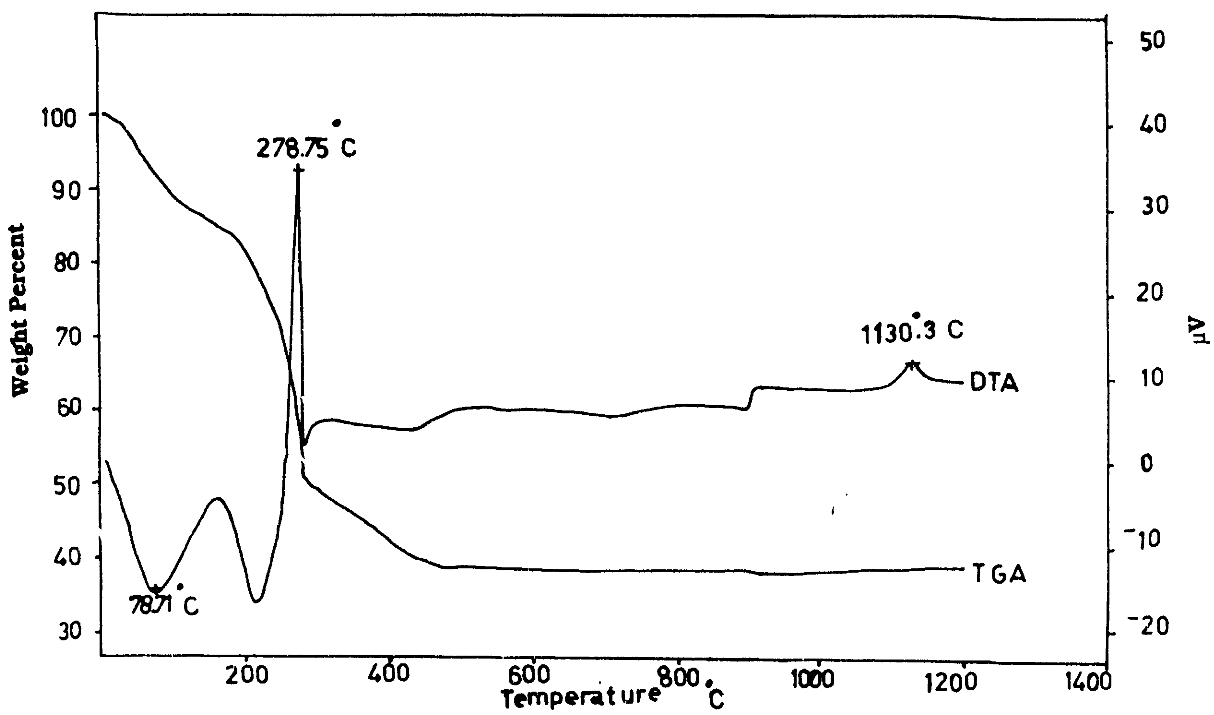

Figure 2. TGA and DTA traces of spray–dried boehmite powder.

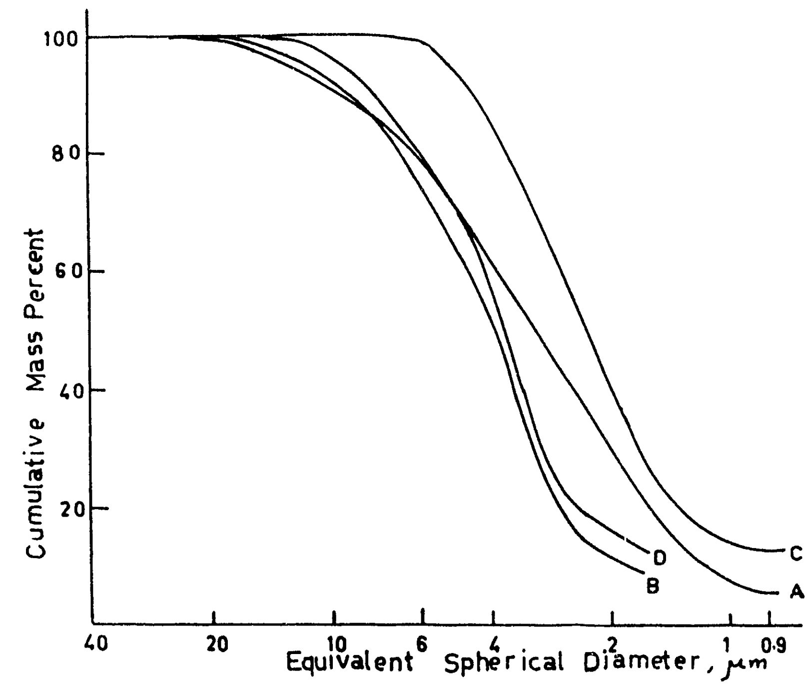

Figure 3. Particle–size distribution curves of calcined powders: (A) as–spray–dried, (B) washed with acetone, (C) washed with isopropanol, and (D) washed with tert–butanol.

sintered Al_2O_3 sheets possess good dielectric properties and are suitable for use as substrate materials in electronic applications.

5. ACKNOWLEDGEMENT

We acknowledge the contributions rendered by Mr. P. Mukundan, Mrs. Prasanna Kumari, and Mr. P. Vijayakumar of the Regional Research Laboratory, Thiruvananthapuram, India. The work at Argonne National Laboratory is supported by the U.S. Department of Energy under Contract No. W–31–109–Eng–38.

REFERENCES

1. B. F. Yoldas, Am. Ceram. Soc. Bull., **54**, 289 (1975).
2. R. D. Dwivedi and G. Gowda, J. Mater. Sci. Lett., **4**, 331 (1985).
3. P. Colomban, J. Mater. Sci., **24**, 3002 (1989).
4. A. C. Pierre and D. R. Uhlmann, J. Am. Ceram. Soc., 70, 28 (1987).
5. H. K. Varma, K. G. K. Warrier, and A. D. Damodaran, Ceramic International, **16**, 73 (1990).
6. T. V. Mani, H. K. Varma, K. G. K. Warrier, and A. D. Damodaran, J. Am. Ceram. Soc., **74**, 1807 (1991).
7. S. K. Ghosh, P. Mukundan, K. G. K. Warrier, and A. D. Damodaran, J. Mater. Sci. Lett., **10**, 119 (1991).

END

DATE
FILMED

10/14/93