

Coating of alumina on cenospheres of fly-ash

PANKAJ K. JAIN, M. N. SAHU and C. B. RAJU

Regional Research Laboratory (CSIR), Bhopal

ABSTRACT

A study is reported that fly-ash behaves as an excellent raw-material for synthesising hollow alumina composite. Coating of alumina onto the surface of cenospheres was accomplished by controlled precipitation around pH-10. Dopants like Ni/Co have also been successfully tried. The resultant co-precipitated composites were then characterized using DTA, XRD, Particle size analysis and specific-gravity measurements. Calcination of co-precipitated samples at 1500°C, for 1h and characterisation of the calcined product also discussed. The results indicate that alumina can be successfully coated on cenospheres.

Key words : Alumina composite, Cenospheres of Fly ash

1.0 INTRODUCTION

A variety of techniques have been employed to deposit coatings from solutions onto suspended particles. Generally, these involve either a physical hetero-coagulation or a direct chemical precipitation. Several heterogeneous precipitation techniques have been investigated to produce thin layers of ceramic coating or ceramic precursors on particles. Kapolnek⁽¹⁾ first developed a controlled aqueous heterogeneous precipitation method by which a thin layer of alumina precursor was deposited onto the surface of SiC whiskers. The coating was then thermally converted into alumina. S. J. Wu and L.C. De Jonghe⁽²⁾ also prepared hollow glass spheres / alumina composites by this method. In the present study, similar technique was used to form a thin layer of alumina onto the surface of cenosphere present in fly ash. These coated cenospheres sintered at higher temperature consist of α -alumina and mullite. Such materials may be useful in high tech engineering applications because of their superior physical and mechanical properties.

Composites containing SiC whisker- Al_2O_3 exhibit greater fracture toughness for safe operations around 1100°C compared to ZrO_2 - Al_2O_3 . It is expected that addition of Si_3N_4 /SiAlON will further improve the performance of these materials compared to the conventional alumina under aggressive environment and high temperature. Addition of 30-40 vol.% of SiC whiskers increased KIC by 40-50%. Alumina based composites are finding many applications in automobile sector for automotive turbocharger, rotor etc. The main advantage in using these materials for structural applications are high strength at high temperatures, corrosion resistance, light weight etc., which will result in im-

proved component performance and energy saving. It is a substitute material in place of metals and polymers for various high tech applications such as abrasive (grinding, polishing), cutting tools, heat shields for rockets and satellites.

Nano-sized alumina particles and in-situ composites of alumina-SiC/ alumina-SiAlON^[3] are presently finding lot of interest for structural engineering and refractory applications compared to the monolithic alumina. This is mainly due to the fact that nano-sized particles offer better sintering properties, leading to near theoretical density and high toughness.

In general, there are some processing techniques for obtaining nano-composite powders with high purity levels viz., Solution techniques, which include sol-gel techniques, precipitation, co-precipitation technique and hydrothermal synthesis.

A. Sol-gel Technique : A sol is dispersion of solid particles in a liquid medium in which atleast some of the dispersed phase is a solid in the size range 1 to 10 nanometers. Sol-gel is a process which converts such a solid to a gelatinous substance and which is usually then dried at low temperature to transform gel to a ceramic material⁽⁴⁻⁷⁾.

The main advantages of Sol-gel Process are better homogeneity in products, high purity, ease of preparing fine powders and lower reaction temperature. In addition, it is possible to prepare many new materials with new compositions in the form of solid, fibres or film⁽⁸⁻⁹⁾.

B. Precipitation, Co-precipitation technique : This technique is limited to the oxide system only. The nature of co-precipitate is critical for the formation of controlled particle size and homogeneous powders⁽²⁾.

C. Hydrothermal Synthesis : This process is applicable only to oxides. This is potentially a superior process for making advanced ceramic powders at low cost e.g.- electro ceramic powders⁽⁹⁻¹³⁾.

Operating Conditions : Temperature : 100-374°C

Pressure : 15 Mpa.

The advantages of Hydro-thermal process are inexpensive raw materials and elimination of impurities. Structural defects associated with milling and the calcination step can be avoided in the process. Powder obtained by this process is fine and more reactive.

More often it has been felt that powder characteristics and their availability are very essential in determining their commercial exploitation. The present situation demands more attention on these two vital aspects for ensuring a real successful attempt in providing a trusted substitute for metallic components. However, despite the fact ceramic materials have superior hardness and toughness at high temperatures, the main weak point is their brittleness due to poor ductility i.e., low fracture toughness compared to metals / alloys. For applications in automotive and aircraft engines, it is very much desirable that a ceramic material should have a minimum fracture toughness of 30 Mpa.√m and high temperature strength i.e. bending strength 700 MPa at 1400°C.

Chemical routes provide more homogeneous nucleation leading to better chemical homogeneity and improved micro-structure. Sub-micrometer sized particles produced in this process will facilitate better sintering properties, achieving near theoretical density and high strength ceramic materials.

It has been reported that the routes viz., hydro-thermal, sol-gel, controlled hydrolysis of metal salts, gas phase reactions have been established to make nano-sized powders of alumina, silica, zirconia, titania, yttria/Ceria stabilised zirconia, β -SiC from silane + acetylene gas composition, alumina-SiC, nano-composite from boehmite by using acetate precursor, mullite (Sol- gel route). Efforts are made to explore the possibilities of synthesising fine powders of composites of alumina-mullite by co-precipitation route and characterise them. Some results are discussed in the following lines.

2.0 EXPERIMENTAL PROCEDURE

Chemical composition and characteristics of fly ash are shown in table 1 and table 2 respectively. Analytical-reagent grade aluminium nitrate of E. Merck was used as a source aluminium. Aluminium hydroxide was precipitated by adding ammonium hydroxide solution to bring pH -10 at 60°C by constant stirring. In some experiments dopants like cobalt and nickel also used which were acting as a catalyst in the precipitation process. Precipitated aluminium hydroxide was dried at 105°C. The dried product was later calcined at 1500°C, 1h, to convert alumina precursor into α -alumina. The dried product at 105°C and calcined products were characterized by Philips X-ray diffractometer using Cu K α and Ni filter and scanning electron microscope (SEM) model JEOL JSM 5600 M for its microstructure. Particle size of the dried, coprecipitated products were examined by Malvern laser partial size analyser. Flow chart of the coating procedure is shown in the process flow chart (Fig -1).

Table 1 : Chemical composition of fly ash

Oxides	Non mag. (wt %)
SiO ₂	65.14%
Al ₂ O ₃	32.50%
Fe ₂ O ₃	2.01%
CaO	Traces
MgO	Traces
Na ₂ O	Traces
K ₂ O	Traces

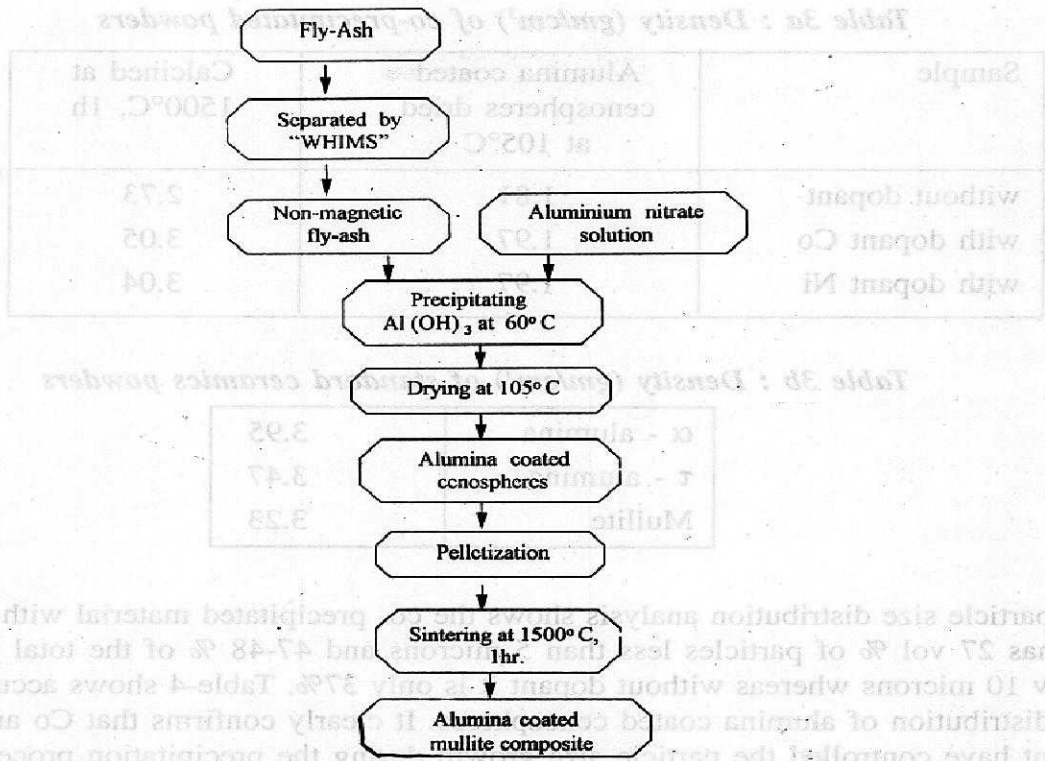


Fig. 1 : Flow chart of coating process and composite preparation

Table 2 : Physical properties of Fly ash

Description	
Density (gm / cm ³)	1.90 - 2.36
Particle size (microns)	< 25
Surface area (gm / cm ²)	max.....3000
	min.....2000

3.0 RESULTS AND DISCUSSION

Table-3 shows the densities of co- precipitated power dried at 105°C for 20h which range from 1.8 to 1.97 gm/ cm². The low value may be due to the hollow nature of the cenospheric particles. Calcined product has higher density of the order 3.04-3.05 gm/cm³. The powder density was recorded a low value of 2.73 gm/ cm³ in the case of sample without any dopant. The introduction of cobalt and nickel has raised the density to 3.05 gm/ cm³.

Table 3a : Density (gm/cm³) of co-precipitated powders

Sample	Alumina coated cenospheres dried at 105°C	Calcined at 1500°C, 1h
without dopant	1.81	2.73
with dopant Co	1.97	3.05
with dopant Ni	1.97	3.04

Table 3b : Density (gm/cm³) of standard ceramics powders

α - alumina	3.95
τ - alumina	3.47
Mullite	3.23

The particle size distribution analysis shows the co-precipitated material with dopants and has 27 vol % of particles less than 5 microns and 47-48 % of the total particles below 10 microns whereas without dopant it is only 37%. Table-4 shows accumulated size distribution of alumina coated cenospheres. It clearly confirms that Co and Ni as dopant have controlled the particle size growth during the precipitation process.

Table 4 : Accumulated particle size distribution of coprecipitated powders (vol%)

Particle size (μm)	Without dopant	With dopant	
		Cobalt	Nickel
<1	10.09	12.52	11.64
<5	22.02	27.21	27.54
<10	37.54	47.68	47.90
<15	53.37	62.83	63.26
<20	62.01	74.83	75.87
<25	70.51	82.42	83.96
<50	91.92	94.61	96.66
<75	95.64	98.24	99.42
<100	97.15	99.12	99.80

In the DTA curve, endothermic effect has been observed in the temperature range 260°C to 297°C and exothermic effect around 290°C to 318°C. The endo effect may be due to the loss of hydrated water, ammonium and hydroxyl ions and the exotherm may be due to phase transition corresponding to conversion of alumina phases. (Fig -2)

X-ray powder diffraction analysis has confirmed the formation of α -alumina [$2d$ (Å°) = 2.09, 2.54, 2.34, 1.71, 1.60, 1.52] and mullite [$2d$ (Å°) = 3.39, 3.43, 5.38, 2.70, 2.21, 1.53] phases at 1500°C at the expense of ϕ - and γ -alumina [$2d$ (Å°) = 2.73, 3.87, 2.29, 1.93, 1.44] formed during the precipitation (Fig.-3 & 4) .

SEM micrograph of the sintered sample with both the dopants and particularly with cobalt has shown a high degree of homogeneity and fine grain structure to the composite material. (Fig-5).

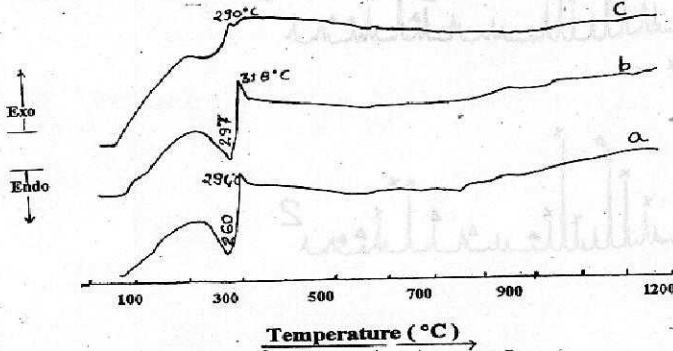


Fig. 2 : Derivatograph of alumina coated cenospheres a) without dopant, b) with dopant Co, c) with dopant Ni

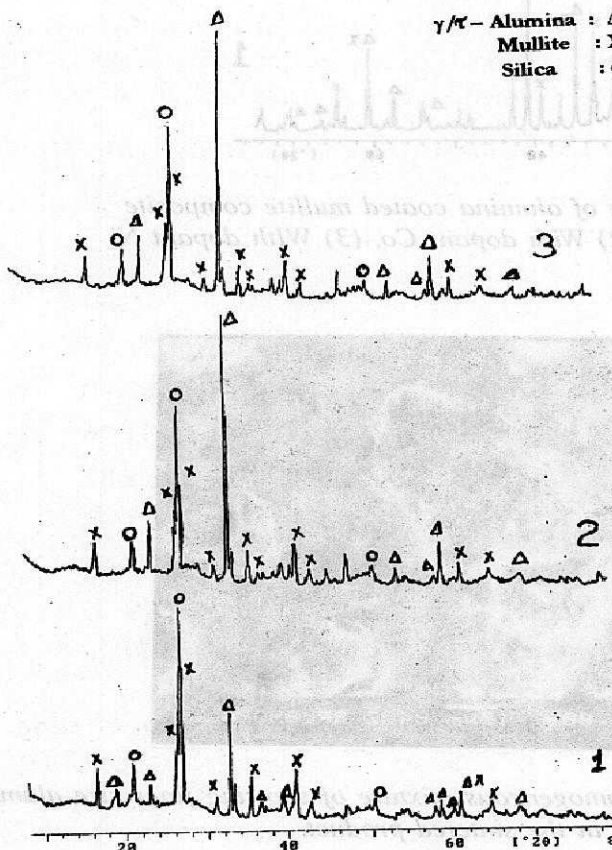


Fig. 3 : XRD pattern of alumina coated cenospheres dried at 105°C (1) Without dopant, (2) With dopant Co, (3) With dopant Ni

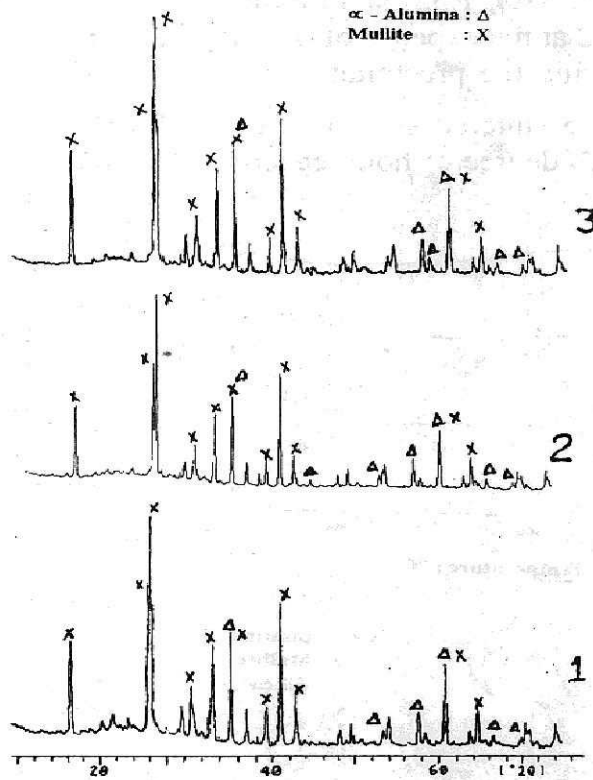


Fig. 4 : XRD pattern of alumina coated mullite composite (1) Without dopant, (2) With dopant Co, (3) With dopant Ni

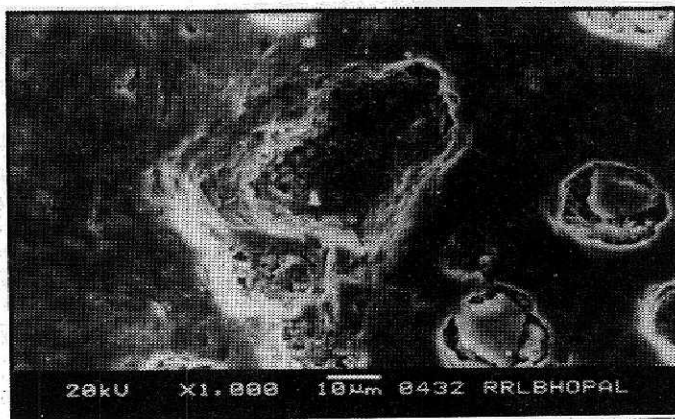


Fig. 5 : SEM micrograph showing homogeneous mixture of showing finer size alumina and mullite in the sintered product.

4.0 CONCLUSIONS

1. Fly ash cenospheres can be effectively used to make alumina-mullite composite powders with high degree of homogeneity.
2. Co and Ni can serve the purpose of dopants for controlling the particle size growth.

5.0 ACKNOWLEDGEMENTS

The authors are very much thankful to Professor (Dr) T. C. Rao Director, RRL Bhopal for his kind permission to present this paper in the seminar.

6.0 REFERENCES

1. Kapolnek D., M. S. thesis, University of California, Berkeley, May 1989.
2. Wu S.J. and Jonghe L.C. De, "Alumina-coated hollow glass spheres/alumina composite", J. Mater.Sci. 32 (1997) 6075-6084.
3. Raju C. B. and Verma S., "Synthesis of In-situ sialon whisker re-inforced ceramic composite - A New process", In British Ceramic Proceeding No. 53: Novel synthesis and promising of ceramics ed. by Prof. F.R. Sale, University of Manchester and UMIST, UK (1994) P. 265-272 Patents.
4. Padmaja P., Sivakumar S., Krishna Pillai P. and K. G. K. Warriar, "Synthesis of porous alumina from boehmite sol" Trans. Ind. Ceram. Soc., Vol.57(6), 1998.
5. Ananthakumar S., Hareesh U. S., Damodaran A. D. and K.G.K.Warrier, "Microwave drying of sol-gel alumina- 30 vol -% SiC precursor for particulate ceramic matrix composite", British Ceram. Trans., Vol.97(5), 1998.
6. Padmaja P., G. M. Anilkumar, P. Krishna Pillai, Damodaran A.D. and Warriar K. G. K., "Formation characteristics and densification behaviour of diphasic mullite gels under various pH conditions", British Ceram. Trans., Vol.97(5), 1998.
7. Nair Jalajakumari, Nair Padmakumar, Van Ommen Jan G., Julian R.H.Ross, and Burggraaf Anthonie J. and Mizukami Fujio, "Influence of peptization and ethanol washing on the pore-structure evolution of sol-gel-derived alumina catalyst supports", J. Am. Ceram. Soc., 81[10], 2709-12, 1998.
8. Pierre Alain C. and Uhlmann Donald R., "Gelation of alumina hydroxide sols", J. Am. Ceram. Soc., 70[1], 28-32, 1997.
9. Lin Yung-Jen and Jiang Bor-Feng, "Sintering and phase evolution of electroless- nickel-cobalt alumina powder", J. Am. Ceram. Soc., 81[9], 2481-84, 1998.
10. Oh Sung - Tag, Sando Mutsuo and Niihara Koichi, "Preparation and properties of alumina / nickel-cobalt alloy nano-composites", J. Am. Ceram. Soc., 81[11], 3013-15, 1998.
11. Sharma Pramod K., Jilavi M.H., Burgard D., Nass R. and Schmid H., "Hydrothermal synthesis of nano sized α - Al_2O_3 from seeded aluminium hydroxide", J. Am. Ceram. Soc., 81[10], 2732-34, 1998.
12. Frey R.G. and Halloran J. W., "Compaction behavior of spray-dried alumina", J. Am. Ceram. Soc., 67[3], 199-203, 1984.
13. Dawson William J., "Hydrothermal synthesis of advanced ceramic powders", Ceramic Bulletin, 67 [10], 1988.