Forming of Alumina Ceramics

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Summary: Alumina ceramic products were made by die pressing, slip casting and extrusion. The products were tested for various physical properties such as percentage shrinkage, bulk density, apparent porosity, water absorption, scratch hardness and thermal conductivity. Increase in sintering temperature resulted in increase in percentage shrinkage of extruded rods and pressed discs from 6.6 % to 11.3 %. Scratch hardness of the extruded rod sample is around 8.5 whereas hardness values of slip cast sample is around 8 on Mohś scale. A simple method has been developed to obtain porous ceramic for thermal insulation purpose of furnaces upto 1600 °C. Porous block made has thermal conductivity value of 0.33 $Wm^{-1}K^{-1}$ and the density of 0.7 gm/cm^3.

Introduction

Alumina ceramics are used in almost every industry in several applications to meet performance requirements, to serve for most metals and plastics. It possesses low thermal conductivity, high electrical resistance, high wear resistance, extreme temperature stability and chemically stable and inert. Ceramic processing is a complicated and influenced by several factors. These factors can be grouped into mainly two categories. One is the processing condition and the other is the intrinsic properties of raw materials. Processing conditions include temperature, pressure, atmosphere and time whereas intrinsic properties encompass raw material purity, particle size distribution, shape and surface area, etc. In the context of the raw material characteristics, the purity and the particle size are the most dominant factors [1].

Die pressed discs were made by using semi dry powder as feed material. A hand operated screw type press was used for making discs. Hydroxyethyl cellulose was used as binder to serve the function of providing strength to green body by forming bridges between the particles [2].

Slip casting was used to make different shapes of crucibles. It is relatively simple and inexpensive method used to produce ceramics. The alumina powder is dispersed in an aqueous solution and poured into plaster of paris moulds. The liquid is gradually absorbed and a solid layer of ceramic is deposited on the mould walls. The layer gets thicken with the passage of time. When desired thickness is obtained, the excess liquid is poured out leaving the powder in a tightly packed green state. Finally the mould is removed and the article is dried and fired.

Extrusion of alumina was carried out in a screw extruder. The screw has to mix the powder and the other additives into a homogeneous mass and generate enough pressure to transport the mixture against the resistance of the die. Shaping of the extruded body is achieved with the head of the extruder screw and the die. The extruder screw head changes the rotational flow of the mixture produced by the screw into and axial flow for extrusion and to produce uniform flow in the die. In the release of the body from the extruder, the die must generate the required cross-section, allow uniform flow across the entire cross-section and ensure a smooth surface [3].

Porous ceramics are of great interest due to their numerous potential applications in adsorption and separation, filtration, refractory insulation for furnaces, as well as hard tissue repair and engineering [4-6].

In the present work, a simplest method has been developed to obtain a porous body with porosity upto 85 % and cell sizes of 1 mm approximately. A

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viscous slip was prepared consisting of ceramic powder, binder and free oxygen releasing hydrogen peroxide. The slip was then poured into stainless steel mould lined with aluminum foil, forming cakes.

Results and Discussion

Grinding raw alumina to achieve finer particle size prior to the formation of ceramic shape and firing is a prime variable affecting density, thermal reactivity and shrinkage during firing.

As supplied, alumina powder was subjected to sieve analysis by using B.S.I.S. test sieves. The powder retained on each of the sieves and that passing through 250 mesh were weighed and are tabulated in Table-1.

Table-1: Sieve analysis of commercially available alumina.

Seive No.	Mesh Size (μm)	% Retention	% Cumulative
70	210	0.03	0.03
100	149	0.045	0.075
150	105	7.86	7.94
200	74	15.28	23.22
250	63	22.36	45.58
-250	63	54.42	100

Particle size distribution of ball milled alumina powder is given in Table-2.

Table-2: Particle size distribution of ball milled alumina powder.

Particle Diameter (μm)	% Cumulative
0.3 - 1	17.6
1 - 6	71.1
6 - 15	11.3

Graphical representation of particle size distribution is also shown in Fig. 1.

Table-3 shows percentage shrinkage of alumina ceramic samples at different temperatures having same holding time of four hours. Rise in sintering temperature resulted in increase of percentage shrinkage. This increase in shrinkage is due to increased matter transport rates during the solid state sintering mechanism. In solid state sintering, the shaped green body is heated to a temperature that is typically 0.5 to 0.9 of the melting point. No liquid is present and atomic diffusion in the solid state produces joining of the particles and reduction of the porosity [7].

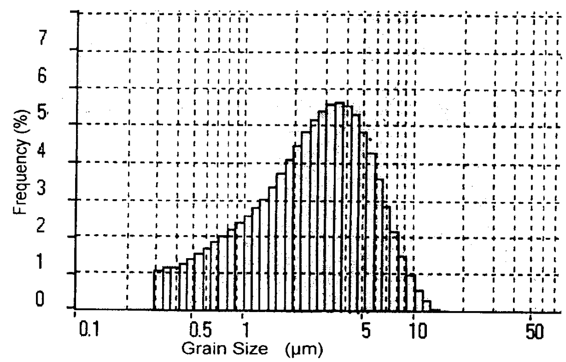

Fig. 1: Particle size distribution of ball milled ground alumina.

Table-4 shows apparent porosity, water absorption and bulk density values of alumina products sintered at 1550 °C having holding time of 8 hours. Results of extruded rod sample show lower apparent porosity and water absorption values whereas higher bulk density values as compared to slip cast samples. This could be due more compaction of alumina granules during extrusion which is not the case in slip casting forming method.

Porous ceramic block (wax coated) floated on the surface of water; therefore the density was calculated by carefully measuring the weight and the dimensions. Density was measured to be 0.7 g/cm^3, which is only 17.5 % of the theoretical density (3.98 g/cm^3) of pure alumina.

Scratch hardness of extruded sample at 1550 °C having holding time of 8 hours is around 8.5 on Mohś scale whereas the hardness value for same sintering temperature and holding time of slip cast sample is around 8 on Mohś scale. More compaction

Table-3: Percentage shrinkage of alumina ceramic samples at different firing temperature.

Sample (soaking time 4 hrs. with different firing Temp.)	Average dimension of rod/disc before firing (mm)	Average dimension of rod/disc after firing (mm)	Difference in dimension (mm)	Shrinkage (%)
Length of extruded rod (1550 °C)	124.0	115.8	8.2	6.6
Dia. of pressed disc at (1600 °C)	51.5	46.5	5	9.7
Dia. of extruded rod (1650 °C)	27.3	24.2	3.1	11.3

Table-4: Properties determination of slip cast and extruded samples.

Properties Studied	Slip Cast Sample (1550 °C, soak time 8 hrs.)	Extruded Rod Sample (1550 °C, soak time 8 hrs.)
Apparent Porosity	33.2	19.6
Water Absorption	12.5	6.7
Bulk Density	2.7	2.9

is attained in case of extruded sample in green state, which is not the case in slip cast forming.

Result of thermal conductivity for porous ceramic containing 85 wt. % Al_2O_3 and 15 wt. % china clay was measured at 500 °C and the average of the two values was 0.33 $Wm^{-1}K^{-1}$ whereas for corundum (Al_2O_3) the value is 24 $Wm^{-1}K^{-1}$ at room temperature [8-10] measured for the same property.

Experimental

Commercial alumina powder made by *Nippon Light Metal Company Ltd. Japan* was used. Ball milling of the alumina powder was carried out for 48 hours. Particle size analyzer model, *Fritsch Company Analystte 22 Germany*, was used to measure particle size distribution of ball milled alumina powder.

Other chemicals used in the experiments were distilled water, hydrochloric acid, hydrogen peroxide, glycerin, polyvinyl alcohol (PVA), hydroxyethyl cellulose (HEC), alumina chloride and china clay (Wattco, England).

Die Pressing

Ball milled alumina powder was mixed with 2 % solution of hydroxyethyl cellulose. The feed material was semi dry powder containing 5 to 7 wt. % water content. Hand operated screw type press was used to make die pressed discs of 51.5 mm diameter and 3 mm thickness (approx.). The sintering schedule was 10 °C/min up to 1000 °C, held there for 30 minutes, then raised up to 1650 °C at same ramp rate (in two and a half hours) and final soaking temperature was maintained at 1650 °C for four hours before the furnace was switched off and allowed to cool to room temperature.

Slip Casting

Alumina powder was ground in ball mill for 48 hours (Refer to Table-2 for particle size distribution). The ground powder was put in a glass winchester with plenty of distilled water. It was shaken thoroughly and left for three days. The supernatant water was syphoned out and concentrated HCl was added (100 cc for 1000 gms of Al_2O_3). It was then further left for 2 days. The binder used in the slips was solid polyvinyl alcohol (PVA). The PVA was dissolved in water before it could be added to the solution up to 2 wt. % of solid. In order to dissolve PVA the water had to be heated to approximately 80 °C. Before the slurry is poured into the plaster-of-paris moulds, it is vacuum treated to remove any air bubbles. The slip cast products (crucibles of different shapes and sizes) were left to dry once removed from plaster of paris moulds. Sintering was carried out in an electric furnace. The temperature was raised to 800 °C at a rate of 10 °C/min and held for 2 hours to burnout the binder. The temperature was further ramped to 1550 °C and held there for 8 hours before the furnace was cooled down to room temperature.

Extrusion

The extrudate was prepared by admixing of 0.2 M aluminum chloride ($AlCl_3$) to 3 wt. % hydroxyethyl cellulose solution and then mixing with the ground alumina powder. It is suggested that addition of $AlCl_3$ coagulate the HEC by the aluminum ions from the $AlCl_3$ solution, hence the smaller difference between yield and final extrusion pressure could be due to reduced organic migration in the direction of extrusion as a result of the coagulation [3, 11]. Prepared feed material was wrapped in plastic bags and stored in saturated humidity prior to extrusion. Rods of 2.73 cm in diameter were extruded in screw extruder with conical shaped die. The extruded rods were dried, first at room temperature and then in a drying oven at 105 °C for overnight. Two different sintering schedules were carried out at the rate of 10 °C /min to 1000 °C with soaking time of 30 minutes. Then the temperatures were further raised by 5 °C /min to 1550 °C and 1650 °C with final soaking time of 4 hours in each case.

Porous Sintered Ceramics

85 wt. % of commercially available alumina (Sieve analysis as shown in Table-1) was mixed with 15 wt. % of china clay (Wattco, England) and a batch of 1 kg was prepared each time for making porous blocks. A viscous slip of powder of above mentioned

composition and water solution of 0.2 polyvinyl alcohol was prepared.

To impart porosity to ceramic body, a known quantity of the slip was continuously mixed with pre-calculated volume of cooled, destabilized 4 % solution of hydrogen peroxide. The slip was then poured into top open stainless steel mould lined with aluminum foil. Strong binder like hydroxyethyl cellulose (1 % solution) was also used in combination with PVA. The moulds containing viscous slip were put into an oven at room temperature and were slowly heated. In a short time, a uniform and steady rising of the mass in the frames occurred, almost like the fermentation of a dough. To ensure free removal of oxygen from all sides, the mould frames were removed as soon as the mass became strong enough to support its own weight. The oven temperature was increased slowly to 80 °C and was maintained there overnight. The cake was then practically dry and ready to be fired.

The porous block of approximate size 13 x 13 x 70 cm was removed from the frames and was slowly heated in an electric furnace to 800 °C and held there for ½ an hour. Then the temperature was raised to 1000 °C with a soaking time of one hour. Finally, the temperature was further raised to 1600 °C and held there for 1 ½ hour before the furnace was switched off and allowed to cool down to the room temperature.

The products developed using different forming methods were tested for the physical properties, *i.e.,* linear shrinkage, bulk density, apparent porosity, water absorption, scratch hardness and thermal conductivity.

The percentage shrinkage was calculated from the difference in diameter or length of the specimen before and after firing divided by the diameter or length of the green body. Bulk density, apparent porosity and water absorption of sintered alumina products were measured according to standard test methods using ASTM C-20-00. To measure the scratch hardness of alumina products, three sets of minerals appearing in Mohs' scale were used. These minerals were Quartz (7 on Mohs' scale), topaz (8 on Mohś scale) and corundum (9 on Mohś Scale).

Thermal conductivity of porous ceramic block was measured using high temperature thermal conductivity tester model HC-60 (digital type), Eko Instruments Trading Co., Ltd. Japan. Test specimen dimensions were 110 mm x 110 mm x 60 mm.

Conclusion

The choice of suitable forming method is determined by various factors which include, ease of forming, cost and quality of the product. Different forming techniques like die pressing, slip casting, extrusion, and a new manufacturing method to make porous high alumina ceramic have been studied in this work.

Die pressing is an economic process for large production runs and is suitable for both simple and complex geometries. Slip casting is a simple method for manufacturing the prototypes and parts with complex shapes whereas extrusion method is used for forming tubes and rods. The novel method developed to manufacture porous ceramic blocks is an achievement in this work which can be used for the production of insulation bricks as constructional material for high temperature furnaces.

Particle size distribution as mentioned in Table-2 was used for forming of ceramics. Higher porosity and water absorption values resulted in lower bulk density values indicate larger particle size and lower sintering temperature used during these studies. Reduction in particle size will help in speeding up sintering process and consequently improve the quality of finished product and make in more economical. Keeping in view the improved grinding mechanisms in order to get finer particle size, future work can be conducted.

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