SYNTHESIS OF ALUMINA POROUS SUPPORTS VIA DIFFERENT COMPACTION ROUTES: VIBRATION AND PRESSING

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ABSTRACT

Porous alumina supports were fabricated using vibration and pressing compaction methods, and their physical and mechanical properties were investigated. After packing of alumina powder with and without silica additive, the samples were sintered at 1325°C - 1625°C for 2 hours. The effects of sintering temperature and silica addition (about 5 mass %) on porosity, thermal conductivity, compressive and flexural strength were studied. Results showed that compaction routes strongly affect sintering and consequently, properties of the samples. Also, samples with high porosity and desirable mechanical properties could be obtained with combination of silica addition and vibration forming. A transition from first stage sintering to intermediate stage has been observed in the temperature domain of 1400-1475°C.

Keywords: porous alumina, compaction, vibration, sintering, mechanical properties, thermal conductivity.

INTRODUCTION

Porous ceramics have many desirable properties such as their light weight, high chemical stability, and low thermal conductivity. These properties are quite attractive for environmental, energy, biotechnology, and other applications. The porous ceramic materials are made by sintering and the physical properties and mechanical strength can be controlled by the microstructure of the sintered powders. To achieve optimal sintered porous ceramics, control of powders parameters, dimensional tolerances, dense and homogeneous packing of powders, as well as of the additives is required [1-3]. Porosity is the main cause for reduction in mechanical properties of ceramic and brittle solids. These classes of ceramics are essential for many industries where high permeability, high surface area, and insulating characteristics are required. The search for porous ceramics with good mechanical strength has stimulated the development of several technologies. The properties of porous ceramics greatly depend on pore morphology, size and distribution [3].

The mechanical properties of porous alumina bodies were correlated with relative density and total porosity [4, 5]. Hashimoto et al. [1] investigated mechanical properties of porous alumina supports fabricated by anisotropic alumina particles with uniaxial pressing at 1 and 3 MPa and heated at 1400°C for 1h. The relative densities of the resulting alumina supports were 25.0 % and 35.5 %, respectively. The compressive strength of the compacts that were uniaxially pressed at 1 and 3 MPa were 0.8 and 4.3 MPa, respectively.

The additives affect properties of sintered alumina. Silica addition decreases shrinkage rate, hardness and toughness of specimens and formation of liquid phase at high temperatures which leads to abnormal grain growth [6-8].

Roudini et al. [9] produced alumina by vibrating the pure powder with narrow size distribution cold isostatic pressing (CIP) and sintering at 1283-1530°C for 2h for synthesis of alumina particle reinforced aluminum composites. They measured only the contiguity, green and
final density of these forms. Their results indicated that the green density of vibrated forms was 0.52 g/cm³ and the final density was 0.52 - 0.60 g/cm³; the contiguity was in 0 - 0.119 range. Despite the existence of a huge number of open-literature investigations on the processing, sintering and properties of porous and dense supports, the synthesis of alumina porous supports via vibration method is more than scarcely discussed.

The forming method, silica addition and sintering temperature dramatically change relative densities and connectivity of alumina particles and consequently, the bending strength, compression strength and thermal conductivity of final samples. It can be concluded that significant improvements in the mechanical properties and thermal conductivity of porous ceramics can be obtained by control of processing (e.g. forming method), of the sintering aids and temperature.

The aim of the present work was the synthesis of porous supports and the study of their physical and mechanical properties. The effects of compaction methods, including vibration and uniaxial pressing, sintering temperatures and silica addition have been investigated.

EXPERIMENTAL

High purity α-Al₂O₃ powder (WDR4, Indal chemical, India) was used as the starting material. The physical properties and chemical composition of this powder declared by the manufacturer are given in Table 1. Two types of granules were prepared for manufacturing of the samples. One was pure alumina powder with properties given in Table 1 and the other mixture of alumina powder and silica (SiO₂) containing 95 mass % Al₂O₃ and 5 mass % SiO₂ (SYLOID AL-1 FP Pharmaceutical Excipient, d₅₀ = 6.8 – 8.1 μm, purity 99.4 %) as an additive. For granulation, 4 mass % PVA (0.2 mass % aqueous solution) was added to the powders, gently blended and aged for 48 h at room temperature. Then, sieved (< 355 μm) granules were used.

Green compacts were formed using the uniaxial pressing and vibration method. For pressed specimens, powders were uniaxially pressed in the pressure range of 2 - 5 MPa in a designed mold, and for vibrated samples, powders were poured in graphite molds and vibrated with a 50 Hz shaker for 5 minutes. Cylindrical green compacts with 18 mm diameter and 45 mm height were produced for the compressive and thermal conductivity tests. Rectangular green compacts with 50.5×12×7 mm³ in size were fabricated for flexural test.

Sintering was performed at 1325, 1400, 1475, 1550 and 1625°C with 2 h soaking time. Heating rates from room temperature to 1000°C and from 1000°C to the sintering temperature were 10°C min⁻¹ and 5°C min⁻¹, respectively. Relative densities of the specimens were determined using mass and dimensions measurements. Porosity was determined with 2 methods: a) by mass and dimensions measurements and b) according to the ASTM C373-88 standard. Three point flexural strength measurements were performed on 58.4×4.70×3.90 mm³ rectangular blocks with a mechanical testing machine (Instron model 4208). Surface area measurements and adsorption isotherms determination were done using a micrometeric apparatus. Structure and microstructure analysis of samples were performed using XRD (Unisantis XMD400) and FE-SEM (HITACHI, S4160) techniques, respectively. Thermal conductivity (W/m K) of specimens were measured with a thermal conduction apparatus (Armfield HT10XC) and calculated by Fourier’s law equation:

\[ q = -K \frac{dT}{dx} \]  

(1)

where, \( q \) is the heat transferred through the sample surface (W m⁻²), \( dx \) is the length (m), and \( dT \) is temperature difference between two heads of samples (°C).

All experiments (except heat conductivity) were performed at least 3 times. Results are presented as the mean ± SD.
RESULTS AND DISCUSSION

A continuous trend of relative density increase and porosity decrease as a function of sintering temperature, both for pressed and vibrated samples, is shown in Fig. 1a and b. Since samples sintered at 1325°C were weak, porosity values of this temperature were not measured. For pressed specimens, porosity has been lower than for vibrated ones due to higher initial compaction of the pressed green compacts. It seems that the difference between porosity values in samples with and without silica, is due to larger mean size of silica and consequently different compactions of green samples.

It can be observed that for vibrated samples, porosity values remains higher than 30 % for sintering temperatures up to 1550°C. For pressed samples, this temperature is 1475°C. A considerable porosity decrease (or relative density increase) due to transition from initial to intermediate stage of sintering is observed both for pressed and vibrated samples within the temperature domain of 1400-1475°C. Within the transition zone, the densification process undergoes acceleration. Similar behavior may also be observed in the shrinking versus sintering temperature curves (Fig. 2).

Surface area and nitrogen adsorption isotherms determined of BET technique versus sintering temperature for vibrated alumina containing SiO₂, are shown in Fig. 3 and Fig. 4, respectively. As seen, a considerable surface...
area and nitrogen adsorption decrease with sintering temperature increase due to open porosity decline is observed.

Funnel shaped corners between large particles can be considered as mesopores (2 - 50 nm) which are good for condense vapor. Mean mesopore size evaluation using nitrogen adsorption isotherms could help the better understanding of the sintering process. Considering a Maxwellian pore volume distribution, the total pore volume \( V_{(p)} \) calculated by the following equation:

\[
V_{(p)} = V_{(0)} \left[ 1 - \left( 1 + \frac{r}{r_0} \right) \exp\left( -\frac{r}{r_0} \right) + \frac{2t}{r_0} \left( \exp\left( -\frac{r}{r_0} \right) - \exp\left( -\frac{r_{\text{max}}}{r_0} \right) \right) \right]
\]

where \( V_{(0)} \) is the total pore volume \( (\text{cm}^3\text{g}^{-1}) \), \( r_0 \) - a constant (nm), \( r \) - the pore radius (nm), \( r_{\text{max}} \) - the threshold pore radius (nm) and \( t \) - the statistical thickness of the adsorbed layer (nm). Using nitrogen adsorption isotherms at sintering temperature and equation (2), the mesopores size distribution could be evaluated at each sintering temperature [10]. The change in the mean mesopores radius as a function of the sintering temperature is shown in Fig. 5. For the last sintering temperature (1625°C) it has not been evaluated due to scattering data. The mean mesopore radius first decreases in the 1400-1475°C range, then increases in the 1475-1550°C temperature range. For this phenomenon, two mechanisms have been suggested. They are shown schematically in Fig. 6. First, sample shrinkage causing reduction of the funnel tip diameter (Fig. 6b) and second - tip filling by different mass transfer mechanisms causing to enlargement of the mesopores (Fig. 6c) [10].

The fracture surface micrographs of specimens are shown in Fig. 7. At 1375°C, particles are partially bonded together with little connectivity and wide porosity for different samples (vibrated/pressed and with/without silica addition) as expected for the initial sintering step of porous ceramics (Fig. 7a &c). In samples without silica, solid state sintering is dominant, as shown in Fig. 7b, but in samples with silica liquid state sintering occurred (Fig. 7d). As sintering temperature increased, porosity decrease and grain growth could be observed (Fig. 7b and d). Obviously, for liquid phase sintered samples, these phenomena were more significant than for the solid state sintered ones.
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The XRD pattern for a sample of alumina with silica additive is shown in Fig. 8. Alumina (Card No: 01-071-1126) is the dominant phase and mullite (Card No: 00-001-613) is a minor phase formed due to reaction between alumina and silica.

Like relative density and shrinkage curves, a continuous trend of compressive and bending strength increase with sintering temperature increase, both for pressed and vibrated samples is shown in Figs. 9 and 10, respectively. Two main parameters affect strengths of samples: porosity and binding nature (solid or liquid phase sintering) of particles. Considering vibrated and pressed samples sintered at 1625°C shows more porosity has led to less strength. Furthermore, in samples with same porosity and different (solid/liquid) state sintering, (for example, pressed samples sintered at 1625°C)

Fig. 7. Microstructure of alumina samples sintered at different temperatures: (a) Pressed sample without silica sintered at 1325°C, (b) Pressed sample without silica sintered at 1625°C (c) Vibrated sample with silica sintered at 1325°C and (d) Vibrated sample with silica sintered at 1625°C.

Fig. 8. XRD pattern of pressed alumina with silica sample sintered at 1625°C.

Fig. 9. Compressive strength versus sintering temperature for pressed and vibrated samples.
particles’ bonding strength is higher when solid state sintering is dominant.

The variation in thermal conductivity of uniaxially pressed and vibrated samples as a function of sintering temperature is shown in Fig. 11. It gives evidence that the sintered alumina at higher temperatures has more thermal conductivity paths between connected particles. Several factors including composition, compaction, grain size and boundaries, rigidity and strength of samples have influence on the thermal conductivity of polycrystalline ceramics. In porous ceramics, porosity is a very important and dominant parameter. With increase of porosity, a dramatic thermal conductivity decrease occurs, as shown in Fig. 11 for pressed and vibrated samples sintered at 1625°C. Moreover, in samples with the same porosity and different (solid/liquid) sintering state, (for example, pressed samples sintered at 1625°C) solid state sintering has led to higher strength of particles’ connections and rigidity and therefore - to increase of thermal conductivity.

CONCLUSIONS

For both pressed/vibrated alumina samples with/without silica addition, a transition from initial to intermediate stage of sintering is observed within the temperature domain of 1475–1550°C. In this region, physical and mechanical properties like surface area, strength and thermal conductivity may strongly change, mainly due to densification progress and porosity decrease.

Vibrated samples without silica sintered at 1550°C can give high porosity (50 %) and appropriate strength. For pressed samples with silica addition, the optimum sintering temperature for giving both proper porosity and strength is 1475°C.

REFERENCES