Thermo-mechanical stability of porous alumina: effect of sintering parameters

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Abstract

Recently, we proposed a two-step heating schedule involving pulse electric current sintering (PECS), a kind of pressure assisted vacuum sintering, and subsequent post-heat treatment in air to fabricate porous alumina support, using commercially available alumina and carbon powders [J. Mater. Res. 18 (2003) 751]. During pressure assisted vacuum sintering, Al$_2$O$_3$–C system of low porosity was obtained and in second stage, i.e. during post-heat treatment in air, carbon particles present in the Al$_2$O$_3$–C system burnt out to form highly porous Al$_2$O$_3$ support. Following our previous brief study, the effects of sintering parameters such as temperature, pressure, and heating rate on the properties of the porous alumina were investigated. The porosity varied between 28 and 38% depending on the sintering parameters. As desired, the pore size distribution did not change with post-heat treatment temperature and hence the mechanical properties as well. It was concurred from this present study that the sintering parameters of PECS greatly influenced pore characteristics and other properties of porous compacts. We admit that the initial composition ratio of powder mixture (Al$_2$O$_3$:C) also plays important role on properties such as porosity, pore size, etc. which is beyond the scope of this present study.

1. Introduction

The thermal stability of porous alumina at high temperature is a crucial challenge for several applications. The necessity to work in high temperature conditions requires the prevention or damaging of catalysts by improving the high temperature stability of the support. Therefore, thermal stability and mechanical properties of the support thus remain key points. Recently, much interest has been shown to catalytic combustion at high temperatures for gas turbines, boilers, and jet engines, and therefore synthesis of catalyst support stable at high temperatures has got an importance [2–4]. In general, commercial catalysts are biphasic; being composed of a support material and one or more active phase component(s). The support provides a porous framework with a pore diameter distribution permitting access to the active sites for the reactants and free exit for the products. In large industrial reactors, the collapse of the structure (catalyst bed) under its own weight should obviously be avoided, because it will result in a severe and not easily corrected pressure drop. Therefore, mechanical strength is required when the catalytic system is submitted to vibrations (car exhaust systems for instance) or to a very high gas or liquid flow velocity. There were many reports, but especially on the thermal stability of porous membranes. Much attention was though paid to improve the mechanical strength of porous support [5–10], there is a lack of reports on the thermal stability of the porous alumina support.

Therefore, the main interest of this work is to develop thermally stable porous alumina support with high strength. The key point of this method is that Al$_2$O$_3$ and carbon powder (Al$_2$O$_3$ + C) compact is heated first in vacuum, instead of air. The approach is schematically illustrated in Fig. 1. Besides traditional methods of developing porosity by burning carbon or fugitive inclusions out in air (Fig. 1), it was proposed earlier [1] that sintering of powder mixture in a low-oxygen atmosphere, for example, in vacuum, and subsequent post-heat treatment in air, leads to porous...
alumina ceramics with pore structure stability. During vacuum sintering, very fine carbon particles are uniformly distributed in alumina matrix either as dispersed particles or as clusters of particles as shown in Fig. 1b. Simultaneously, alumina grains form a strong grain boundary interfaces through volume diffusion. These well-defined surface facets denote the final sintering geometry. When vacuum sintered compacts are further post-heat treated in air, carbon burns out to leave pores. The cluster of agglomerated fine carbon particles would result in large pores, which may prevent the shrinkage of the structure and consequently causes an increased porosity with fully developed neck structure, as shown in Fig. 1b. In this case, the extensive interconnectivity between the particles would prevent substantial consolidation. Therefore, the size of alumina grains after both sintering schedule would remain the same. In continuation to our previous work [1], this study demonstrates in detail, the effect of sintering parameters, such as temperature, heating rate and applied pressure, on pore characteristics and mechanical properties of porous alumina.

2. Experimental procedures

2.1. Fabrication of porous alumina

Porous alumina compacts were fabricated using a two-step sintering process. The starting powders were alumina \( (d_{50} = 0.23 \, \mu m, \text{Taihei Chemicals Co. Ltd, Japan}) \) and carbon black \( (d_{50} = 20 \, nm, \text{Mitsubishi Chemical Corp., Tokyo, Japan}) \). For the fabrication of porous alumina compacts, the following composition of powder mixture was used: 90 and 10 wt.% of alumina and carbon, respectively. The mixture was first wet ball milled in ethanol for 24 h using alumina media. The wet milled slurry was dried in a rotary evaporator at 75 °C and subsequently dried in an oven at 110 °C for 24 h. The dried powder was sieved and used for compaction. Sintering was performed in a pulse electric current sintering equipment, and the experimental details of pulse electric current sintering were explained previously [10,11]. For the present study, the following sintering conditions were considered: (i) temperature \(-1400 \, ^\circ C\), soaking time \(-5 \, min\), pressure \(-5.5 \, MPa\) and heating rate \(-100 \, ^\circ C/min\) (hereafter the specimens sintered under these conditions will be referred as AlC-1); (ii) temperature \(-1500 \, ^\circ C\), soaking time \(-5 \, min\), pressure \(-5.5 \, MPa\) and heating rate \(-100 \, ^\circ C/min\) (hereafter the specimens sintered under these conditions will be referred as AlC-2); (iii) temperature \(-1500 \, ^\circ C\), soaking time \(-5 \, min\), pressure \(-15 \, MPa\) and heating rate \(-100 \, ^\circ C/min\) (hereafter the specimens sintered under these conditions will be referred as AlC-3) and (iv) temperature \(-1500 \, ^\circ C\), soaking time \(-5 \, min\), pressure \(-15 \, MPa\) and heating rate \(-200 \, ^\circ C/min\) (hereafter the specimens sintered under these conditions will be referred as AlC-4). The vacuum sintered compacts were then post-heat treated (post-sintering) in air at different temperatures between 800 and 1300 °C, for a holding time of above 10 h. The weight loss was measured after both heating schedules. The linear shrinkage was evaluated by measuring the axial dimensions. 

2.2. Characterization

Density measurements were carried out by the Archimede’s method using water as medium. The relative density of the vacuum sintered samples \( (\rho_{vs}) \) was calculated by the rule of mixtures considering the theoretical densities of alumina \( (3.989 \, g/cm^3) \) and carbon \( (2.26 \, g/cm^3) \), while the relative density of the porous alumina compacts \( (\rho_{porous}) \) (after post-heat treatment in air) was calculated by

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**Fig. 1.** Schematic illustration of pore formation during (a) conventional sintering and (b) two-step sintering (vacuum and post-heat treatment in air); P, pore; A, alumina; C, carbon.
considering the theoretical density of alumina alone. i.e.\[ \rho_{vs} = \frac{w_{Al_2O_3} + w_C}{\left( \frac{w_{Al_2O_3}}{\rho_{Al_2O_3}} \right) + \left( \frac{w_C}{\rho_C} \right)} \] where \( w \) and \( \rho \) are the weight fraction and the density of the phases, respectively. X-ray diffraction analysis was carried out for both vacuum sintered and post-heat treated samples, in order to identify any trace of new phases and/or carbon. The surface area measurements were carried out for the porous compacts using BET method, by means of N\(_2\) adsorption, at 77 K (Model No. AS3B-Kr, Quantachrome Corp., Boynton Beach, FL). The surface area was measured by multiple point BET, after outgassing at 350°C for more than 1 h. The pore size distribution of the sintered porous Al\(_2\)O\(_3\) compacts was determined by Hg porosimetry (Autopore 9220, Shimadzu Corp., Japan). The elastic modulus of porous Al\(_2\)O\(_3\) specimens was measured by the pulse echo method, according to JIS 1602. The values represent the average value of at least six measurements. The fracture surface of porous alumina was analysed by scanning electron microscopy (SEM, Model S-5000, Hitachi Ltd., Tokyo, Japan).

### 3. Results and discussion

#### 3.1. Fabrication of porous compacts

The characteristic results of the properties of vacuum sintered samples (pulse electric current sintering (PECS), in this study) and post-heat treated samples are given in Table 1. It is observed from Table 1 that there is no appreciable change in the properties of AlC-1 and AlC-2 porous compacts. That is, when the applied pressure is as low as 5.5 MPa, increase in temperature does not enhance the densification of Al\(_2\)O\(_3\)–C ceramics, and their relative density (75% of the theoretical density) remains the same. But sufficient increase in either pressure and/or heating rate, i.e. from 5 to 15 MPa and from 100 to 200°C/min, respectively, has little effect on densification (AlC-3, 83% and AlC-4, 86% of the theoretical density), though the specimens are not completely densified. All these specimens after vacuum sintering had a weight loss of less than 2%. This negligible weight loss might be the evaporation of Al\(_2\)O\(_3\), which forms by reaction between Al\(_2\)O\(_3\) and C due to low oxygen partial pressure [12], according to the following reaction:

\[ \langle Al_2O_3 \rangle + 2 \langle C \rangle \leftrightarrow \{ Al_2O \} \uparrow + 2 \{ CO \} \uparrow \] (2)

The formation of Al\(_2\)O is more probable than formation of other existing gaseous products (such as AlO, Al\(_2\)O\(_2\)), according to thermodynamic calculations using the Barin’s data of Gibbs free energies of pure substances [13]. However, the occurrence of this reaction was less feasible than almost all the carbon particles were retained in the alumina matrix. When the compacts were subjected to post-heat treated in air at different temperatures between 800 and 1300°C, for more than 10 h, the porosity varied from ~28 to 39%. This increase in porosity for the post-heat treated specimens is reasonable; the carbon particles burn out according to the following reaction,

\[ 2\langle C \rangle \leftrightarrow 2\{ CO \} \uparrow \] (3)

It must be pointed out here that the diffusion of Al\(_2\)O\(_3\) grains predominantly takes place during sintering in non-oxidizing atmosphere itself, but not during the successive sintering in air while burning out of carbon. There was no shrinkage observed after the second stage, while the weight loss was around 9–9.5% for all the compacts. This implies that the total amount of carbon burnt out in all the compacts remains

| Post-heat treatment temperature (°C) | AlC-1 | AlC-2 | AlC-3 | AlC-4 |
|------------------------------------|-------|-------|-------|-------|
|                                   | Porosity (%) | Surface area (m\(^2\)/g) | Pore size (µm) | Surface area (m\(^2\)/g) | Pore size (µm) | Surface area (m\(^2\)/g) | Pore size (µm) | Surface area (m\(^2\)/g) | Pore size (µm) |
| PECS (1500)                        | 17.5  | –     | 17.5  | –     | 17.5  | –     | 16.2  | –     | –     | –     |
| 800                                | 36.1  | 2.06  | 38.2  | 1.5   | 30.4  | 1.8   | 29    | 1.1   | 0.19 |
| 900                                | 37.3  | –     | 36.4  | 1.8   | 30.3  | 1.9   | 29.2  | 1.2   | 0.12 |
| 1000                               | 38.6  | 3.36  | 36.9  | 1.5   | 31.5  | 3.41  | 29.4  | 1.5   | 0.15 |
| 1100                               | 38.2  | –     | 30.5  | –     | 30.7  | –     | 28.7  | –     | 0.11 |
| 1200                               | 37.2  | –     | 35.7  | 1.4   | 28.4  | –     | 28    | –     | 0.11 |
| 1300                               | 34.9  | 1.91  | 30.7  | –     | 28.7  | –     | 28    | –     | 0.11 |

AlC-1: sintering temperature, 1400°C; pressure, 5.5 MPa; heating rate, 100°C/min; AlC-2: sintering temperature, 1500°C; pressure, 5.5 MPa; heating rate, 100°C/min; AlC-3: sintering temperature, 1500°C; pressure, 15 MPa; heating rate, 100°C/min; AlC-4: sintering temperature, 1500°C; pressure, 15 MPa; heating rate, 200°C/min.
the same, i.e. carbon that was added with alumina burnt out completely. As anticipated, AlC-3 and AlC-4 specimens, i.e. the compacts sintered at high pressure and high heating rate, had a lower volume fraction of porosity when compared with the other two specimens. When specimens were post-heat treated at respective temperatures ranging from 800 to 1300 °C for above 10 h, there was very little or no reduction in porosity of the specimens. This shows a character of non-dependency of porosity as a function of post-heat treatment temperature. It could be suggested that porosity corresponds to initial amount of carbon and the sintering condition in first stage.

3.2. X-ray diffraction

The XRD patterns for specimens vacuum sintered at 1500 °C and post-heat treated at 800, 1000 and 1300 °C are shown in Fig. 2. It can be seen that there was no reaction between Al₂O₃ and C during vacuum sintering. The peak indicated by arrow in Fig. 2 corresponds to unknown phase, might be attributed to carbon containing phase. The specimens after post-heat treatment did not show any trace of newly formed or carbon containing peaks. This confirms the complete burnt out of carbon particles in the specimens.

3.3. Surface area and pore size distribution

The pore size distributions of the porous compacts are shown in Fig. 3. Fig. 3a shows the pore size distributions of specimens post-heat treated at 1300 °C with respect to their sintering conditions and Fig. 3b shows the pore size distributions of AlC-3 specimens with respect to post-heat treatment temperature. Fig. 3a reveals that the average pore size was dependent on sintering parameters and Fig. 3b reveals that the average pore size of specimens remained same for all post-heat treated temperatures, though there was an increase in pore volume with an increase in post-heat treatment temperature. It is generally understood from Fig. 3 that all specimens had narrow pore size distribution and sizes of few pores fell on both side of the sharp peak (not clearly seen due to multiple graphs). As can be observed in Table 1, the surface area of the specimens did behave similarly and it did not change with post-heat treatment temperature. This clearly demonstrates the stability in terms of pore structure and physical properties of porous compacts fabricated in this study.

3.4. Microstructure

The microstructure analysis by SEM (Fig. 4) gives a clear understanding of the mechanism of pore structure evolution during a two-step sintering process. Fig. 4a shows the SEM micrograph of the vacuum sintered compact. The vacuum sintering of the mixture of alumina and carbon, and subsequent heat treatment in air leads to a homogeneous porous structure interconnected by well-defined faceted alumina grains. In vacuum sintered specimens, we still observe carbon in the alumina matrix uniformly distributed either as very fine particles or as clusters of carbon particles. As a consequence, the compacts could not be fully sintered at 1500 °C. Desirably, the carbon particles located between the alumina grains either as a fine particle or as a cluster of particles, pin the grain boundary mobility of alumina grains and this is the reason for the hindered grain growth in these specimens. Fig. 4b and c are SEM micrographs of porous alumina specimen after post-heat treatment in air at 1000 and 1300 °C, respectively, showing many interconnected pore channel and large voids. Figs. 4b and c are typical examples of sintering occurring in a many-particle system where the particles have a fully developed neck structure. These well-defined surface facets denote the final sintering
geometry. In this case, the extensive interconnectivity between the particles has prevented substantial consolidation. Therefore, the size of the alumina grains after both sintering schedules remains same, proving that no grain growth occurred after the second step. As an apparent end-density phenomenon is noted, it may be reasoned out from the microstructure that the grains have adhered to each other and sintered with apparent ‘reorientation’ of the sintered particles to form low energy interfaces. As a consequence, in Table 1, the median pore size and the surface area of the specimens did not vary with an increase in post-heat treatment temperature. However, the pore characteristics depend mainly on the sintering condition. The arrows indicated in Fig. 4d referred to necks grown in porous alumina. It can be clearly seen that cracks occurred through necks.

3.5. Mechanical properties

Fig. 5 shows the results of the mechanical properties of porous alumina specimens. It is observed that the mechanical properties are independent on the sintering temperature. To make a point here, the fracture strength does not either depend on the porosity of the specimens, but is closely related with sintering parameters that include temperature, pressure and heating rate. There is no significant difference between AIC-1 and AIC-2 specimens in their values. AIC-3 and AIC-4 specimens showed a significant improvement in their strength and modulus. This improvement is probably attributed to the formation of strong bonding between contiguous alumina grains due to

![Fig. 4. SEM micrographs of porous alumina compacts sintered in vacuum (1500 °C) post-heat treated in air (1000 °C) post-heat treated in air (1300 °C) showing strong neck as well as crack occurring at the neck region.](image)

![Fig. 5. Effect of post-heat treatment temperature on the mechanical properties of porous alumina (holding time: 10 h).](image)
high pressure and high heating rate during the PECS process. Previously [11], it has also been documented that the sintering parameters of PECS greatly influence densification, grain size, microstructure and hence the mechanical properties of ceramics. The sintered porous alumina specimens exhibited high strength (250 MPa) than previously cited values (~150 MPa) [6–9]. The porous alumina specimens having a porosity of 28% possessed a fracture strength of as high as 250 MPa. This is because, both gaseous products of the reactions (2) and (3) move towards the sample surface. During this migration, they might condense at the powder surfaces with high chemical potential by reverse chemical reaction and thus form strong necks between the particles (evaporation–condensation mechanism of sintering) [12]. That is, there is a higher partial pressure of oxygen near the sample surface than inside the ceramic body. Therefore, on the surface the back oxidation of Al2O can occur as follows,

\[
\{\text{Al}_2\text{O}_3\}^{\text{solid}} + \{\text{O}_2\}^{\text{gas}} \rightarrow \{\text{Al}_2\text{O}_3\}^{\text{solid}}
\]  

This results in the development of the dense surface layer, as clearly seen on the SEM micrographs (Fig. 4b–d). This mechanism increases the strength of the sample but it does not increase the sample density. Furthermore, in the present work, failure was observed to occur always at the necks between particles, as shown in Fig. 4d. It has been shown [13–16] that the fracture strength of porous ceramics is determined by the actual load-bearing area or the minimum solid area. Therefore, the increase in fracture strength is reasonable. These well-grown necks subsequently increased the elastic modulus of the porous alumina specimens and found to be not dependent on post-heat treatment temperature. As there was no change in porosity between specimens post-heat treated at different temperatures, there was a little or no variation in strength and modulus values of these specimens with an increase in the post-heat treatment temperature (Fig. 5). And this concurs the stability of mechanical properties of porous alumina compacts.

4. Conclusion

By optimizing the sintering parameters in the proposed two-step sintering process, a desired volume fraction of porosity could be attained. Besides, the sintering parameters influence the porosity and pore characteristics of the specimens. Due to strong grain bonding between the hexagonal alumina grains, the porous compacts exhibit very high strength and modulus. The fracture strength of the porous specimens is closely related to the sintering parameters. The thermal stability and the improved mechanical properties of the porous alumina compacts fabricated by this method are very much appreciated. As apparently there is no shrinkage between vacuum sintering and post-heat treatment in air, this method can be helpful in designing complicated porous structure. Another important aspect of this study is, the porous compacts are initially sintered at very high temperatures and hence, the application temperature of this porous compacts is also high.

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