Formation of porous Al$_2$O$_3$–SiO$_2$ composite ceramics by electrostatic assembly

Wai Kian TAN$^{1,†}$, Keita TSUZUKI$^2$, Atsushi YOKOI$^1$, Go KAWAMURA$^2$, Atsunori MATSUDA$^2$ and Hiroyuki MUTO$^{1,2,††}$

$^1$Institute of Liberal Arts and Sciences, Toyohashi University of Technology, Toyohashi, Aichi 441–8580, Japan
$^2$Department of Electrical and Electronic Information Engineering, Toyohashi University of Technology, Toyohashi, Aichi 441–8580, Japan

Porous ceramics possess many unique properties that are used for multifunctional applications. This study reports on a feasible formation of Al$_2$O$_3$–SiO$_2$ composite ceramics using an electrostatic assembly technique without any use of pore former. Homogeneously SiO$_2$-particles-decorated Al$_2$O$_3$ composites were first obtained using electrostatic assembly. The amount of SiO$_2$ added was varied at 12 and 40 vol.%. The Al$_2$O$_3$–SiO$_2$ composite powders were then pressed into green bodies and sintered at different temperatures from 1300 to 1600 °C. The morphologies, open porosity and crystallinity as well as the mechanical properties of the Al$_2$O$_3$–SiO$_2$ composite ceramics were systematically characterized. The microstructural observation demonstrated that the porosity was altered by changing the amount of SiO$_2$ added as well as sintering temperature. A mullite phase was observed after sintering at 1600 °C. The elastic modulus and yield stress were found to correlate with the open porosity of the Al$_2$O$_3$–SiO$_2$ composites.

©2020 The Ceramic Society of Japan. All rights reserved.

Key-words : Composite particles, Electrostatic assembly, Porous ceramics, Al$_2$O$_3$, SiO$_2$

[Received March 25, 2020; Accepted May 8, 2020]

1. Introduction

Ceramics possess excellent characteristics such as a high degree of hardness, good heat resistance, corrosion resistance and chemical resistance that enables their usage in various applications. Recently, researchers have focused on the innovative processing technologies of porous ceramics in order to improve their properties. Porous ceramics possess unique mechanical properties that cannot be achieved with dense ceramic structures. Various fabrication techniques have been used to produce porous alumina ceramics such as sol-gel, organic foam, and freeze-casting. One of the conventional methods for porous ceramics fabrication is partial sintering. A homogeneous porous ceramic can be obtained by tailoring the microstructure such as size and arrangement of the ceramic particles, to permit a narrow size distribution. The inability to obtain a homogeneous distribution during the mixing stage prior to partial sintering remain the biggest obstacle in the fabrication of porous ceramics. Conventional mixing method such as mechanical milling often results in the formation of unwanted agglomeration and poor materials distribution, which eventually generates inferior ceramic properties. One solution is to use homogeneously designed precursor composite particles, obtained by electrostatic assembly. This method has been used for feasible controlled composite particles formation, aerosol deposited film with desired optical properties, efficient thermal conductive composite materials and infrared filtering composite materials. In this study, composite particles consisting of alumina (Al$_2$O$_3$) and silica (SiO$_2$) with different coverage percentages were fabricated and sintered in order to investigate the feasible formation of porous Al$_2$O$_3$–SiO$_2$ ceramics without the use of any pore-forming agent. By carefully designing the ceramic particles, a dense green body was obtained prior to sintering in order to promote better mechanical properties. Besides that, porous ceramics with controllable microstructures have also been used for applications such as heat insulation, sound dampening, and bio-ceramics as well as, catalyst carriers for lightweight structural components. In the design of porous ceramics, not only is the pore distribution important, but the continuous or graded/inclined porosity also plays an important role in the final properties of the ceramics due to a compromise between the load resistance of the dense layer and the insulating porous layer. The motivation of this study is to look at the formation of...
porous Al₂O₃–SiO₂ ceramics without the use of pore former which could cause aggregation and influence the pore distribution. This can be achieved using electrostatic assembly, which allows the amount control of secondary particles (SiO₂) decoration onto the primary particles (Al₂O₃). Using Al₂O₃ that has a larger particle size as the primary particles with a high sintering temperature and smaller SiO₂ particles as secondary particles with a low sintering temperature, the formation of a bridge-like interconnected porous ceramics structure was targeted after sintering of the green body. Alumina-mullite has been attracting researchers’ attention due to its improved thermal and mechanical properties. Porous alumina-mullite composite was also produced as opposed to most reported work that focused on the formation of dense alumina-mullite structure. Different volume percentages of SiO₂ addition to Al₂O₃ was carried out and the porosity as well as the mechanical properties of the porous Al₂O₃–SiO₂ ceramics were investigated systematically as a function of sintering temperature.

2. Experimental procedures

2.1 Materials

The experiments were carried out using commercially available monodispersed spherical SiO₂ particles (average particle diameter 0.25 μm, Ube EXSYMO) and Al₂O₃ particles (average particle size 1.5 μm, Sumitomo Chemical Co., Ltd.). The polycation and polyanion used were polydiallyldimethyl ammonium chloride (PDDA) (average molecular weight 100,000 to 200,000, Sigma-Aldrich) and polyodium styrenesulfonate (PSS) as polyanion (average molecular weight 70,000, Sigma-Aldrich), respectively. 3)

2.2 Formation of Al₂O₃–SiO₂ composites by electrostatic assembly

The Al₂O₃ and SiO₂ particles were used as the primary and secondary particles, respectively in the electrostatic assembly process. The surface charge of the primary Al₂O₃ particles were first adjusted using PSS and PDDA,11) while the secondary SiO₂ particles were adjusted with the immersion sequence of PDDA and PSS.3) After that, the Al₂O₃ and SiO₂ particles possessed positive and negative surface charge, respectively. The detail about the surface charge modification as well as experimental conditions used are reported elsewhere.3,11) Figure 1 shows the images of the starting precursors and the schematic of the Al₂O₃–SiO₂ composites formation. The Al₂O₃–SiO₂ composites were obtained after mixing both suspensions and stirring at room temperature. In this study, 12 and 40 vol.% of SiO₂ particles were added to Al₂O₃ particles. The green body obtained using these composite powders was sintered at temperatures of 1300, 1400, 1500 and 1600 °C prior to characterization.

2.3 Preparation and sintering of green body

Prior to the sintering process, the slip casting method was used to produce the green bodies of the composite powders. The obtained composite particle suspension was poured into a vinyl chloride container placed on gypsum, and allowed to stand overnight to obtain a cylindrical green body (diameter 10 mm, height 3 mm). The obtained green body was then placed into a furnace and sintered at a temperature range from 1300 to 1600 °C for 2 h in the atmosphere.

2.4 Materials characterization

The cross sectional view of the sintered body was observed using an S-4800 Field Emission Scanning Electron Microscope (FE-SEM, Hitachi S-4800). The porosity of the sintered body was obtained using Archimedes method. The open porosity (Pₒ) was calculated according to Eq. (1). The sintered body was first immersed into boiling water for 3 h to remove the entrapped air within the sample, and the weight obtained was W₁. After that, the sample was weighed again after wiping the moisture from the pellet’s surface. The weight obtained was taken as W₂. Finally, the wet sample was allowed to dry in an oven overnight and the dry weight obtained was W₃. The values of W₁, W₂ and W₃ were used for the open porosity calculation according to Eq. (1).

\[ Pₒ = \frac{W₂ - W₃}{W₂ - W₁} \times 100 \% \] (1)

X-ray diffraction (XRD) characterization was done using an X-ray diffractometer (Rigaku RINT 2500) with Cu Kα radiation (30 kV, 20 mA) from 2θ = 15–45° at a scan rate of 2° min⁻¹. In order to determine the mechanical properties of the sample obtained after sintering at different temperatures, an indentation test was carried out. Each indentation test was repeated three times. A Rockwell indenter that consisted of a diamond (Ei = 1050 GPa, ν = 0.20) with a nominal radius of curvature, R = 200 μm embedded in a conical tip with an apex angle of 120° was used for the measurement. The indentation equipment used was A & D, RTF-1250 (Tokyo, Japan).

3. Results and discussion

3.1 Morphological observation

The morphologies of the Al₂O₃–SiO₂ composites obtained after electrostatic assembly are shown in Fig. 2.
From the higher magnification SEM images which are shown in inset of Figs. 2(a) and 2(b), it can be seen that SiO$_2$ particles were adsorbed homogeneously on the surface of Al$_2$O$_3$ particles. The zeta potential for Al$_2$O$_3$ and SiO$_2$ after polyelectrolyte adsorption was approximately $+50$ mV and $-50$ mV, respectively.\textsuperscript{3,11} As-received SiO$_2$ particles exhibit a zeta potential of approximately $-30$ mV and for electrostatic assembly, a zeta potential of higher than $+/-40$ mV is preferred for a stable electrostatic adsorption process.\textsuperscript{6,12} By comparing Figs. 2(a) and 2(b), it can be seen that the amount of SiO$_2$ particles decorated on the surface of the Al$_2$O$_3$ was different, indicating the possible control of secondary particles adsorption onto the primary Al$_2$O$_3$ particle. The composite particle powders, which consisted of 12 and 40 vol.% SiO$_2$ were sintered after green body compaction. The morphologies of the sintered porous Al$_2$O$_3$–SiO$_2$ ceramics are shown in Fig. 3 with higher magnification images shown as an inset. The samples obtained after sintering at 1300, 1400, 1500 and 1600°C are labelled as Figs. 3(a)–3(d) respectively. The composite particles with 12 and 40 vol.% SiO$_2$ additions are marked with (i) and (ii), respectively. By comparing the SEM images sintered at 1300°C in Figs. 3(a)(i) and (ii), it can be observed that a porous structure was formed, the size of the Al$_2$O$_3$ particle was approximately 1.5 µm, and the SiO$_2$ particles that were positioned between the Al$_2$O$_3$ particles appeared to be sintered, forming a bridge-like structure as shown in the inset. In the three-dimensional linkage of the Al$_2$O$_3$ particles, open pores were formed, resulting in the formation of porous structured Al$_2$O$_3$–SiO$_2$ ceramic composites. At the higher sintering temperature of 1400 to 1600°C, the bridge-like interconnected structure appeared to be thicker. This was due to the higher densification phenomenon that occurred at the interface between Al$_2$O$_3$ and SiO$_2$ when higher activation energy was supplied with a higher sintering temperature. At 1600°C, a thick and short interconnected necking structure was obtained due to partial melting of SiO$_2$ particles at the interface of Al$_2$O$_3$.

3.2 The relationship between sintering temperature and the open porosity of Al$_2$O$_3$–SiO$_2$ composite ceramics

The open porosity values obtained for the Al$_2$O$_3$–SiO$_2$ composites with 12 and 40 vol.% SiO$_2$ using Eq. (1) were plotted against sintering temperature. The graph obtained is shown in Fig. 4. From the results, it can be confirmed that the degree of densification increased with sintering temperature from 1300 to 1600°C as the open porosity values reduced with the higher sintering temperature. Both samples with 12 and 40 vol.% SiO$_2$ addition exhibited a similar trend, which tallies with the SEM observations obtained. It is noteworthy that the overall open porosity values for Al$_2$O$_3$–SiO$_2$ composites with 12 vol.% were higher compared to those of 40 vol.% This is due to a higher pore volume generation, as lesser SiO$_2$ particle content would lead to reduced crosslinking. This also shows that the open porosity of the Al$_2$O$_3$–SiO$_2$ composites can be altered by adjusting the amount of SiO$_2$ addition.

3.3 Crystallinity of the Al$_2$O$_3$–SiO$_2$ composite ceramics

Figure 5 shows the XRD patterns of the Al$_2$O$_3$–SiO$_2$ composite ceramics with 12 vol.% SiO$_2$ addition after sintering at 1300 to 1600°C. The XRD pattern for the Al$_2$O$_3$–SiO$_2$ composite sintered at 1300°C only exhibited peaks of α-Al$_2$O$_3$. Similar observation is reported by Li et al., from sintering of Al$_2$O$_3$–SiO$_2$ microspheres obtained by rotary atomizer spray drying.\textsuperscript{13} Upon higher sintering temperature of 1400 and 1500°C, a peak that correlated to SiO$_2$ cristobalite was observed at 22°.\textsuperscript{13} Upon sintering at 1600°C, the peak related to cristobalite disappeared while a mullite phase was observed indicating mullite formation.\textsuperscript{14} The XRD peaks that correlate to Al$_2$O$_3$ also reduced when the mullite phase appeared, which corroborates with the findings of Li et al.\textsuperscript{13} The mullite phase is thought to be generated at the surface contact area of Al$_2$O$_3$ and SiO$_2$. On the other hand, the XRD patterns for the Al$_2$O$_3$–SiO$_2$ composites with 40 vol.% SiO$_2$ added are shown in Fig. 6. Although a similar trend was observed with the 12 vol.% sample, by comparing the XRD intensity ratio of alumina and mullite phase for both Al$_2$O$_3$–SiO$_2$ composite ceramics (12 and 40 vol.%), obtained after sintered at 1600°C, the ratio of Al$_2$O$_3$; mullite was 75:25 and 61:39 for the samples with 12 and 40 vol.% SiO$_2$ addition, respectively. This further confirms that higher amounts of mullite were generated when more SiO$_2$ particles were added into the composites which promoted the formation of mullite compounds.
Fig. 3. SEM images showing the morphologies of the Al₂O₃–SiO₂ composites obtained after sintering at (a) 1300, (b) 1400, (c) 1500 and (d) 1600 °C, respectively. The images labelled (i) and (ii) represent the vol.% of SiO₂ added at 12 and 40 vol.%, respectively.
3.4 Mechanical properties of the porous Al₂O₃–SiO₂ composite ceramics

The elastic modulus of the porous Al₂O₃–SiO₂ composite ceramics obtained against sintering temperature is shown in Fig. 7. The results obtained indicated that elastic modulus for both samples increased with sintering temperature. For the composite sample with 12 vol.% addition of SiO₂, the elastic modulus increased gradually from approximately 20 to 100 GPa at sintering temperatures from 1300 to 1600 °C. As for the composite sample with 40 vol.% SiO₂ addition, the elastic modulus ranged from approximately 50 to 200 GPa which marked a 100% increment from the 12 vol.% SiO₂ added composite at the same temperature range. The elastic modulus also exhibited a more exponential increment from approximately 70 to 200 GPa from 1400 to 1600 °C. The increment is due to the onset of mullite formation which possesses good mechanical properties leading to higher elastic modulus when heat-treated beyond 1500 °C.15) Higher sintering temperature is also reported to promote mullite formation which improved the bending strength.14) Ma et al. also reported that the porosity sharply reduced upon annealing beyond 1500 °C due to densification and mullization process, that caused volume expansion leading to enhanced mechanical properties.14) This abovementioned observation also correlates with the SEM images shown in Fig. 3(d)(ii), where shorter and thicker interconnected necking structures were observed upon sintering of the 40 vol.% added SiO₂ composite powders at 1600 °C. The highest degree of local densification with a dense structure formation was observed in Fig. 3(d)(ii). Although exhibiting a high elastic modulus, the dense structure was not an ideal porous ceramic. A similar trend was also obtained for the yield stress of the porous Al₂O₃–SiO₂ composite ceramics as shown in Fig. 8. The yield stress for 12 and 40 vol.% SiO₂ added composites were between the ranges of 0.8–4.1 and 2.1–7.8 GPa, respectively. In order to compare the relationship between the open porosity of both 12 and 40 vol.% SiO₂ added, Al₂O₃–SiO₂ composite ceramics against the elastic modulus and yield stress obtained, the graphs of elastic modulus and yield stress are plotted against open porosity and shown in Figs. 9(a) and 9(b), respectively. The graph shows that the elastic modulus reduced from approximately 200 to 15 GPa with open porosity from 14 to 43%. The samples produced with 12 vol.% SiO₂ addition exhibited lower elastic modulus and higher open porosity values. A similar trend was observed for yield
stress, as shown in Fig. 9(b) which concludes that the elastic modulus and the yield strength of the porous Al$_2$O$_3$–SiO$_2$ composite ceramics were intercorrelation of the sintering temperature, the microstructure and the open porosity.~~

### 4. Conclusions

The formation of porous Al$_2$O$_3$–SiO$_2$ composite ceramics was demonstrated using electrostatic assembly. SiO$_2$ particles with different volume percentages of 12 and 40 vol.% were decorated onto the primary Al$_2$O$_3$ particles to obtain the composite particles powder, that were used to form the green body prior to sintering. The morphologies, crystallinity, open porosity and mechanical properties of the sintered bodies obtained at different annealing temperatures from 1300 to 1600°C were reported. Interconnected bridge-like structures were observed after sintering, forming porous Al$_2$O$_3$–SiO$_2$ composite ceramics. The findings obtained demonstrated that porosity could be controlled by adjusting the sintering temperature as well as the amount of SiO$_2$ added during the electrostatic assembly stage. The microstructure and the porosity of Al$_2$O$_3$–SiO$_2$ composite ceramics were crucial factors in determining the mechanical properties of the porous ceramics. This study demonstrated the feasibility of fabricating porous composite ceramics with good homogeneity without using any pore former. This technique will not only reduce contamination but also allow porosity control, which directly influences the physical properties of the composite ceramics.

### Acknowledgements

Prof. Hiroyuki Muto and Dr. Wai Kian Tan would like to acknowledge Japan Society for Promotion of Science (JSPS) Grant-in-Aid for Scientific Research JP18H01706 and KAKENHI Early-Career Scientist JP18K14013 for funding of this research work.

### Declaration Funding

Japan Society for the Promotion of Science (JSPS) Grant-in-Aid for Scientific Research JP18H01706, JSPS KAKENHI Early-Career Scientist JP18K14013, Toyohashi University of Technology Research Support Fund and Science of New-Class of Materials Based on Elemental Multiplicity and Heterogeneity (Grant No. 18H05452) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT, Japan).

### References

1. M. S. Ali, M. A. A. Hanim, S. M. Tahir, C. N. A. Jaafar, M. Norkhairunnisa and K. A. Matorri, *J. Ceram. Soc. Jpn.*, 125, 402–412 (2017).
2. T. Ohi and M. Fukushima, *Int. Mater. Rev.*, 57, 115–131 (2012).
3. W. K. Tan, Y. Araki, A. Yokoi, G. Kawamura, A. Matsuda and H. Muto, *Nanoscale Res. Lett.*, 14, 297–306 (2019).
4. W. K. Tan, Y. Shigeta, A. Yokoi, G. Kawamura, A. Matsuda and H. Muto, *Appl. Surf. Sci.*, 483, 212–218 (2019).
5. A. Yokoi, W. K. Tan, T. Kuroda, G. Kawamura, A. Matsuda and H. Muto, *Nanomaterials*, 10, 134–143 (2020).
6. W. K. Tan, A. Yokoi, G. Kawamura, A. Matsuda and H. Muto, *Nanomaterials*, 9, 886–896 (2019).
7. S. Meille, M. Lombardi, J. Chevalier and L. Montanaro, *J. Eur. Ceram. Soc.*, 32, 3959–3967 (2012).
8. C. Petit, L. Montanaro and P. Palmero, *Int. J. Appl. Ceram. Techn.*, 15, 820–840 (2018).
9. A. R. Studart, U. T. Gonzenbach, E. Tervoort and L. J. Gauckler, *J. Am. Ceram. Soc.*, 89, 1771–1789 (2006).
10. I. Zake-Tiluga, R. Svinka and V. Svinka, *Ceram. Int.*, 40, 3071–3077 (2014).
11. W. K. Tan, N. Hakiri, A. Yokoi, G. Kawamura, A. Matsuda and H. Muto, *Nanoscale Res. Lett.*, 14, 245–252 (2019).
12. C. Q. Peng, Y. S. Thio and R. A. Gerhardt, *Nanotechnology*, 19, 505603 (2008).
13. N. Li, X.-Y. Zhang, Y.-N. Qu, J. Xu, N. Ma, K. Gan, W.-L. Huo and J.-L. Yang, *J. Eur. Ceram. Soc.*, 36, 2807–2812 (2016).
14. J. Ma, X. Xi, C. He, W. Chen, W. Tian, J. Li, C. Wang, B. Luo, A. Shui and K. Hua, *Ceram. Int.*, 45, 17946–17954 (2019).
15. B. Dong, M. Yang, F. Wang, L. Hao, X. Xu, G. Wang and S. Agathopoulos, *Mater. Lett.*, 240, 140–143 (2019).
16. K. Yoshida, H. Tsukidate, A. Murakami and H. Miyata, *Journal of Solid Mechanics and Materials Engineering*, 2, 1060–1069 (2008).