Enhancement of Porosity and Strength of Porous Al_2O_3 Ceramics by $\text{Al}(\text{H}_2\text{PO}_4)_3$ Addition

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ABSTRACT

Porous alumina ceramics with addition of 0, 5, 10, 15, and 20 wt% $\text{Al}(\text{H}_2\text{PO}_4)_3$ were sintered at 1300, 1350, and 1400°C. The effects of the $\text{Al}(\text{H}_2\text{PO}_4)_3$ addition on crystal phases, water absorption, open porosity, pore size distribution, microstructures, and flexural strength were studied extensively. The experimental results revealed that only characteristic peaks of corundum were indexed in the XRD patterns of the as-prepared porous ceramics. The water absorption and open porosity of the porous Al_2O_3 ceramics increased remarkably with an increase in $\text{Al}(\text{H}_2\text{PO}_4)_3$ addition. The flexural strength first increased to a maximum value when 5 wt% $\text{Al}(\text{H}_2\text{PO}_4)_3$ was added and then decreased as additional $\text{Al}(\text{H}_2\text{PO}_4)_3$ was further added. SEM images showed that the average Al_2O_3 grain size in the porous ceramics changed in an opposite way as the flexural strength. The porous Al_2O_3 ceramics with 10 wt% $\text{Al}(\text{H}_2\text{PO}_4)_3$ addition exhibited comparable flexural strength to the ceramics without $\text{Al}(\text{H}_2\text{PO}_4)_3$ addition, although the latter had much higher porosity.

Key words : Ceramics, Porous materials, Al_2O_3 , $\text{Al}(\text{H}_2\text{PO}_4)_3$

1. Introduction

Porous ceramics have been used widely in many areas of industry involving catalyst carriers, membrane supports, filters, and biomaterials.^{1–3)} For these applications, many excellent properties including high porosity and good mechanical strength are typically required.³⁾ Generally, higher porosity tends to result in a certain decrease in mechanical strength.⁴⁾ Thus, it is important to improve the mechanical strength of porous ceramics with higher porosity, and many studies have been carried out to investigate the relationship between porosity and mechanical strength of porous ceramics.^{5–9)} For example, Chang⁷⁾ reported that fine Al_2O_3 grains with a lower degree of agglomeration could increase the bending strength of porous Al_2O_3 ceramics with a slight increase in porosity. Liu⁸⁾ found that pores smaller than 2 μm were helpful for improving strength whereas pores larger than 14 μm had the opposite effect. Tang⁹⁾ developed a routine including directional freeze casting and annealing in a tertiary butyl alcohol (TBA)–water–sucrose system that could significantly improve the compressive strength of porous alumina ceramics. However, until now, the effects of $\text{Al}(\text{H}_2\text{PO}_4)_3$ addition on the porosity and flexural strength of porous Al_2O_3 ceramics had not been investigated in detail. In this work, $\text{Al}(\text{H}_2\text{PO}_4)_3$ was used as an

additive to fabricate porous Al_2O_3 ceramics, and the effects of $\text{Al}(\text{H}_2\text{PO}_4)_3$ addition on the porosity and flexural strength of the ceramics were studied extensively.

2. Experimental Procedure

Al_2O_3 powders with purity > 99.0 wt% were used in this work. The average particle size of these powders was about 0.9 μm . The Al_2O_3 powders were mixed with 0.5 wt% polyvinyl alcohol (PVA) solution (concentration of 5 wt%) and chemically pure $\text{Al}(\text{H}_2\text{PO}_4)_3$ with additions of 0, 5, 10, 15, and 20 wt%. Then, green rectangular bodies of 5.0 mm × 10.0 mm × 50.0 mm were bidirectionally pressed under the pressure of 35 MPa. After drying at 50°C for 10 h, the green bodies were heated to 1300°C, 1350°C, and 1400°C at a heating rate of 5°C/min and then soaked for 2 h in air.

The water absorption and open porosity of the as-prepared Al_2O_3 ceramics were measured using Archimedes principle. Ignition loss (IL) was calculated by measuring the weight of the bodies before and after sintering. Flexural strength was tested via a three-point bending test (ATOGRAPH AG-I, Shimadzu) with a support distance of 30.0 mm and cross-head speed of 0.50 mm/min. The crystal phase compositions of the sintered Al_2O_3 ceramics were determined with an X-ray diffractometer (XRD; D8 Advance, Bruker, Germany) using a Ni-filtered $\text{Cu K}\alpha$ radiation source ($\lambda = 0.154178$ nm). The microstructures of fracture surfaces of the sintered specimens were characterized with a field emission scanning electron microscope (FESEM; Sirion 2000, FEI, Netherlands). Pore size distribution was determined by mercury porosimetry (AutoPore IV 9510,

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3. Results and Discussion

3.1. XRD

Figure 1 shows the XRD patterns of the 1350°C sintered ceramics with various additions of Al(H₂PO₄)₃. As can be seen from Fig. 1, all peaks in the five patterns can be attributed to the characteristic peaks of corundum (α-Al₂O₃, JCPD S 46-1212), and no appreciable peaks of Al(PO₃)₃ or AlPO₄ were found, indicating that most of the added Al(H₂PO₄)₃ was eventually decomposed into Al₂O₃, H₂O, and P₂O₅ during the course of sintering. The chemical reaction can be described as follows:

Thus, it can be inferred that the as-produced H₂O and P₂O₅ in the form of gas evaporated out of the ceramics during sintering and that only solid Al₂O₃ remained. Therefore, only the characteristic peaks of α-Al₂O₃ occur in the patterns.

Figure 2 presents XRD patterns of the ceramics with addition of 20 wt% Al(H₂PO₄)₃ sintered at 1300, 1350, and 1400°C. As shown in Fig. 2, only characteristic peaks of corundum (α-Al₂O₃, JCPD S 46-1212) occur for the ceramics

Fig. 1. XRD patterns of the 1350°C sintered ceramics with additions of 0, 5, 10, 15, and 20 wt% Al(H₂PO₄)₃.

Fig. 2. XRD patterns of the ceramics with addition of 20 wt% Al(H₂PO₄)₃ sintered at 1300, 1350, and 1400°C.

sintered at the three temperatures, revealing that the added Al(H₂PO₄)₃ was eventually decomposed into Al₂O₃, H₂O, and P₂O₅ during the course of sintering.

3.2. Properties of the porous ceramics

The properties, including water absorption, open porosity, bulk density, and flexural strength, of the as-prepared porous ceramics are summarized in Tables 1, 2, and 3. As shown in the tables, the water absorption, open porosity, and bulk density of the porous Al₂O₃ ceramics increased remarkably with increasing Al(H₂PO₄)₃ addition from 0 to 20 wt%, indicating that the gaseous H₂O and P₂O₅ resulting from decomposition of the Al(H₂PO₄)₃ increased open porosity. Meanwhile, the flexural strength of the ceramics first increased significantly with increasing Al(H₂PO₄)₃ addition from 0 to 5 wt%, although the open porosity increased remarkably. Additionally, compared to that of the ceramics without Al(H₂PO₄)₃ addition, the porous ceramics with 10 wt% Al(H₂PO₄)₃ addition exhibited no appreciable deterioration in flexural strength, despite the remarkable increase in open porosity. Subsequently, the flexural strength of the porous ceramics decreased slightly with further increase in Al(H₂PO₄)₃ addition. In conclusion, addition of 5–10 wt% Al(H₂PO₄)₃ was significantly advantageous to the flexural

Table 1. Properties of the Al₂O₃ Ceramics Sintered at 1350°C with Various Additions of Al(H₂PO₄)₃

Al(H ₂ PO ₄) ₃ addition (wt.%)	Ignition loss (wt.%)	Water absorption (%)	Open porosity (%)	Bulk density (g/cm ³)	Relative density (%)	Flexural strength (MPa)
0	0.2	14.2	33.8	2.5	65.6	19.0 ± 0.3
5	4.3	15.7	37.6	2.3	60.4	21.6 ± 0.2
10	8.6	18.5	41.8	2.2	57.1	19.8 ± 0.2
15	12.8	20.0	44.1	2.1	55.1	17.8 ± 0.3
20	16.9	24.3	46.5	2.0	52.5	15.6 ± 0.3

Table 2. Properties of the Al_2O_3 Ceramics Sintered at 1300°C with Various Additions of $\text{Al}(\text{H}_2\text{PO}_4)_3$

$\text{Al}(\text{H}_2\text{PO}_4)_3$ addition (wt.%)	Water absorption (%)	Open porosity (%)	Bulk density (g/cm^3)	Relative density (%)	Flexural strength (MPa)
0	16.0	36.5	2.4	62.3	16.9 ± 0.4
5	16.4	38.7	2.2	57.7	17.1 ± 0.3
10	18.3	39.4	2.1	55.1	15.4 ± 0.3
15	19.9	41.1	2.0	52.5	13.3 ± 0.3
20	22.5	44.2	1.9	49.8	12.8 ± 0.3

Table 3. Properties of the Al_2O_3 Ceramics Sintered at 1400°C with Various Additions of $\text{Al}(\text{H}_2\text{PO}_4)_3$

$\text{Al}(\text{H}_2\text{PO}_4)_3$ addition (wt.%)	Water absorption (%)	Open porosity (%)	Bulk density (g/cm^3)	Relative density (%)	Flexural strength (MPa)
0	11.9	31.6	2.7	70.1	36.8 ± 0.2
5	11.7	32.5	2.6	67.2	36.5 ± 0.3
10	13.3	33.4	2.4	62.3	33.4 ± 0.3
15	15	35.5	2.2	57.7	31.5 ± 0.3
20	18.4	38.5	2.1	55.1	29.3 ± 0.3

strength as well as the open porosity of the porous Al_2O_3 ceramics sintered at 1350°C .

3.3. SEM characterization

Figure 3 shows the SEM microstructures of fracture surfaces of the porous Al_2O_3 ceramics with various additions of $\text{Al}(\text{H}_2\text{PO}_4)_3$ sintered at 1350°C . As revealed by Fig. 2, more

pores were observed in the fracture surfaces with increasing addition of $\text{Al}(\text{H}_2\text{PO}_4)_3$, in good agreement with the experimental results shown in Table 1. Moreover, the average grain size of Al_2O_3 became appreciably smaller as the $\text{Al}(\text{H}_2\text{PO}_4)_3$ addition increased from 0 to 5 wt%, which may be, at least partly, responsible for the higher flexural strength of the latter than of the former, because flexural

Fig. 3. SEM microstructures of fracture surfaces of the porous Al_2O_3 ceramics sintered at 1350°C with various $\text{Al}(\text{H}_2\text{PO}_4)_3$ additions. (a) 0 wt%, (b) 5 wt%, (c) 10 wt%, (d) 20 wt%.

Fig. 4. Pore size distribution of the porous Al_2O_3 ceramics sintered at 1350°C with various $\text{Al}(\text{H}_2\text{PO}_4)_3$ additions. (A) 0 wt%, (B) 5 wt%, (C) 10 wt%, (D) 20 wt%

strength was in proportion to $d^{-1/2}$ (d : grain size) despite the higher porosity of the former.¹⁰⁾ With further $\text{Al}(\text{H}_2\text{PO}_4)_3$ addition, the porosity and average Al_2O_3 grain size of the porous ceramics became larger, so the flexural strength became lower. It is worth noting that the ceramics with 10 wt% $\text{Al}(\text{H}_2\text{PO}_4)_3$ addition exhibited flexural strength comparable to that of the ceramics without $\text{Al}(\text{H}_2\text{PO}_4)_3$, although the latter had much higher porosity. Thus, it is reasonable to conclude that addition of 5–10 wt% $\text{Al}(\text{H}_2\text{PO}_4)_3$ can enhance the flexural strength and open porosity of the Al_2O_3 ceramics.

3.4. Pore size distribution

Figure 4 shows the pore size distribution of the porous Al_2O_3 ceramics sintered at 1350°C with various $\text{Al}(\text{H}_2\text{PO}_4)_3$ additions. As revealed by Fig. 4, the pore size distribution of the porous Al_2O_3 ceramics with various $\text{Al}(\text{H}_2\text{PO}_4)_3$ additions was bimodal. Furthermore, the pore sizes corresponding to the two peaks of the Al_2O_3 porous ceramics both increased appreciably with an increase in the amount of $\text{Al}(\text{H}_2\text{PO}_4)_3$ addition. In other words, the $\text{Al}(\text{H}_2\text{PO}_4)_3$ addition enlarged the average pore size of the porous Al_2O_3 ceramics, which could be mainly attributed to the evaporation of gaseous H_2O and P_2O_5 resulting from the decomposition of $\text{Al}(\text{H}_2\text{PO}_4)_3$ during sintering.

4. Conclusions

Porous Al_2O_3 ceramics were successfully fabricated with 0, 5, 10, and 20 wt% $\text{Al}(\text{H}_2\text{PO}_4)_3$ additions. The open porosity and average pore size of the as-sintered porous ceramics increased remarkably with an increase in $\text{Al}(\text{H}_2\text{PO}_4)_3$ addition. The flexural strength of the porous ceramics first

increased to a peak value when 5 wt% $\text{Al}(\text{H}_2\text{PO}_4)_3$ was added and then decreased as additional $\text{Al}(\text{H}_2\text{PO}_4)_3$ was added. The average Al_2O_3 grain size of the porous ceramics changed in an opposite way as the flexural strength. It should be noted that the ceramics with 10 wt% $\text{Al}(\text{H}_2\text{PO}_4)_3$ addition exhibited flexural strength comparable to that of the ceramics without $\text{Al}(\text{H}_2\text{PO}_4)_3$ addition, although the latter had much higher porosity.

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REFERENCES

1. E. C. Hammel, O. L.-R. Ighodaro, and O. I. Okoli, "Processing and Properties of Advanced Porous Ceramics: An Application Based Review," *Ceram. Int.*, **40** [10] 15351–70 (2014).
2. T. Ohji and M. Fukushima, "Macro-Porous Ceramics: Processing and Properties," *Int. Mater. Rev.*, **57** [2] 115–31 (2012).
3. K. Ishizaki, S. Komarneni, and M. Nanko, *Porous Materials, Process Technology and Applications*; Kluwer Academic Publishers, London, 1998.
4. N. Miyazaki and T. Hoshide, "Influence of Porosity and Pore Distributions on Strength Properties of Porous Alumina," *J. Mater. Eng. Perform.*, **27** [8] 4345–54 (2018).
5. W. Qin, C. Peng, M. Lv, and J. Wu, "Preparation and Properties of High-Purity Porous Alumina Support at Low Sintering Temperature," *Ceram. Int.*, **40** [8] 13741–46 (2014).
6. Y. Feng, K. Wang, J. F. Yao, P. A. Webley, S. Smart, and H. Wang, "Effect of the Addition of Polyvinylpyrrolidone as a Pore-Former on Microstructure and Mechanical Strength of Porous Alumina Ceramics," *Ceram. Int.*, **39** [7] 8833–39 (2013).
7. Q. Chang, Y. Yang, X. Zhang, Y. Wang, J. Zhou, X. Wang, S. Cerneaux, L. Zhu, and Y. Dong, "Effect of Particle Size Distribution of Raw Powders on Pore Size Distribution and Bending Strength of Al_2O_3 Microfiltration Membrane Supports," *J. Eur. Ceram. Soc.*, **34** [15] 3819–25 (2014).
8. J. Liu, Y. Li, Y. Li, S. Sang, and S. Li, "Effects of Pore Structure on Thermal Conductivity and Strength of Alumina Porous Ceramics Using Carbon Black as Pore-Forming Agent," *Ceram. Int.*, **42** [7] 8221–28 (2016).
9. Y. Tang, M. Mao, S. Qiu, K. Zhao, and W. Chen, "Fabrication of Porous Alumina by Directional Freeze Casting and Annealing in TBA–Water–Sucrose System," *Ceram. Int.*, **44** [14] 17566–70 (2018).
10. Z. Guan, T. Zhang, and J. Jiao, *Physical Properties of Inorganic Materials*; Second Ed., Tsinghua University Press, Beijing, 2011.