A Novel Method to Fabricate Porous Single Phase O’-sialon Ceramic and Improve its Mechanical Property

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Abstract: Nowadays, the O’-sialon ceramics are synthesized by the reaction of Si₃N₄, SiO₂ and Al₂O₃. However, it is difficult to achieve the single phase materials. Here, we have successfully developed porous single phase O’-sialon ceramics by pre-oxidation combined with gas-pressure sintering method. The effects of β-Si₃N₄ powder on the microstructure, phase evolution, mechanical property were investigated. The result illustrated that the main crystal phase of the porous ceramics was composed of the single O’-sialon phase. The pores were well distributed and generated from the decomposition of Si₂N₂O. The elongated O’-sialon grains were found and formed around pore walls. Additionally, the addition of β-Si₃N₄ powder was beneficial for improving the bending strength because of the reduction of porosity and pore size. The porous O’-sialon ceramics with uniform pores obtained the excellent bending strength when the β-Si₃N₄ powder was 6 wt%.

Keywords: Porous O’-sialon ceramic; Pre-oxidation; β-Si₃N₄ powder; Pore.

1. Introduction

In terms of structural materials, generally, pore always is considered as a defect which significantly degrades mechanical properties [1-3]. However, the existence of pores with well-designed pore channel also makes critical contributions on the ceramic material in many applications, to some extent. O’-sialon ceramics with porous structure can be described as Si₂₋ₓAlₓO₁₋ₓN₂₋ₓ (Si₂₋ₓAlₓO₁₋ₓN₂₋ₓ, 0<X≤0.3), and are solid solutions of the Si₂N₂O and Al₂O₃. They with desirable properties, e.g., good chemical stability, high strength and hardness, good dielectric property, and high thermal shock resistance [4-6] have huge prospects and can be employed extensively for several important engineering applications including insulators, gas filter, separation membranes, and catalyst support [7-11].

In the past, various synthesis methods have been reported to fabricate porous ceramics, such as adding pore-former agents method, freeze casting method, slip casting method, reaction bonded method and partial sintering method, etc [12-16]. However, no published literatures have been mentioned on porous ceramic developed by pre-oxidation combined with gas-pressure sintering. Furthermore, most of the scholars devoted to investigating porous α-SiAlON, β-SiAlON and multiphase sialon ceramics [17-19], which mainly intended to pursue mechanical properties and dielectric property as well as thermal conductivity. Additionally, in the case of the study of O’-sialon ceramics, they mostly referred to multiphase ceramics with other additives, such as TiO₂/(O’+β’)-sialon ceramic [20], O’-

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sialon/Si$_3$N$_4$ ceramic [21], and O’-sialon/TiC ceramic [22]. However, there were no works on the porous single phase O’-sialon ceramics.

In the present work, the porous O’-sialon ceramics are fabricated by pre-oxidation combined with gas-pressure sintering. A small amount of β-Si$_3$N$_4$ powders are adopted, which improved mechanical property. Furthermore, this work also studies the effects of different contents of β-Si$_3$N$_4$ powder on phase evolution and mechanical property, and the formation mechanism of pores.

2. Materials and Experimental Procedures

α-Si$_3$N$_4$ powders (including α-phase content >95 wt.%, O content =1.5 wt.%, average particle size=0.5 µm, UBE, Japan), β-Si$_3$N$_4$ powders (including β-phase content >93 wt.%, O content =1.3 wt.%, Fe content =0.014 wt.%, Ca content =0.010 wt.%, Al content =0.008 wt.%, Mg content <50 ppm, Na content <45 ppm and Ti content <10 ppm, average particle size =1.5 µm, HeFei Aijia New Material Co., Ltd., China) were used as raw materials. The Al$_2$O$_3$ and Y$_2$O$_3$ were as sintering agents and their weight ratio was fixed at 4:6 [23-25]. In our previous study, the high content of β-Si$_3$N$_4$ was not helpful for improving mechanical property. To improve mechanical property of O’-sialon ceramics, therefore, the low content of β-Si$_3$N$_4$ contents ranging from 0 wt.% to 8 wt.% was added into α-Si$_3$N$_4$ powders in this research.

All the raw materials were mixed and milled with high purity Si$_3$N$_4$ balls in anhydrous alcohol for 12 h in a rein plastic bottle. After being milled, the slurry was dried, followed by sieving through a 200-mesh screen. The mixtures were uniaxially pressed into rectangular bars following isostatic pressing at 200 MPa. Afterwards, these green bodies were subjected to oxidation at 1200 °C with 10 °C/min heating rate for a dwell time of 0.5 h in a muffle furnace. These pre-oxidation samples were immersed in a powder bed included of Si$_3$N$_4$ and BN within a graphite crucible, while Si$_3$N$_4$: BN weight ratio was defined at 1:1 and sintered in a furnace (Highmulti-5000, Fujidempa Co. Ltd, Osaka, Japan) at 1750 °C for 2 h with a heating rate of 5 °C/min under a nitrogen pressure of 3 MPa.

The Archimedes principle was carried out to calculate the porosity for sintered samples, in which deionized water was regarded as an immersing medium. The phase compositions of sintered samples were recorded by X-ray diffraction with a scanning speed of 10 °/min in the range of 10°-90° (XRD, D/MAX-2400X, Rigaku Co., Tokyo, Japan). The O’-sialon phase present in the samples was identified with the assistance of JCPDS database. The microstructure of samples was characterized by a field emission scanning electron microscope (SEM, JSM-35C, JEOL., Tokyo, Japan). The bending strength of samples was evaluated by three point bending in a testing machine (Instron1195, Instron Co., London, UK) with a span of 20 mm at a crosshead speed of 0.5 mm/min. Six samples were utilized to test, from which the average value of the bending strength was calculated.

3. Results and Discussion

3.1 Phase evolution of porous O’-sialon ceramics

Fig. 1 shows the phase evolution of porous O’-sialon ceramics as a function of β-Si$_3$N$_4$ contents. As revealed by XRD patterns, these patterns of porous ceramics were fully similar and had no significant change, which was determined as the O’-sialon phase (JCPDS: 42-1492) as a whole with the increase in β-Si$_3$N$_4$ contents. There was no evidence of the presence of any crystalline grain boundary phase suggesting that these sintering agents probably formed into the glassy phase.
3.2 Microstructural evolution of porous O'-sialon ceramics

Fig. 2 shows the typical fracture surface of porous O'-sialon ceramics as a function of \( \beta\)-Si\(_3\)N\(_4\) contents. In this sintering process, it could be observed significantly that the pores were well distributed for all samples. This indicated that pre-oxidation combined with gas-pressure sintering method was a good approach to fabricate porous ceramics. More specifically, for sample without \( \beta\)-Si\(_3\)N\(_4\), most of the pores were irregular and the pore size was relatively large as displayed in Fig. 2a. As the \( \beta\)-Si\(_3\)N\(_4\) increased, the irregular pores transformed slightly too spherical-shaped ones and the pores size gradually decreased. Additionally, the number of small and spherical-shaped pores began to increase as displayed in Fig. 2b-d. It was worth noting that the spherical-shaped pores were perfectly distributed in the sintered sample with 6 wt% \( \beta\)-Si\(_3\)N\(_4\) and pore size was also distributed uniformly. However, further increased \( \beta\)-Si\(_3\)N\(_4\) to 8 wt%, the large pore enhanced again within the sample because pore was sensitive to the addition of \( \beta\)-Si\(_3\)N\(_4\) as shown in Fig. 2e. These results above suggested that the addition of \( \beta\)-Si\(_3\)N\(_4\) could control the formation and uniform distribution of spherical-shaped pores to some extent. One possible explanation for this result might be mainly due to pinging effect of pore on the grain boundaries [26, 27]. Specifically, the grain boundary migration was pinned by pores. As a result, those pores on the grain boundaries could not form easily the aggregation growth, which gave rise to the generation of uniform and small pores.

The pore size distribution of porous O'-sialon ceramics with different contents of \( \beta\)-Si\(_3\)N\(_4\) powders was presented in Fig. 3. As it shown, without adding \( \beta\)-Si\(_3\)N\(_4\) (Fig. 3a), the pore size of samples was relatively larger and the average value of their was about 101.89 µm, and corresponding the number of pore size more than 100 µm was higher. With the increase of \( \beta\)-Si\(_3\)N\(_4\), the pore size gradually reduced from 90.67 µm to 69.47 µm as shown in Fig. 3b-d. In addition, the number of large pores over 100 µm also declined constantly. In the sample with 6 wt.% \( \beta\)-Si\(_3\)N\(_4\), nearly all the pores were less than 100 µm. Further increased \( \beta\)-Si\(_3\)N\(_4\) to 8 wt.%, the pores size became large again and was appropriately 85.14 µm and the larger pores were also appeared as observed in Fig. 3e. Therefore, according to the above result, it
could be summarized that the moderate addition of $\beta$-Si$_3$N$_4$ was helpful for fabricating the uniform pores and controlling the formation of the large pores (>100 µm).

![Fig. 2. SEM micrographs of Fracture surface of porous sialon ceramics with different contents of $\beta$-Si$_3$N$_4$ powders.](image)

**Fig. 2.** SEM micrographs of Fracture surface of porous sialon ceramics with different contents of $\beta$-Si$_3$N$_4$ powders, (a) 0 wt.%; (b) 2 wt.%; (c) 4 wt.%; (d) 6 wt.%; (e) 8 wt.%.

![Fig. 3. Pore size of porous sialon ceramics with different contents of $\beta$-Si$_3$N$_4$ powders.](image)

**Fig. 3.** Pore size of porous sialon ceramics with different contents of $\beta$-Si$_3$N$_4$ powders.

To distinguish clearly O’-sialon grain, the isolated spherical-shaped pore was enlarged in the high magnification as presented in Fig. 4a, a large number of elongated grains were found and formed around pore walls. In order to further clarify the elongated grains, the elongated grain was characterized by EDS as displayed in Fig. 4b. It could be seen that the elongated grain was composed of O, Al, Si, and N elements, which was confirmed that the elongated grain was definitely O’-sialon phase. This result was an agreement with the result of XRD analysis. Additionally, the element mappings proved well that the O, Al, Si, and N elements were distributed uniformly as shown in Fig. 4c.
3.3 Properties of porous O’-sialon ceramics

The porosity and bending strength of porous O’-sialon ceramics vs β-Si$_3$N$_4$ contents were shown in Fig. 5. As could be seen, the porosity had a decline trend together with bending strength enhancing when the addition of β-Si$_3$N$_4$ was between 0 wt.% and 6 wt.%. Conversely, when the β-Si$_3$N$_4$ exceeded 6 wt.%, both of them showed a reverse tendency. When the addition of β-Si$_3$N$_4$ was 6 wt.%, the porosity had the lowest value of 43.2 %, and bending strength achieved the highest value of 56.1 MPa.

![Fig. 5. Porosity and bending strength of porous O’-sialon ceramics as a function of β-Si$_3$N$_4$ contents.](image-url)
Analyzing the above results, for sample added β-Si₃N₄ from 0 wt.% to 6 wt.%, the porosity decreased evidently, which was primarily due to the reduction in the number of large pores (>100 µm). Whereas the increment in porosity of sample with 8 wt.% β-Si₃N₄ was attributed to the generation of large pores (>100 µm) again as shown in Fig. 2. However, the bending strength was associated closely with both porosity and pore size. Based on the empirical formula of porous ceramic described by Ryshkewitch as follows Equation (1) [28]:

$$\sigma = \sigma_0 \exp(-\beta p) \quad (1)$$

Where $\sigma$ is bending strength; $\sigma_0$ is bending strength for ceramic without pores; $\beta$ is structural parameter; $p$ is the porosity for ceramic. As indicated by this equation, the bending strength of O’-sialon ceramics decreased exponentially with the increase in porosity. According to Fig. 5, we could conclude that the bending strength degraded, which was due to the increment of porosity. Additionally, the pore size was also an important factor depending on the bending strength of O’-sialon ceramics. It was also well accepted that the larger the pore size was, the more serious the mechanical property decreased. It was obviously found that the pore size increased constantly as shown in Fig. 3. As a result, the bending strength reduced. Therefore, both porosity and pore size were two major factors for influencing the bending strength of porous O’-sialon ceramics in our research. The O’-sialon ceramic in this work exhibited more excellent mechanical property than those reported earlier [29].

### 3.4 Formation mechanism of pore

![Fig. 6. A schematic diagram of the formation mechanism of pore.](image)

To control effectively the microstructure of porous O’-sialon ceramics, it was significant to explore the formation mechanism of the pore in porous O’-sialon ceramics. A schematic diagram of the formation mechanism of pore was presented in Fig. 6. It was well conducted that the O’-sialon ceramics were derived from the reaction of the Si₂N₂O and Al₂O₃ as expressed by Equation (2) [30]. In this work, Si₂N₂O was mainly generated through a typical process where Si₃N₄ was dissolved and reacted with the SiO₂ component of the liquid phase as described in Equation (3) in the second stage. The liquid phase was formed by the Y₂O₃, Al₂O₃ and SiO₂. Besides, the formation of parts of SiO₂ was from oxidizing α-Si₃N₄ as following Equation (4) in the first stage. In the formation process of O’-sialon ceramics, the Si₂N₂O played an important role for the preparation of porous O’-sialon ceramics. On the one hand, the Si₂N₂O was the essential raw material to form O’-sialon. On the other hand, the Si₂N₂O was regarded as the source of pore. In particular, the formation of pores was from the
decomposition of Si$_2$N$_2$O when the sintering temperature was over 1700 °C. Therefore, two types of pores were observed as shown in the points “1” and “2” of Fig. 6 that was spherical-shaped pore and irregular one. This phenomenon suggested that their formation process was significantly distinctive. The irregular pore was formed by the combination of two or several small pores, while spherical-shaped pore originated from the decomposition of Si$_2$N$_2$O as shown in Equation (5) in the third stage. In addition, it was worth noting that the strut of irregular pore gradually disappeared, which resulted in the production of large pore as observed in the point “3” of Fig. 6. The strut of the point “4” of Fig. 6 was still reminded. Therefore, we proposed one possible formation mechanism of pore. The generation of pore was closely correlated with the pinning effect of pore. When the sample without or with a small amount of β-Si$_3$N$_4$, the pinning effect was not obvious. The grain boundaries could be swept through the pores, which resulted in the aggregation growth of pores on multiple grain boundaries. Therefore, the pore size was relatively large. By contrary, for sample with high level of β-Si$_3$N$_4$, the pinning effect became remarkable; the grain boundaries migration was pinned severely by pores. As a result, those pores on the grain boundary could not promote easily the aggregation growth, which gave rise to the generation of uniform and small pores.

\[ 0.98\text{Si}_2\text{N}_2\text{O}(s)+0.02\text{Al}_2\text{O}_3(s) \rightarrow \text{Si}_{1.96}\text{Al}_{0.04}\text{O}_{1.04}\text{N}_{1.96}(s) \]  
\( (2) \)

\[ \text{Si}_3\text{N}_4(s)+\text{SiO}_2(s) \rightarrow 2\text{Si}_2\text{N}_2\text{O}(s) \]  
\( (3) \)

\[ \text{Si}_3\text{N}_4(s)+3\text{O}_2(g) \rightarrow 3\text{SiO}_2(s)+2\text{N}_2(g) \]  
\( (4) \)

\[ 2\text{Si}_2\text{N}_2\text{O}(s) \rightarrow \text{Si}_3\text{N}_4(s)+\text{SiO}(g)+0.5\text{O}_2(g) \]  
\( (5) \)

4. Conclusion

In this research, porous O’-sialon ceramics were synthesized successfully by pre-oxidation combined with gas-pressure sintering method. The XRD patterns and SEM images indicated that the porous O’-sialon ceramics were composed of the elongated O’-sialon grains. The well-distributed pores were observed in porous O’-sialon ceramics and the pore walls were surrounded by elongated O’-sialon grains. The irregular and large pores and spherical-shaped ones were generated, which was attributed to the pinning effect of pores. Additionally, the addition of β-Si$_3$N$_4$ could effectively tailor the pore volume and pore size. With the increase of β-Si$_3$N$_4$ from 0 wt.% to 8 wt.%, both pore volume and pore size firstly declined and then enhanced. The porosity and bending strength of the prepared porous O’-sialon ceramics with 6 wt.% β-Si$_3$N$_4$ obtained optimum performance and reached 43.2 % and 56.1 MPa, respectively. The improvement of bending strength was resulted from the reduction of porosity and pore size. This method was a feasible way to prepare porous O’-sialon ceramics.

Acknowledgments

The work was supported by the Key Research and Development Plan of Shaanxi Province (2017GY-118).

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Сијалонска керамика са унiformном порозношћу показује одличну снагу савијања са 6 wt%. β-Si₃N₄ праха.

Кључне речи: порозна O’-сијалонска керамика, пре-оксидација, β-Si₃N₄ прах, поре.

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