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Effect of processing on toughness of Ca α-sialon ceramics

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The influence of processing on microstructural development of Ca α-sialon composition ($Ca_xSi_{12-3x}Al_{3x}O_xN_{16-x}$) with $x = 1.8$ was studied by dwelling at different intermediate temperatures before reaching the final sintering temperature. The microstructural observation results have showed the different aspect ratios of elongated grains obtained by the various processing conditions, reflecting the effect of the number of nuclei of α-sialon on morphology of grains during sintering. Improved toughness was achieved by applying low temperature dwelling for Ca α-sialon compositions with low x values. The toughness showed an increase of 33% and 16% for $x = 0.6$ and 1.0 compositions respectively with middle dwelling processing at 1350°C for 3 h before reaching 1750°C for 1 h by hot-pressing. © *2000 Kluwer Academic Publishers*

1. Introduction

The brittle nature of ceramics has prompted many researchers to explore various possibilities to enhance their toughness. One great breakthrough is the in-situ toughening of Si_3N_4 and SiC based ceramics by elongated grains developed during the sintering process [1]. The elongated grains result in enhanced toughness owing to such mechanisms as crack bridging, crack deflection and grain pullout [2]. The commercialization of β-Si_3N_4 and its solid solution β-sialon is a successful application of this research.

Another solid solution of Si_3N_4 is α-sialon with the general formula $M_xSi_{12-(m+n)}Al_{(m+n)}O_nN_{16-n}$, where M represents calcium, lithium, magnesium, yttrium and most rare earth elements [3]. Comparing to its β counterpart, α-sialon has the advantage of high hardness and the potential of cleaning up grain boundaries. However, engineering application of α-sialon has been limited by its frequently occurred equi-axed grain morphology associated with low toughness and reliability [4]. Recent findings of elongated α-sialon microstructure have opened up new possibility to obtain more synergistic ceramics with both high hardness and high toughness [5, 6]. It has been found in our previous work that compositions with high x values in the Ca doped system are more readily to evolve into elongated α-sialon grains [7]. To achieve the goal of tailoring the microstructure and hence improving the toughness of the α-sialon ceramics, a further understanding of the processing-microstructure-property relationship is needed. In this paper, a study of the influence of processing conditions on microstructure of Ca-α-sialon with $x = 1.8$ composition was made by dwelling at different intermediate temperatures during sintering, which serves as reference to achieve toughening effect on α-sialon compositions having low x values.

2. Experimental

The compositions investigated in this study lie on the join line Si_3N_4-CaO:3AlN with the general formula $Ca_xSi_{12-3x}Al_{3x}O_xN_{16-x}$. The corresponding samples were termed by their x value, such as C60 for $x = 0.6$, C100 for $x = 1.0$ and C180 for $x = 1.8$. Starting powders were Si_3N_4 (UBE E-10, Japan, 2.0 wt% O), AlN (1.3 wt% O) and $CaCO_3$ (99%). Powder mixtures were milled in an agate mortar with absolute alcohol for 2 h, and dried before sintering.

Both pressureless sintering and hot-pressing were conducted in a graphite resistance furnace in flowing nitrogen for selected compositions. Compacted columnar pellets were cold isostatically pressed at 200 MPa and a packing powder mixture of 60wt% Si_3N_4 : 30wt%AlN : 10wt%BN was used in a graphite crucible for pressureless sintering. For studying reaction sequences of C180, the samples were sintered at the temperatures ranging from 1350°C to 1800°C for 2 h. Some C180 samples were fired at intermediate temperatures, 1350, 1450, 1550 and 1650°C, respectively for 1 h before reaching the final temperature (1800°C) by the same sintering technique in order to compare the difference in microstructure. Hot-pressing with an applied pressure of 20 MPa was used for $x = 0.6$ and 1.0 compositions for both the phase evolution (1350 to 1750°C for 1 h) and dwelling at intermediate temperature before final sintering (1750°C for 1 h). For each run in either pressureless sintering or hot-pressing, a holding time of 0.5 hour at 1150°C was applied to decompose $CaCO_3$ in starting powders into CaO and CO_2, the latter being expelled with the flowing nitrogen.

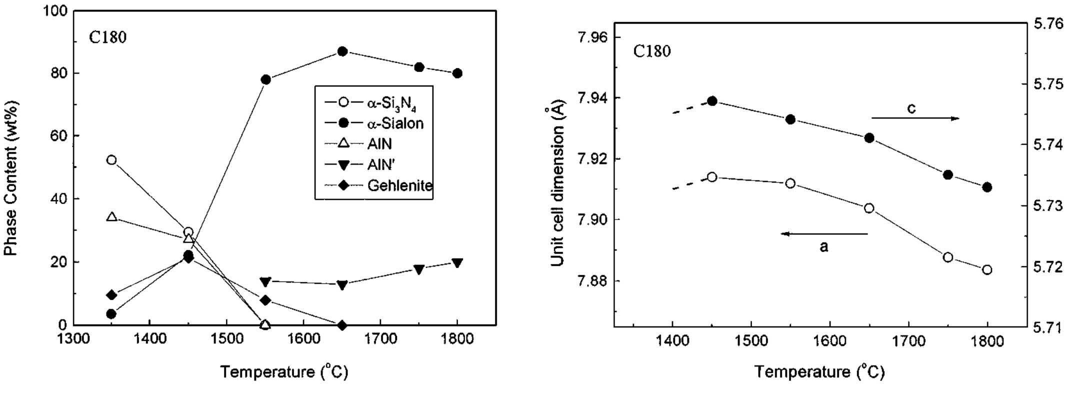
Phase identification was performed on an RAX-10 diffractometer using Cu K_α radiation. Semi-quantitative analysis was made on the crystalline phase content based on the calibration curves. XRD patterns were also obtained by Guinier-Hägg camera (Cu $K_{\alpha 1}$ radiation, $\lambda = 1.5405981$ Å) film data to determine the accurate lattice parameters of α-sialon for selected samples. Fracture toughness was measured on polished surfaces of hot-pressed samples at room temperature using a Vickers diamond indenter under a load of 98 N (10 kg). The mean values of at least three measurements represented the property data for each specimen. Microstructural observation was carried out on a KYKY-2000 scanning electron microscope (Keyi Inc., China) equipped with an energy dispersive spectrometer (LINK ISIS). Polished surfaces of the prepared samples were etched in molten NaOH and then carbon coated prior to observation.

3. Results and discussion

3.1. Phase evolution of Ca α-sialon with high x composition

Phase assemblages and the corresponding α-sialon cell dimensions of C180 pressureless-sintered at different temperatures are shown in Fig. 1. As expected, the content of Si_3N_4 and AlN in the starting powder decreased with the increase of sintering temperature, whereas the amount of α-sialon started to increase above 1350°C. Gehlenite ($Ca_2Al_2SiO_7$) was the only intermediate crystalline phase observed during sintering. No starting powders remained after sintering at 1550°C for 2 h and gehlenite disappeared after sintering at 1650°C for 2 h, indicating completion of the reaction. Based on the reaction sequence of Ca-α-sialon, it was noted that the formation of α-sialon at the early stage of sintering occurred simultaneously with the formation and dissolution of the intermediate gehlenite phase. As a result, there existed the competition for Ca between the formation of α-sialon and gehlenite. On the other hand, with the redissolution of gehlenite at higher temperatures, both the amount and viscosity of the transient liquid were greatly enhanced and decreased respectively, thus promoting the further formation of α-sialon. In the final phase assembly, α-sialon was the dominant phase, together with a small amount of AlN-polytype phase. This is in agreement with the recently established two dimensional Ca α-sialon plane, in which α-sialon compositions with high x value are compatible with nitrogen rich AlN or AlN polytypoid phases [8].

The trace amount of α-sialon in the 1350°C sintered sample made it difficult to accurately determine the cell dimensions. By comparing the strong peak (102) of α-sialon phase between the 1350°C and the 1450°C spectrums, it was seen that the latter gave slightly higher d value, corresponding to larger α-sialon cell dimensions. At temperatures exceeding 1450°C, the α-sialon cell dimensions showed a monotonic decrease. As is known, the formation of α-sialon is a solution-precipitation process. During the precipitation the α-sialon grains nucleate and subsequently grow into large sizes. In the early sintering period, all the Ca cation and part of the Si, Al, O and N cations in the starting powders dissolved to form the transient liquid. Thus the low α-sialon content and the abundant Ca concentration in the liquid produced larger α-sialon cells at low temperatures. Further increase of α-sialon content at higher sintering temperatures led to decrease of the α-sialon cell dimensions. The decrease of α-sialon cell dimensions even after 1650°C should be attributed to the formation of AlN polytypoid, which exhausted Al and hence forces some Ca to enter the grain boundary phase. According to the results of phase evolution and the cell dimensions of α-sialon at the different sintering



(a) (b)

Figure 1 Phase evolution of pressureless sintered C180 composition at different temperatures for 2 h. (a) Phase assemblages; (b) Corresponding α-sialon cell dimensions. Note: (a) Here AlN′ denotes AlN polytypoid; (b) The dotted line represents the estimated α-sialon cell dimensions at temperatures lower than 1450°C.

temperatures as shown in Fig. 1, it was noted that at 1450°C, both the α-sialon cell dimensions and the gehlenite content reached the maximum. The variation of cell dimensions of α-sialon with sintering temperatures imparts potential for the microstructural control through processing, as will be discussed below.

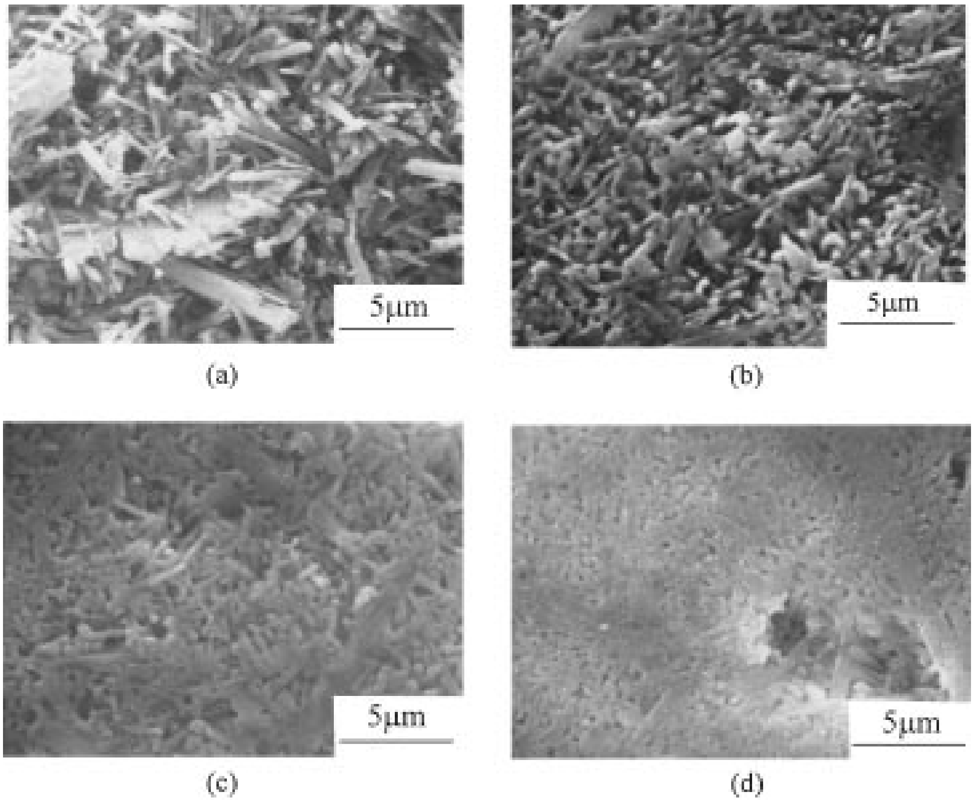
3.2. Microstructural response of Ca α-sialon to different processing

For C180 composition, dwelling at intermediate temperatures (1350–1650°C) for 1 hour was adopted prior to pressureless sintering at 1800°C for 2 hours. The resultant microstructure, especially the morphology of α-sialon grains, showed marked distinction between samples with the different intermediate temperatures sintering as seen in Fig. 2. Samples undergoing a low-temperature dwelling (1350°C and 1450°C) revealed a microstructure with more obvious elongated α-sialon grain morphology, whereas in samples undergoing a high-temperature dwelling (1550°C and 1650°C), abundant α-sialon grains were present with relatively low aspect ratio.

The above difference in microstructures developed under different sintering conditions is attributed to some of the features observed in the reaction sequence of the material. As mentioned above that at low temperatures (1350°C or 1450°C), both the nucleation of α-sialon seeds and formation of gehlenite occur in the system, but they have to compete for Ca. The competition of these two processes produces fewer α-sialon nuclei, which are more fully developed during dwelling than those formed after the dwelling, thus leading to inhomogeneous microstructure with obvious elongated grain morphology. At temperatures exceeding 1450°C, considerable amounts of α-sialon nuclei have already been formed as α-sialon content reaches the higher level shown in Fig. 1. Dwelling at these temperatures mainly benefits the growth of α-sialon grains. But too many nuclei would result in significant grain impingement during growth and give less freedom for the anisotropic growth of α-sialon grains, thus producing abundant α-sialon grains with decreasing aspect ratios.

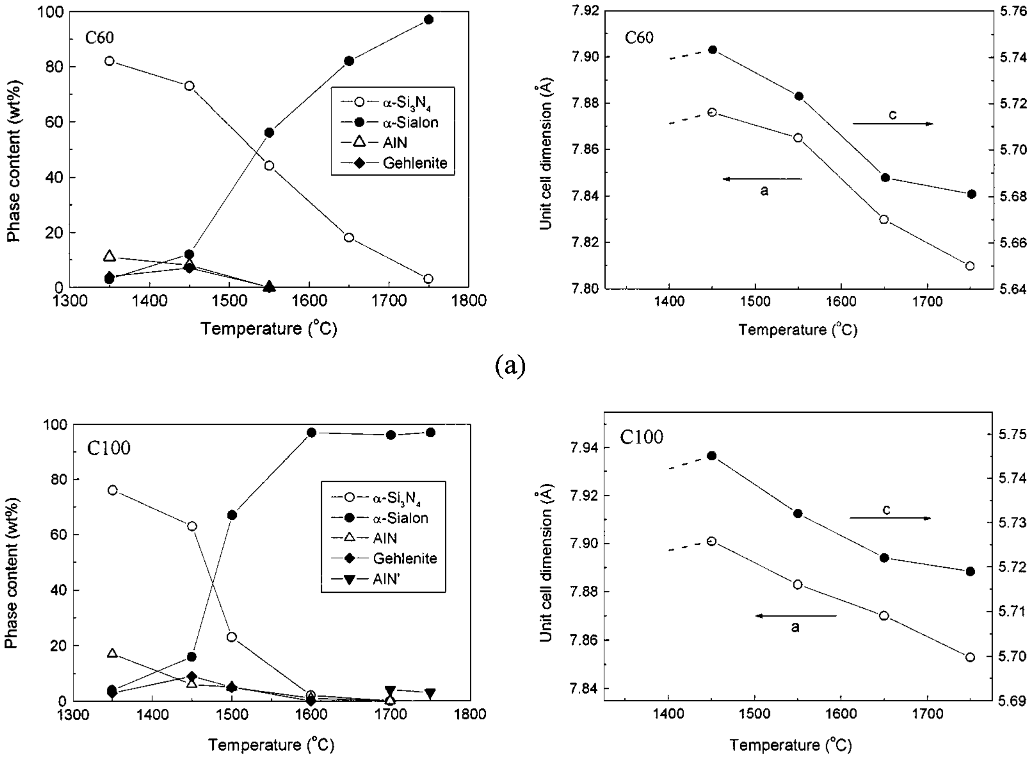
3.3. Toughening of Ca α-sialon composition with low x values

As discussed above, the amount and aspect ratio of α-sialon grains can be tailored through intermediate dwelling processes. This prompted a further study of the effect of the elongated grain morphology on fracture toughness in the Ca α-sialon system. It should be noted that the mechanical properties, especially hardness, of Ca α-sialon with high x compositions are relatively low owing to large amounts of residual glass formed after sintering. On the other hand, hot-pressed Ca α-sialons with low x values would possess high hardness, while their toughness would be relatively low owing to the frequently occurred equi-axed grain morphology. Therefore, from the viewpoint of engineering application, it is of more significance to explore the toughening possibility of α-sialon ceramics to compositions with low x values. To test the applicability of the processing-microstructure relationship derived from high x composition to low x compositions, the reaction sequence and cell dimensional changes of C60



(a) (b)
(c) (d)

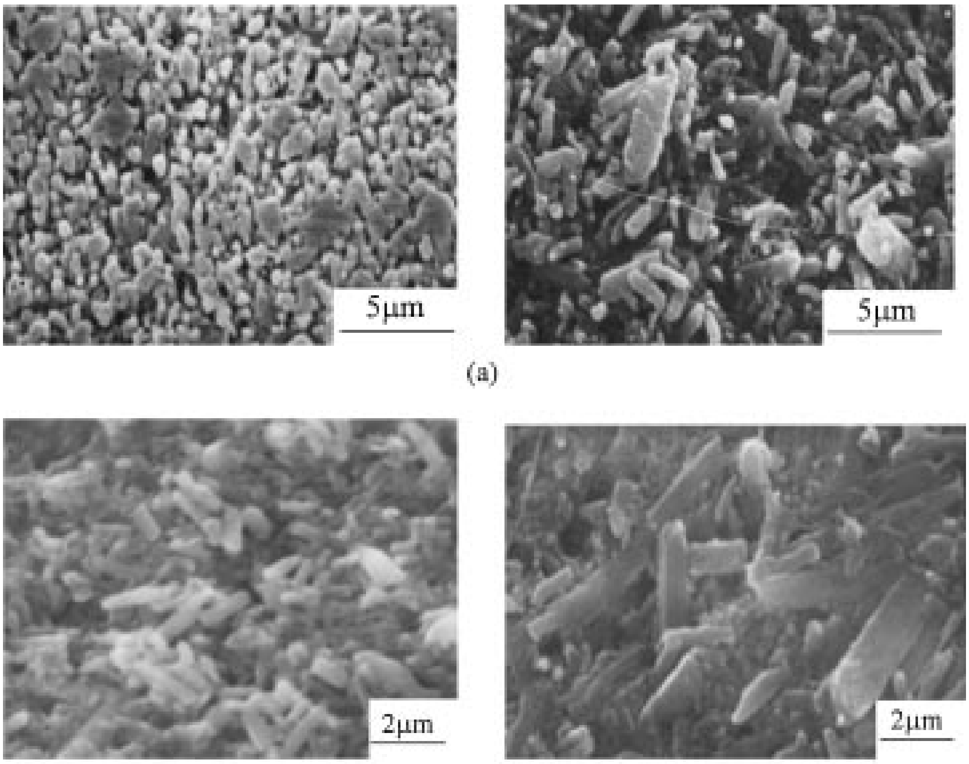
Figure 2 Influence of middle dwelling on microstructure of pressureless sintered C180 composition (1800°C/2 h). (a) 1350°C/1 h; (b)1450°C/1 h; (c)1550°C/1 h; (d) 1650°C/1 h.



(a)

(b)

Figure 3 Phase evolution of hot-pressed (a) C60 and (b) C100 compositions. Note: left, phase assemblages; right, α-sialon cell dimensions.



(a)

(b)

Figure 4 SEM micrographs of hot-pressed (a) C60 and (b) C100 compositions (1750°C/1 h, 20 MPa) with (right) and without (left) middle dwelling at 1350°C for 3 h.

and C100 were also studied and compared with C180, as shown in Fig. 3. The final phase assembly of C100 was α-sialon and traces of AlN polytypoid while that of C60 consisted of nearly 100% α-sialon. Due to the decrease of transient liquid in these compositions with low x values, the temperature for complete reaction rose from 1650°C for C180 to 1700°C for C100 and 1750°C for C60. On the other hand, a similar trend concerning the α-sialon cell dimensions of C60 and C100 was observed. Both the gehlenite content and α-sialon cell

TABLE I Fracture toughness of hot-pressed Ca α-sialons under different processing conditions

	$K_{1c}(\text{MPa}\cdot\text{m}^{1/2})$	
Processing	$x = 0.6$	$x = 1.0$
HP 1750°C/1 h	4.2	4.9
HP 1350°C/3 h + 1750°C/1 h	5.6	5.7

dimensions reached the maximum at 1450°C, followed by a monotonic decrease with increasing temperatures. This indicates that the same rule should apply to the Ca α-sialon compositions with both high and low x values concerning the phase evolution and microstructural development.

It is known from previous studies on β-sialon and α-sialon/β-sialon ceramics that a bimodal microstructure, with large elongated grains embedded in a fine-grained matrix, contributes to improved toughness of the material [9]. From the earlier discussion, it is seen that dwelling at low temperatures produced a less homogeneous microstructure with a few grains experiencing more obviously anisotropic growth. The intermediate dwelling was therefore fixed at 1350°C for 3 hours, followed by hot-pressing at 1750°C for 1 hour to C60 and C100 compositions. Preliminary property test showed a further improvement in toughness in the samples after the two-stage firing. The fracture toughness of C100 composition rose from 4.9 $\text{MPa}\,\text{m}^{1/2}$ to 5.7 $\text{MPa}\,\text{m}^{1/2}$ and that of C60 from 4.2 $\text{MPa}\,\text{m}^{1/2}$ to 5.6 $\text{MPa}\,\text{m}^{1/2}$ (see Table I), showing an increase of 16% and 33% respectively in comparison to those without middle dwelling. Fig. 4 are their corresponding SEM micrographs. The α-sialon grains showed more pronounced growth and the aspect ratio of grains was greater than that without dwelling. It is supposed that a few of α-sialon nuclei preferentially formed during the dwelling process and they also experienced preferential growth thereafter. The toughness enhancement, therefore, is attributed to the formation of a few coarse elongated α-sialon grains.

4. Conclusion

Possibility of toughness enhancement of Ca α-sialon ceramics through processing has been illustrated. By dwelling at different intermediate temperatures before reaching the final sintering temperature, the elongated grains of Ca α-sialon with the different aspect ratios were observed. A dwelling process at low temperatures prior to sintering at elevated temperatures encourages the preferential growth of a few elongated α-sialon grains and results in enhanced toughness for hot-pressed Ca α-sialon compositions with low x values.

Acknowledgments

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References

1. M. MITOMO and G. PETZOW, *MRS Bulletin* **2** (1995) 19.
2. P. F. BECHER, *J. Am. Ceram. Soc.* **74** (1991) 255.
3. S. HAMPSHIRE, H. K. PARK, D. P. THOMPSON and K. H. JACK, *Nature* **274** (1978) 880.
4. T. Y. TIEN, in "Silicon Nitride Ceramics Scientific and Technological Advances," edited by I. W. Chen, P. H. Becher, M. Mitomo, G. Petzow and T. S. Yen (MRS, Pittsburgh, PA, 1993) p. 51.
5. I. W. CHEN and A. ROSENFLANZ, *Nature* **389** (1997) 701.
6. C. WOOD, H. ZHAO and Y. B. CHENG, *J. Am. Ceram. Soc.* **82** (1999) 421.
7. Y. W. LI, P. L. WANG, D. S. YAN and Y. B. CHENG, *J. Inorg. Mater.* **6** (1999) 893 (in Chinese).
8. C. L. HEWETT, Y. B. CHENG, B. C. MUDDLE and T. B. TRIGG, *J. Am. Ceram. Soc.* **81** (1998) 1781.
9. M. MITOMO, *Key Eng. Mater.* **161–163** (1999) 53.

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