Journal of the European Ceramic Society 20 (2000) 939–944

Inhomogeneous grain growth and elongation of Dy-α sialon ceramics at temperatures above 1800°C

C. Zhang*, K. Komeya, J. Tatami, T. Meguro

Department of Materials Chemistry, Yokohama National University, 79-5 Tokiwadai, Hodogayaku, Yokohama 240-8501, Japan

Received 4 May 1999; accepted 4 July 1999

Abstract

A series of samples with dysprosium α-sialon compositions and different amounts of sintering additives has been fabricated from α-Si$_3$N$_4$, AlN, Al$_2$O3 and Dy$_2$O$_3$ starting powders, using pressureless sintering (PLS) at 1800°C plus gas pressure sintering (GPS) at the same and higher temperatures under a relatively low gas pressure of 0.9 MPa N$_2$. The resultant α-sialon grains show significantly different features, such as regularly fine and equiaxed, elongated, and even a few extraordinarily large with high aspect ratio grains in the fine matrix, which has rarely been observed in α′ ceramics. It is suggested that the temperature strongly influences the grain morphologies of α-sialon, playing an important role particularly in the latter stage of the "nucleation-growth" process. Such a kind of microstructural morphology as mixed with equiaxed and elongated grains toughens the α-sialon ceramics and leaves them still hard as usual. Overly high temperature treatment leads to the preferential growth of a few grains which become excessively large and long, and do not significantly improve the materials toughness. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Grain size; Mechanical properties; Sialon; Sintering

1. Introduction

Alpha sialon ceramics (symbolized as α′), iso-structure with α-Si$_3$N$_4$, contains two large isolated interstices in which some large metal ions can be accommodated.[1] The general formula of α′ is represented as M$_x$Si$_{12-(m+n)}$Al$_{m+n}$O$_n$N$_{16\text{-}n}$ with $x \leqslant 2$, where M is a metal cation and x is related to its valence v according to the relationship $x = m/v$. The elements M which have been reported to stabilize α′ are Li, Ca, Mg, Y and most lanthanide elements[2,3] except La, Ce, Pr and Eu. In comparison with beta sialon (β′ Si$_{6\text{-}z}$Al$_z$O$_z$N$_{8\text{-}z}$), α′ promises high hardness because its structure consists of a longer stacking sequence of ABCD than the AB in -Si$_3$N$_4$, giving longer Burgers vector for dislocations,[4] which makes it particularly suitable for cutting tool or bearing parts.

α-Sialon has been observed and recognized to possess equiaxed morphology and to be very difficult to grow into elongated grains like β-sialon since it was successfully synthesised some 20 years ago. Partly for this reason, it is relatively poor in toughness because such a microstructure lacks the toughening mechanisms such as crack-deflection and bridging,[5,6] which usually take effect in those ceramics containing needle-like grains, such as β-sialon. In order to broaden the application of this material, much emphasis has been placed on forming some elongated grains in the α-sialon matrix. So-called in situ self-reinforced multiphase α′-β′ is one of the most significant achievements in this endeavour. The hardness and fracture toughness can be adjusted to a required value by carefully altering the α′ and β′ phase ratio in the final products.[7] However, this kind of mechanical property "tailoring" is at the expense of some of the high quality of α-sialon. Moreover, the phase design seems not so easy to achieve because of the unstable nature of α-sialon phase, especially in light rare earth systems, makes it difficult to control the phase distribution after sintering.

Most recently, a slight change has taken place in the concept of α-sialon ceramics. A coarse and elongated microstructure of α′ was found in some laboratories during the past 3 or 4 years.[8–11] The most attractive results were reported by Chen and Rosenflanz in *Nature* in 1997.[12] They used β-Si$_3$N$_4$ as starting powder to synthesize α-sialon ceramics, resulting in a minimum of α′ nuclei.

---

* Corresponding author.

PII: S0955-2219(99)00208-3

These few grains could be kept from running into each other at the early stage of firing and thus grow in one direction. In this unique way, the α-sialon ceramics consisting of almost all elongated grains were made. They exhibited significant improvement in toughness and strength, but the hardness still remained extremely high. A special sort of technique based on the similar nucleation-controlling principle was adopted by a research group in Monash University, Australia to yield calcium α-sialon having this morphological feature as well.[13,14]

It is well known that the formation of α-sialon grains form Si_3N_4 and their growth are through the process of solution-diffusion-reprecipitation, which is relevant to many factors, such as the composition, viscosity and quantity of the liquid phase, as well as the sintering temperature. The whole sintering process can be roughly divided into two steps, nucleation and growth. Until now, research papers on sintering temperature and the amount of liquid phase, the most important factors, which favor the elongation of grains, particularly during the second stage, i.e. growth period, are still scarce. Based on this consideration, the present work was designed and conducted to identify these factors and to explore the possibility of fabricating the α-sialon ceramics with coarse and long shape grains by the regular and inexpensive sintering method, gas pressure sintering (GPS) under low gas pressure and pressureless sintering (PLS), and from the conventional raw powders, mainly α-Si_3N_4. Highly desirable properties, with an optimum combination of hardness and toughness, were also expected.

In this experiment, the dysprosium was chosen to form the α-sialon ceramics, and $Dy_2O_3 + Al_2O_3$ (mol ratio as 3/5) was used as the additive to promote densification. In some previous works concerning this system, results showed that the formation of Dy-α′ had a kinetic priority during sintering. Hereby the single phase Dy-ceramic was easy to acquire and its grain feature was typically fine and equiaxed.[15,16]

2. Experimental procedure

The starting materials used were Si_3N_4 (Ube, SN-E10), AlN (Tokuyama, grand F), Al_2O_3 (Sumitomo, AKP-50) and Dy_2O_3 (Shin-Etsu, DY-03-180). The minor oxygen contents on the surface of Si_3N_4 and AlN were taken into account in making compositions. The mixed powder with an α-sialon composition of $Dy_{0.33}Si_{9.3}Al_{2.7}O_{1.7}N_{14.3}$ (i.e. $m = 1$, $n = 1.7$) and different amounts of extra Dy_2O_3 plus Al_2O_3 (corresponding to $Dy_3Al_5O_{12}$, abbreviated DyAG) as sintering additives were ball-milled with ethanol for 24h using sialon balls, and then dried and passed through a sieve with an opening hole of 300 μm. The powders were uniaxially pressed in a steel mold of ϕ 15 mm, followed by a cold isostatic press under a pressure of 200 MPa. PLS and the successive GPS firings were carried out in a graphite-resistance furnace. The heating program is indicated in Fig. 1. During GPS treatment, the second stage of the firing cycle, the temperature rose from 1800 to 1900°C for G2 and 2000°C for G3, or was kept at 1800°C for G1, immediately after the PLS for 1.5 h and the nitrogen gas pressure was increased from 0.1 to 0.9 MPa simultaneously. The samples were kept for another 1 h under these conditions. In order to compare the microstructural morphology, some compositions were sintered only by PLS without GPS firing. The bulk densities of the samples were measured by the Archimedes principle, and the phases were identified by X-ray diffraction (Rigaku, CuKα). Hardness and indentation fracture toughness were measured by the Vickers method using a diamond indenter under a load of 100 N. The microstructure observations were performed with a JEOL JSM-5200 scanning electron microscope on polished and etched sample surfaces.

3. Results and discussions

3.1. Sintering behaviors and phase compositions

All the compositions listed in Table 1, were almost fully densified through PLS plus successive GPS treatment at

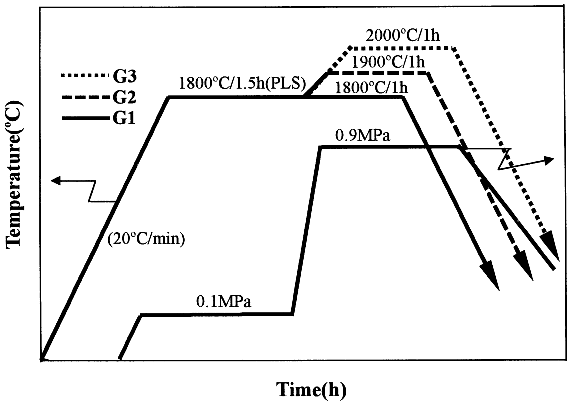

Fig. 1. Schematic diagram of sintering patterns to fabricate Dy-α sialon ceramics by PLS plus GPS.

Table 1
Compositions and densities of Dy-sialon ceramics sintered at three temperature stages

Sample No.	DyAG additive content (wt%)	D/D_{th} (%)		
		G1	G2	G3
D1	2.5	88.1	96.8	96.7
D2	5.0	98.5	98.6	98.8
D3	7.5	99.0	99.1	98.9
D4	10.0	98.3	98.5	98.2

[a] G1: 1800°C/1.5 h (0.1 MPa N_2) + 1800°C/1 h (0.9 MPa N_2).
[b] G2: 1800°C/1.5 h (0.1 MPa N_2) + 1900°C/1 h (0.9 MPa N_2).
[c] G3: 1800°C/1.5 h (0.1 MPa N_2) + 2000°C/1 h (0.9 MPa N_2).

both 1900 and 2000°C for 1 h under 0.9 MPa nitrogen gas pressure. The prepared samples sintered at 1800°C show a little lower density except for sample D1, in which the 2.5 wt% additives seem insufficient to form enough liquid phase at that temperature, causing the as-fired body to be less densified. Thus, it is obvious that GPS at higher temperatures promotes the densifying process towards the end.

The XRD patterns in Fig. 2 confirm that only α′ phase exists in almost all specimens. The only exception is that a small amount of M′ ($Dy_2Si_{3\text{-}X}Al_XO_{3+X}N_{4\text{-}X}$, $x = 0 \rightarrow 0.6$) phase appears in sample D4, which was subjected to GPS at 2000°C. At that high temperature, much liquid phase must have formed, especially in this composition to which excess 10 wt% oxides were added, and the nitrogen concentrated in the liquid phase increases accordingly. Due to the limited solubility of nitrogen in the glass phase after cooling, the excessive nitrogen would precipitate as a certain nitride compound which is responsible for the presence of M′ phase[17] instead of DyAG (non-nitrogen containing phase as designed) in the final sintered body. Furthermore the M′ phase has been proved to coexist with both α- and β-sialon according to subsolidus phase relationships in the system Dy_2O_3–Si_3N_4–AlN–Al_2O_3.[18]

3.2. Morphology of the α-sialon ceramics

The whole sintering process of α-sialon ceramics can primarily be divided into two steps, nucleation and growth. The former is considered to finish at a temperature lower than that at which the latter process mostly takes place.[14] In regard to this experiment, it is reasonable to believe that all specimens have completed the former process after PLS at 1800°C for 1.5 h. The GPS firing should only further develop the growth of the grains. The firing temperature and the amount of additives are supposed to be the two major factors. Fig. 3, shows the microstructural morphologies of sample D3, GPS treated at 1800, 1900 and 2000°C, together with the same composition as only PLS treated for 1.5 h for comparison. The sample GPSed at 1800°C is composed of fine and equiaxed grains, simply inheriting the feature before being GPS treated [see Fig. 3 (a)]. However, the morphology of the 1900°C fired sample obviously indicates that inhomogeneous grain growth of α′ has occurred during the treatment at higher temperature. Once the treating temperature becomes extremely high, up to 2000°C, the microstructural feature shows an absolutely different pattern. Several grains preferentially grow extra large, ranging from 2 to 10 μm in diameter and 10 to 100 μm in length.

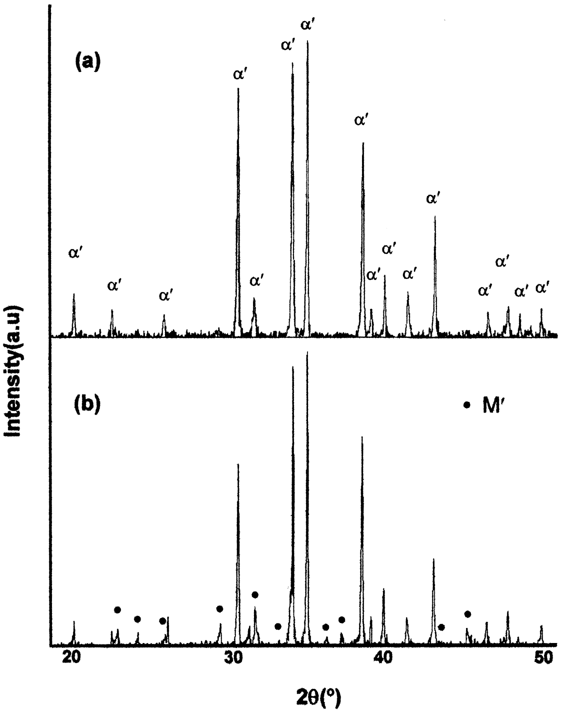

Fig. 2. XRD patterns: (a) typically for all samples except D4(G3) showing only α′ phase existing in those as-fired bodies and (b) for D4(G3), a small amount of M′ phase crystallizing out.

The α-sialon grains form and grow from Si_3N_4 generally via a liquid phase, through the process of solution-diffusion-reprecipitation, and the growth process is somewhat diffusion controlled. Therefore, the higher temperature would certainly favor the grain growth because it supplies more energy to the system to increase the mass transport at grain boundaries. The various changes in viscosity and quantity of the liquid phase which depend partly on temperature will also encourage grain growth when the temperature is elevated. In this study, it seems that more "driving force" for grain growth is concentrated on only a few grains, resulting in them being abnormally extra large, and the extension of such grains is undoubtedly along one direction, which is of great interest to us. Fig. 4, displays the fine grains adjacent to an extra large grain in sample D3 (G3), showing no appreciated grain grow for the matrix.

Research work on the nucleation and growth of equiaxed α-sialon has already been reported.[19] Heterogeneous nucleation and epitaxial growth mode are generally accepted to be the case in most α′ ceramics. After carefully examining the yttrium α′ hot-pressed at 1825°C, Xu et al.[20] found that the deformed structure existed in the elongated grain with a normal size of 9–12 μm in length and 1.5–3 μm in width. They thus concluded that changes of chemical bonding conditions, especially on the (001) plane resulted in the faster deposition of atoms on the (001) plane than on other planes. This might partly explain the observation in this study because higher temperature firing will certainly sustain more distortions in the system, making several α′ grains to grow extraordinarily large. More efforts should be made on TEM before the growth mechanism for such extra large α-sialon grains can be clearly identified.

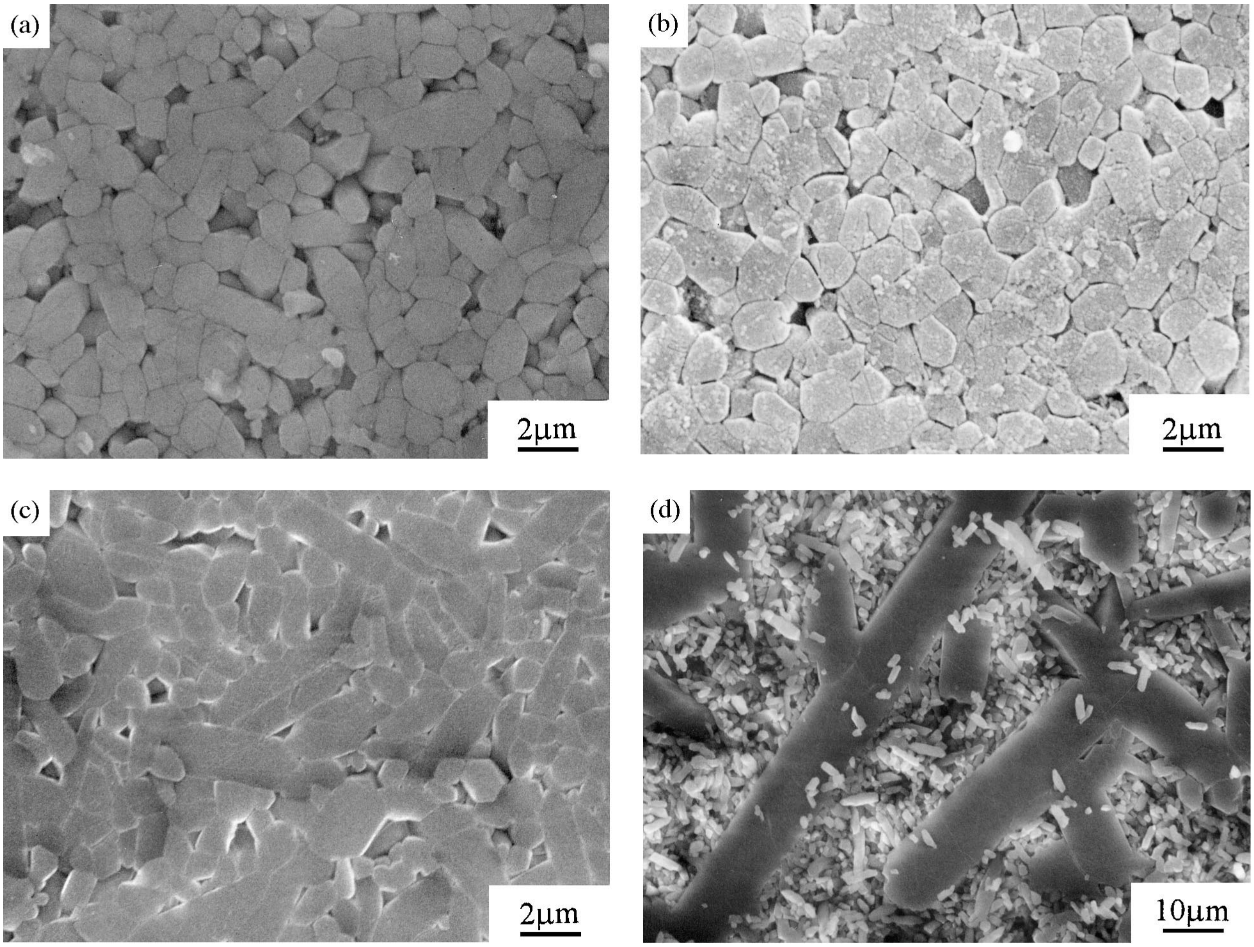

Fig. 3. Microstructural morphologies of composition D3 by different sintering treated: (a) PLS at 1800°C for 1.5 h without GPS firing, (b) PLS plus GPS at 1800°C for 1 h, (c) PLS plus GPS at 1900°C for 1 h and (d) PLS plus GPS at 2000°C for 1 h.

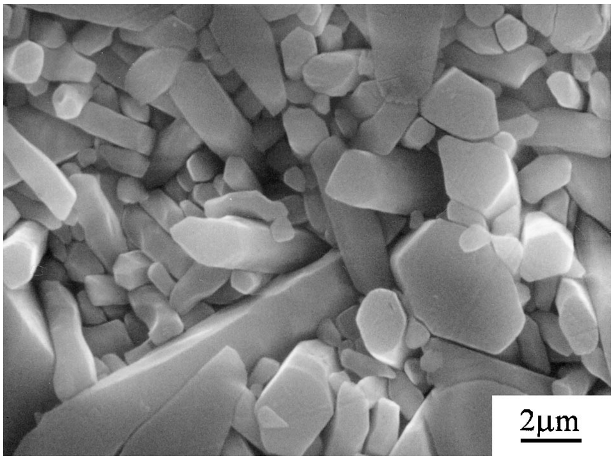

Fig. 4. Microstructural morphology of composition D3 sintered by GPS at 2000°C for 1 h (G3), indicating the matrix grains adjacent to extra large grain are still fine.

Although so-called discontinuous or exaggerated grain growth has been well explained in classical text book,[21] and was observed in the β-Si_3N_4 and β-sialon systems by other researchers,[22,23] no paper describing extraordinarily large α-sialon grain ceramics has yet been found.

Compared to treatment temperature, additive content is a minor factor in developing the α′ to high ratio aspect. Fig. 5, clearly shows the same extra large grains existing in the matrix of D1 treated at 2000°C, only fewer in quantity.

3.3. Mechanical properties

Figs. 6 and 7 plot the hardness and fracture toughness of all samples except for the less densified one, as a function of the sintering additive content at different GPS firing temperatures. Apparently, all samples show the typically high hardness value of α-sialon ceramics, above 1800 HV_{10}. A small decrease in hardness with the increase in GPS treatment temperature could be attributed to there being more liquid phase formed at higher temperature. As a result, there is more glass phase in the sintered bodies after cooling, thus softening the materials to some degree. Also, the same reason causes the variations in hardness among different compositions using the same GPS temperature, i.e. the decrease of

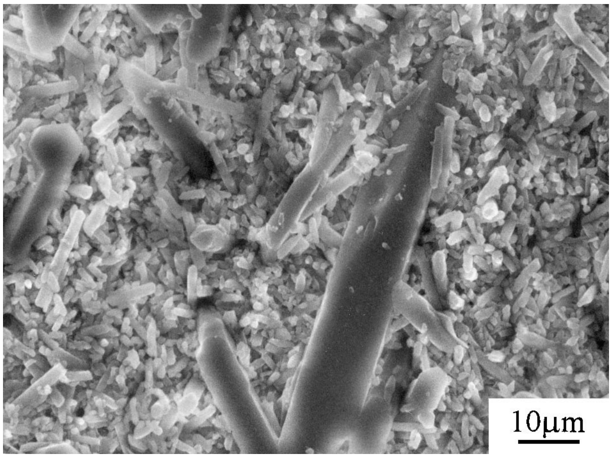

Fig. 5. Microstructural morphology of composition D1 sintered by GPS at 2000°C for 1h (G3), showing the existence of extraordinarily large α' grains.

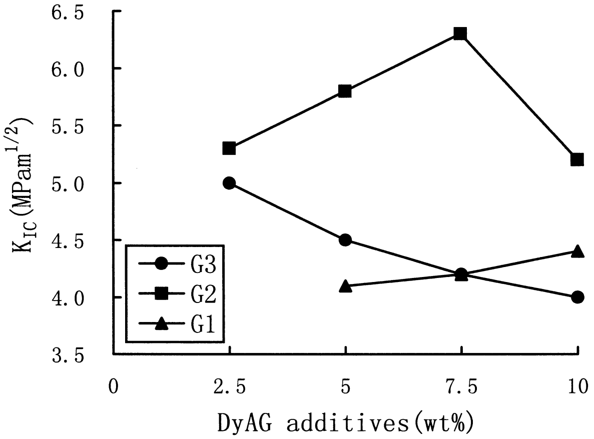

Fig. 7. The fracture toughness of samples GPS fired at three temperatures vs DyAG contents.

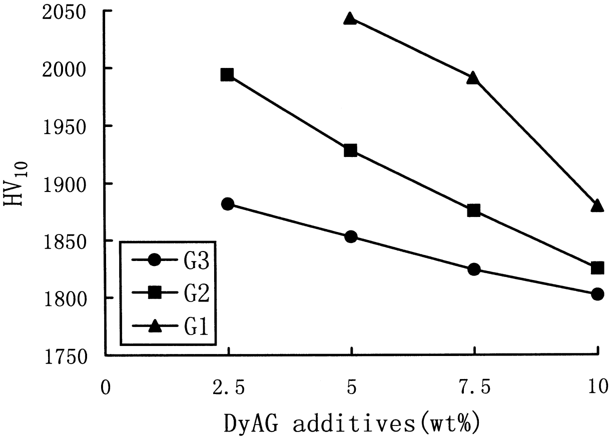

Fig. 6. The hardness of samples GPS fired at three temperatures vs DyAG contents.

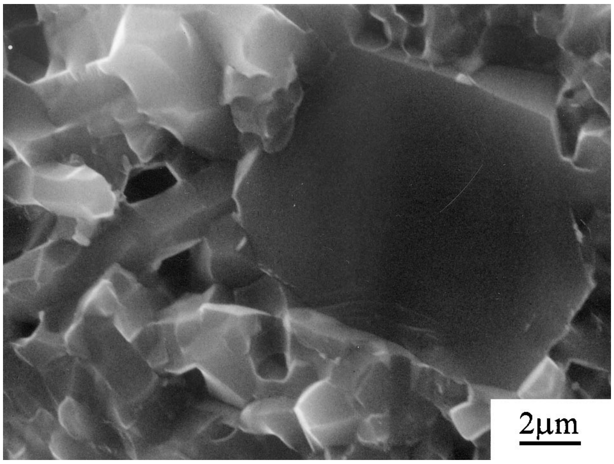

Fig. 8. Fracture surface of composition D3 sintered by GPS at 2000°C for 1 h (G3), revealing the brittle fracture of large grain.

hardness with the increase of additive content. The different behavior in toughness for each specimen is obvious. As indicated in Fig. 7, the samples produced by GPS firing at 1900°C are appreciably tougher than those produced by the other two approaches. The peak appears at 7.5 wt% content composition, values 6.2 MPa·m$^{1/2}$. The variations in toughness could be attributed to the microstructural characteristic as mentioned above. The samples treated at 1900°C were mixed with identical equiaxed and elongated grains, which are assumed to contribute a great deal to the toughening mechanisms in sialon ceramics. However, as indicated in Fig. 8, once crack propagation encounters excessively large α' grain existing in compositions GPSed at 2000°C, it will simply break the grain, implying that such grain does not facilitate crack deflection and/or bridging. Furthermore, large defects generated by extra large α' grains might reduce the toughness.

It should be noted that all the compositions prepared in this work are slightly liquid-rich. Some glass phase must have remained on the grain-boundary which will weaken the ceramics at high temperature. However, post-heat-treatment at relatively low temperature will cause designed DyAG phase to crystallize out according to the subsolidus phase relationships in the Dy–Si–Al–O–N system.[15,18] Since DyAG has a high melting point and good oxidation resistance, it is supposed to eliminate that influence and keep mechanical properties and materials chemically stable at elevated temperatures. Further investigation is in progress.

4. Conclusions

Dysprosium α-sialon ceramics were fabricated by PLS at 1800°C plus GPS at the same and higher temperatures. The higher temperature GPS obviously promoted full densification. The α-sialon was detected as the only crystallized phase for almost all as-fired bodies, excluding composition with the most DyAG added and GPS fired at 2000°C, in which a small amount of M phase appeared. With the increase of firing temperature, some grains developed into elongated grains, while the remaining matrix was unchanged. Several extraordinarily large grains, up to 100 μm in length and 10 μm in width, were observed in the samples fired at 2000°C. Compared with temperature, the microstructural feature was not so sensitive to the amount of additive, suggesting that the grain growth of is somewhat temperature-determining. As-sintered bodies exhibited typically high hardness, above 1800 HV_{10}. Fracture toughness was strongly relevant to the microstructural morphology. Elongated grains increased the toughness in the samples GPS sintered at 1900°C with the highest measured value at 6.2 $MPa{\cdot}m^{1/2}$. No expected toughening effect was found from the extra large grains. On the contrary, toughness decreased with the increase of such large grains, probably as a result of large defects being generated in the materials.

Acknowledgements

The authors would like to thank Dr. Y-B.Cheng (Monash University, Australia) for helpful discussions.

References

1. Hampshire, S., Park, H. K., Thompson, D. P. and Jack, K. H., α'-sialon ceramics. *Nature*, 1978, **274**, 880–882.
2. Huang, Z. K., Tien, T. Y. and Yan, D. S., Subsolidus phase relationships in the Si_3N_4–AlN–rare earth oxide system. *J. Am. Ceram. Soc.*, 1986, **69**, C241–242.
3. Wang, P. L., Sun, W. Y. and Yen, T. S., Sintering and formation behaviour of R-α-sialons (R = Nd, Sm, Gd, Dy, Er and Yb. *Eur. J. Solid State Inorg. Chem.*, 1994, **t.31**, 93–104.
4. Lewis, M. H., Fung, R. and Taplin, D. M. R., Indentation plasticity and fracture of Si_3N_4 ceramics alloys. *J. Mater. Sci.*, 1981, **16**, 3437–3446.
5. Lange, F. F., Fracture toughness of Si_3N_4 as a function of the initial α-phase content. *J. Am. Ceram. Soc.*, 1979, **62**(7–8), 428–430.
6. Himsolt, G., Knoch, H., Huebner, H. and Kleinlein, F. W., Mechanical properties of hot-pressed silicon nitride with different grain structure. *J. Am. Ceram. Soc.*, 1979, **62**(1–2), 29–32.
7. Ekstrom, T. and Ingelstrom, N. Characterisation and properties of sialon materials. In *Nonoxide Technical and Engineering Ceramics*, ed. S. Hampshire. Elsevier Applied Science, London, 1986, pp. 231–253.
8. Nordberg, L. O. and Ekstrom, T., Hot-pressed MoSi2-particulate-Reinforced α-sialon Composites. *J. Am. Ceram. Soc.*, 1995, **78**(3), 797–800.
9. Shen, Z. J., Ekstrom, T. and Nygren, M., Ytterbium–stabilised α-SIAlON ceramics. *J. Phys. D: Appl. Phys.*, 1996, **29**, 893–904.
10. Wang, H., Cheng, Y-B., Muddle, B. C., Gao, L. and Yen, T. S., Preferred orientation in hot-pressed Ca α-sialon ceramics. *J. Mater. Sci. Lett.*, 1996, **15**, 1447–1449.
11. Zhang, C., Sun, W. Y. and Yan, D. S., Fabrication of Dy-α-sialon ceramics. *J. Mater. Sci. Lett.*, 1998, **17**, 583–586.
12. Chen, I-W. and Rosenflanz, A., A tough SiAlON ceramics based on α-Si_3N_4 with a whisker-like microstructure. *Nature*, 1997, **389**(16), 701–704.
13. Hewett, C. L., Cheng, Y-B., Muddle, B. C. and Trigg, M. B., Phase relationships and related microstructural observations in the Ca–Si–Al–O–N system. *J. Am. Ceram. Soc.*, 1998, **81**(7), 1781–1789.
14. Wood, C. A., Zhao, H. and Cheng, Y-B., Microstructural development of Calcium α-SiAlON ceramics with elongated grains. *J. Am. Ceram. Soc.*, 1999, **82**(2), 421–428.
15. Zhang, C., Sun, W. Y. and Yan, D. S., Optimizing mechanical properties and thermal stability of Ln-α-β-sialon by using duplex Ln elements (Dy and Sm). *J. Eur. Ceram Soc.*, 1999, **19**(1), 33–39.
16. Sun, W. Y., Chen, H. G. and Yan, D. S., Kinetic study on β-sialon-DyAG ceramics. *Mater. Sci. Lett.*, 1997, **16**, 1853–1855.
17. Cheng, Y-B. and Thompson, D. P., Aluminium-containing nitrogen melilite phase. *J. Am. Ceram. Soc.*, 1994, **77**(1), 143–148.
18. Sun, W. Y., Yan, D. S., Gao, L., Mandal, H. and Thompson, D. P., Subsolidus phase relatioships in the system Dy_2O_3–Si_3N_4–AlN–Al_2O_3. *J. Eur. Ceram Soc.*, 1996, **16**, 1277–1280.
19. Hwang, S-L. and Chen, I-W., Nucleation and growth of α'SiAlON on α-Si_3N_4. *J. Am. Ceram. Soc.*, 1994, **77**(7), 1711–1718.
20. Xu, F. F., Wen, S. L., Nordberg, L.-O. and Ekstrom, T., Nucleation and growth of the elongated α'-SiAlON. *J. Eur. Ceram Soc.*, 1997, **17**, 1631–1638.
21. Kingery, W. D., *Introduction to Ceramics*. John Wiley and Sons, Inc, New York, London, 1960 pp. 363–369.
22. Hirosaki, N., Akimune, Y. and Mitomo, M., Effect of grain growth of β-silicon nitride on strength, Weibull modulus, and fracture toughness. *J. Am. Ceram. Soc.*, 1993, **76**(7), 1892–1894.
23. Park, D-S., Lee, S-Y., Kim, H-D., Yoo, B-J. and Kim, B-A., Extra-large grains in the silicon nitride ceramics doped with yttria and hafnia. *J. Am. Ceram. Soc.*, 1998, **81**(7), 1876–1880.