Journal of the European Ceramic Society **12** (1993) 431–434

Phase Transformation from α′- to β′-Sialon by Liquid Infiltration in Y–Si–Al–O–N System

Sang-Moo Han, Suk-Joong L. Kang*

Department of Ceramic Science and Engineering, Korea Advanced Institute of Science and Technology, Taejon 305-701, South Korea

&

Yong-Tae Lee

High Temperature Materials Laboratory, Korea Institute of Machinery and Materials, Changwon 641-010, South Korea

(Received 22 March 1993; accepted 15 June 1993)

Abstract

The formation of β′-sialon from α′-sialon during infiltration of a glass matrix has been investigated. Sintered α′-sialon containing large grains of about 5 μm has been resintered within a glass matrix of which the composition is in equilibrium with β′-sialon. During resintering the glass matrix has penetrated into sintered α′-sialon specimen and induced the transformation of α′- into β′-sialon. No trace of α′ is found within β′ grains formed. The nucleation of β′ grains is thus believed to occur not on the preexisting α′ grains but in the penetrated glass matrix. The concentration of Al in β′ grains increases from their centre towards their edge, implying that the glass matrix has continuously penetrated with resintering time. Continuous penetration of glass matrix and thus a concentration gradient in the penetrated glass is also confirmed by a directional growth of 12H polytype grains formed between transformed β′ and bulk glass matrix.

Die Bildung von β′-Sialon aus α′-Sialon während der Infiltration einer Glasmatrix wurde untersucht. Gesintertes α′-Sialon, mit etwa 5 μm großen Körnern, wurde in einer Glasmatrix, deren Zusammensetzung im Gleichgewicht mit β′-Sialon ist, nachgesintert. Während des Nachsinterns drang die Glasmatrix in die gesinterten α′-Sialon Proben ein und induzierte die Transformation von α′- in β′-Sialon. Es konnte kein α′ in den β′-Körnern hachgewiesen werden. Es wird daher angenommen, daß die Keimbildung von β′-Körnern nicht in den bereits existierenden α′-Körnern, sondern in der eindringenden Glasmatrix stattfindet. Die Al-Konzentration in den β′-Körnern nimmt vom Zentrum zu den Rändern hin zu, was bedeutet, daß die Glasmatrix kontinuierlich während der Nachsinterzeit eindringt. Das kontinuierliche Eindringen der Glasmatrix und damit ein Konzentrationsgradient im eingedrungenen Glas wird ebenfalls duch das gerichtete Wachstum der 12H Polytyp-Körner bestätigt, die sich zwischen dem umgewandelten β′ und der massiven Glasmatrix bilden.

Les auteurs ont étudié la formation du sialon β′ à partir du sialon α′ durant l'infiltration d'une matrice vitreuse. Le sialon α′ fritté, contenant de gros grains avoisinant 5 μm environ, a été refritté à l'intérieur d'une matrice vitreuse dont la composition est en équilibre avec le sialon β′. Durant le refrittage, le verre a pénétré l'échantillon de sialon α′ fritté et a induit la transformation sialon α′ → sialon β′. On n'a relevé aucune trace de sialon α′ dans les grains de sialon β′ formés. La nucléation des grains de β′ est donc attribuée, non pas aux grains de α′ pré-existants, mais bien au verre pénétrant dans le fritté. La concentration en Al des grains de β′ augmente depuis le centre vers les côtés, ce qui implique que le verre a continuellement pénétré le solide durant tout le refrittage. Cette continuelle pénétration du verre et donc un gradient de concentration dans le verre pénétré, est aussi confirmée par une croissance directionnelle de grains du polytype 12H formés entre le sialon β′ transformé et la matrice de verre.

1 Introduction

One of the major research subjects for Si_3N_4-based ceramics has been the phase transformation from α

* To whom correspondence should be addressed.

Journal of the European Ceramic Society 0955-2219/93/$6.00

to β'[1-4] because α-Si_3N_4 powder has usually been used to get β'-sialon products. The phase transformation is now understood to occur by solution of α and reprecipitation of β' through a liquid matrix.[5,6] The liquid matrix which forms by reactions between impurity silica, sintering additives and also possibly Si_3N_4 plays in fact the major role for the transformation.[5,7-11]

Probably the most definitive experimental support for the solution–reprecipitation process and the role of liquid matrix is the uneven concentration of elements in single crystal β' grains formed in the liquid matrix.[10,11] Decreasing Al concentration from the centre of β' grains towards their edge for the garnet and cordierite sialon systems[10] and the Si_3N_4–Al_2O_3–Nd_2O_3 system[11] can be understood as a result of changing the liquid composition with sintering temperature and time and the grain growth by material precipitation from liquid, i.e. solution–reprecipitation process.

Another experimental support for the precipitation of materials from liquid matrix is the cored structure of α'- and β'-sialons.[12-14] Observed α- (or β') Si_3N_4 cores within α'- (or β'-) sialon grains[12] appear to demonstrate that the grains were grown by material precipitation and the α'- or β'-sialon nuclei might form on pre-existing α- or β-Si_3N_4 starting powders. As far as the nucleation sites are concerned during the phase transformation from α to β, two possibilities may be considered: pre-existing α or liquid matrix. The previously published cored-microstructure (α within α' and β within β')[12] suggests the former possibility, however, many investigations[2-5] have proposed the latter possibility without any microstructural evidence.

In the present study, the nucleation and growth of β'-sialon during the transformation from α' to β' has been investigated. Since the transformation is rapid and the resulting microstructure is very fine in usual sintering of fine powder mixtures, it may be difficult to determine the transformation mechanism. In this study, large α'-sialon grains were induced to transform into β'-sialon by resintering in a liquid matrix of which the composition is in equilibrium with β'-sialon.

2 Experimental Procedure

Specimens were prepared from commercial α-Si_3N_4 (LC-10, H. C. Starck, Berlin, Germany), AlN (A Grade, H. C. Starck, Berlin, Germany), Al_2O_3 (AKP-30, Sumitomo Chemicals, Tokyo, Japan), and Y_2O_3 (Shin-etsu Chemical Co., 99·99%, Tokyo, Japan) powders. Fifty grams of 77·9 Si_3N_4–13·7 AlN–8·4 Y_2O_3(wt%) powder mixtures were ball-milled for 30 min in a planetary ball mill containing 100 g Al_2O_3 balls and full of ethyl alcohol for the preparation of α'-sialon. Approximately 1·5 g of dried slurry was compressed in a steel die of 15 mm in diameter and isostatically pressed under 200 MPa. The compact was packed with Si_3N_4 powder and sintered in a graphite furnace at 1700°C for 24 h under 0·3 MPa N_2 pressure in order to obtain α'-sialon with large grain size. Sintered α'-sialon was packed with 15 g of 14·4 Si_3N_4–4·2 AlN–40·8 Al_2O_3–40·6 Y_2O_3 (wt%) powder mixture and resintered at 1700°C for various times up to 32 h in 0·3 MPa N_2 to induce the transformation from α' to β'. The chemical composition of the packing powder corresponds to a glass composition which is in equilibrium with β'-sialon at the resintering temperature. The sintered and resintered specimens were etched in an NaOH molten melt at 400°C. The phases present were identified by X-ray diffraction (XRD) using CuKα and their chemical composition was determined by energy dispersive X-ray spectroscope (EDX) attached to scanning electron microscope (SEM) and scanning transmission electron microscopy (STEM) with the reaction beam diameter of 5 μm and 1 μm, respectively. The relative amount of transformed β' ($\beta'/(\alpha'+\beta')$) was determined by the formula $(I_{101}(\beta')+I_{210}(\beta'))/(I_{102}(\alpha')+I_{210}(a')+I_{101}(\beta')+I_{210}(\beta'))$,[15] where each term is the intensity of diffracted beam for a specific plane and phase.

3 Results and Discussion

The microstructure of sintered α'-sialon showed more or less equiaxed grains of about 5 μm in size containing little glassy phase, as shown in Fig. 1. The chemical composition of the α' phase measured by EDX analysis was $Y_{0.5}Si_{9.75}Al_{2.25}O_{0.75}N_{15.25}$. During resintering of the α'-sialon packed with 14·4 Si_3N_4–4·2 AlN–40·8 Al_2O_3–40·6 Y_2O_3 (wt%) powder mixture, the liquid formed penetrated into the

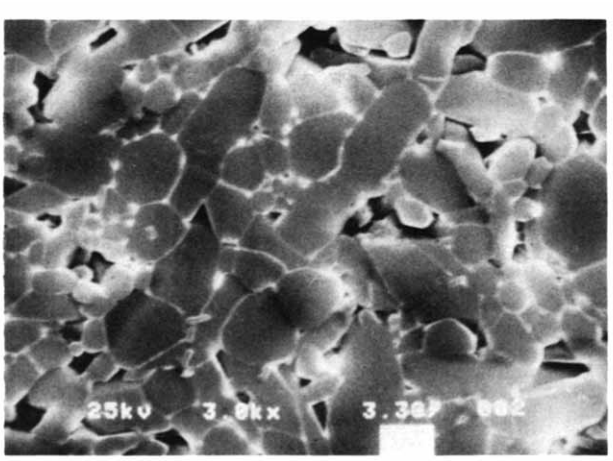

Fig. 1. α'-sialon sintered at 1700°C for 24 h under 0·3 MPa N_2.

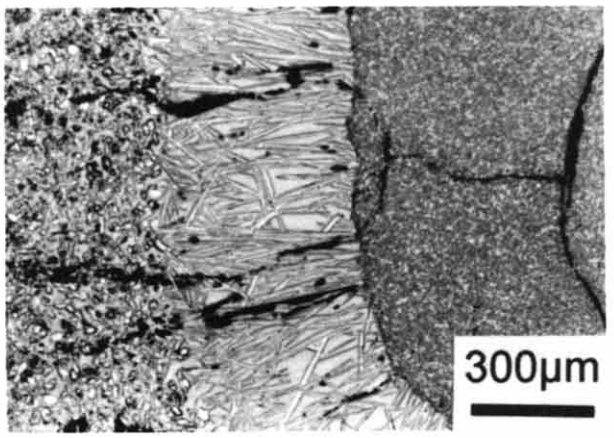

Fig. 2. Optical micrograph of the sample resintered at 1700°C for 32 h under 0·3 MPa N_2. From left, regions of bulk glass matrix, 12H polytype grains, and transformed β′ grains.

specimen and the fraction of β′-sialon ($\beta'/(\alpha' + \beta')$) increased sigmoidally with resintering time. After 32 h resintering, α′-sialon transformed completely into β′-sialon. Between the transformed β′ and bulk glass matrix of which a fraction had been crystallised during cooling, 12H ($SiAl_5O_2N_5$) sialon polytype grains were present, as shown in Fig. 2.

Figure 3 shows large and well-faceted growing β′ grains and small dissolving α′ grains in a specimen resintered for 8 h. (The β′ and α′ grains can be easily distinguished by observing the distribution of yttrium under SEM or STEM.) The cored structure[12–14] which was observed previously (in α–α′ or β–β′ solutions) is not formed in our α′–β′ transformation. TEM micrographs, such as Fig. 4, also show that any second phase or heterogeneity is not present within the transformed β′ grains. The cation composition of β′ grains was measured more than 30 times by an EDX attached to STEM with the reaction beam diameter size of 1 μm. No yttrium was detected within any single crystal β′-sialon, indicating that no α′ grain was entrapped within β′-grains during the transformation from α′ to β′. Yttrium was present only in the glass matrix. This experimental

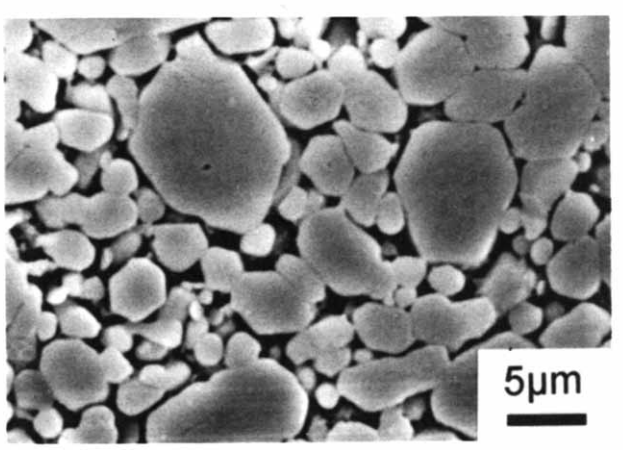

Fig. 3. SEM micrograph of the specimen resintered at 1700°C for 8 h. Large, faceted grains are β′ and small grains α′.

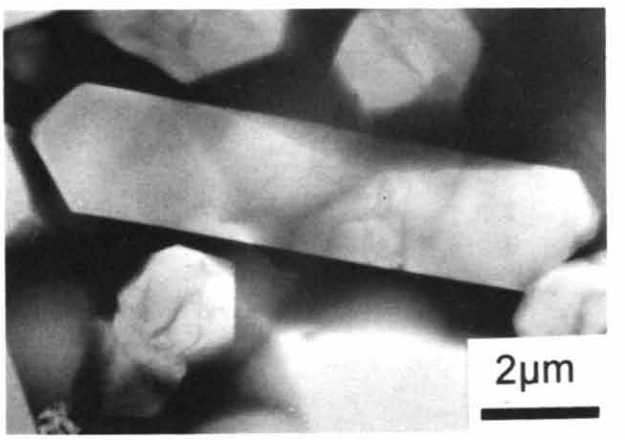

Fig. 4. TEM micrograph of transformed β′-sialon grains in specimen resintered for 32 h.

observation may imply that the nucleation and growth of β′ grains occur mostly within and from the penetrated glass matrix, and not on the pre-existing α′ grains, in contrast to the case of α–α′ or β–β′ transformation. It also appears that the old α′ phase is very unstable to dissolve out completely without any entrapment of the phase within newly formed β′ grains.

The compositional change of the penetrated liquid matrix during resintering may be presumed by measuring the variation of the aluminium concentration in single crystal β′-sialon grains formed.[11] Contrary to the previous investigations,[10,11] the Al concentration increased from the centre of grains towards their edges, as shown in Fig. 5. In usual sintering of β′-sialon, a liquid containing Al oxide forms first and the Al oxide in the liquid is consumed with the formation of β′-sialon. The result of such a consumption of Al oxide in the liquid is a decrease in Al concentration from centre towards edge of single crystal β′ grains.[11] In our experiment, on the other hand, the liquid which induces the α′ to β′ transformation is supplied from the outside of the α′ compact. With resintering time the bulk liquid matrix seems to penetrate continuously into the sintered α′ compact, resulting in higher Al con-

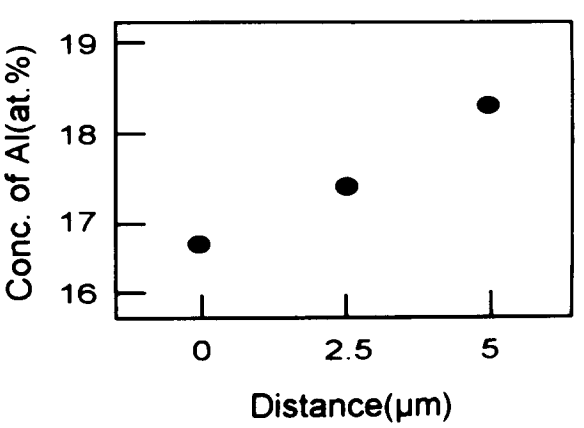

Fig. 5. Al concentration in a single crystal β′ grain. The abscissa represents the distance from the centre of the hexagonal grain.

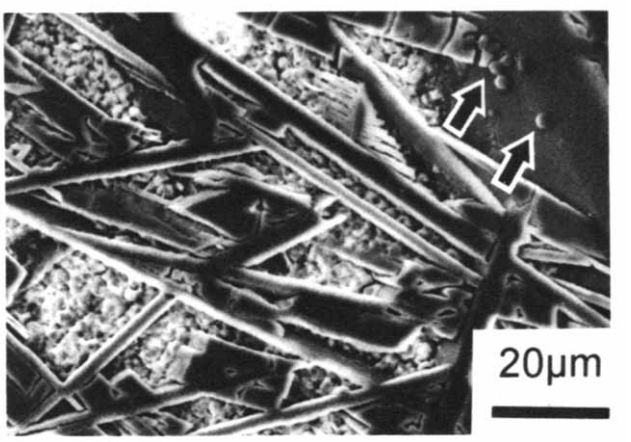

Fig. 6. Entrapped β'-sialon grains (indicated by arrows) in fast-growing 12H($SiAl_5O_2N_5$) plate-like grains.

centration in the penetrated liquid matrix between grains and therefore precipitation of β' phase with higher Al concentration.

The 12H ($SiAl_5O_2N_5$) sialon polytype formed between transformed β' and bulk liquid matrix were plate-like, as shown in Figs 2 and 6. From the region near the bulk matrix phase towards the transformed β' compact, most of the 12H grains appear to be aligned towards the β'-region, suggesting that the grains are directionally grown. Such a directional growth implies again a concentration gradient in the matrix and also a continuous penetration of liquid matrix during resintering. A similar directional growth of plate-like $CaO.6Al_2O_3$, an intermediate phase, was also observed during reaction between $CaO.MgO.SiO_2$ glass and Al_2O_3.[16] Within some 12H grains small sialon grains were entrapped as shown in Fig. 6, indicating that the growth of 12H grains in longitudinal direction is very fast. The entrapped grains were found to be β'-sialon by an observation of element distribution which showed no presence of yttrium within the grains. The non-existence of any α' fragment within β' grains shows, on the other hand, that the growth of β' grains is not fast enough to trap the dissolving α' fragments, as we have observed in the microstructures (Figs 3 and 4).

4 Summary

During resintering of sintered α'-sialon ($Y_{0.5}Si_{9.75}Al_{2.25}O_{0.75}N_{15.25}$) in a liquid matrix of which the composition is in equilibrium with β'-sialon at the resintering temperature, the liquid has infiltrated into the α' specimen and the α' phase has transformed into β'. Despite the large grain size, about 5 μm, of the α'-sialon no trace of the α' is found in any transformed β', suggesting that the nucleation and growth of the β' phase does not occur on pre-existing α' grains but in the liquid matrix. Increasing Al concentration within single crystal β' grains from their centre towards their edges indicates continuous infiltration of liquid matrix into the α' compact during the transformation and growth of β' grains. Directional growth of the 12H ($SiAl_5O_2N_5$) sialon polytype towards the sintered compact also indicates concentration gradient in the liquid matrix in the same direction during resintering and phase transformation.

Acknowledgment

This work was supported by the Korea Science and Engineering Foundation (KOSEF).

References

1. Lange, F. F., Relation between strength, fracture energy, and microstructure of hot-pressed Si_3N_4. *J. Am. Ceram. Soc.*, **56** (1973) 518–22.
2. Jack, K. H., The characterization of α'-sialons and the α-β relationships in sialons and silicon nitrides. In *Proceedings of the NATO Advanced Study Institute on Nitrogen Ceramics Progress in Nitrogen Ceramics*, ed. F. L. Riley. Nijihoff, The Hague, The Netherlands, 1983, pp. 45–60.
3. Natansohn, S. & Sarin, V. K., The α-to-β transformation in Si_3N_4 powders. In *Proceedings of the Second International Conference Ceramic Powder Processing Science*, ed. H. Hausner, G. L. Messing & S. Hirano. Deutsche Keramische Gesellschaft, Köln, Germany, 1989, pp. 433–44.
4. Hwang, C. J. & Tien, T.-Y., Microstructural development in silicon nitride ceramics. In *Preparation and Properties of Silicon Nitride Based Materials*. Publ. Trans. Tech., Switzerland, 1989, pp. 84–109.
5. Hampshire, S. & Jack, K. H., The kinetics of densification and phase transformation of nitrogen ceramics. *Proc. Brit. Ceram. Soc.*, **31** (1981) 37–49.
6. Hampshire, S., *The Sintering of Nitrogen Ceramics*. The Parthenon Press, UK, 1986, pp. 164–70.
7. Terwilliger, G. R. & Lange, F. F., Pressureless sintering of Si_3N_4. *J. Mater. Sci.*, **10** (1975) 1169–74.
8. Gazza, G. E., Hot-pressed Si_3N_4. *J. Am. Ceram. Soc.*, **56** (1973) 662.
9. Gazza, G. E., Katz, R. N. & Priest, H. F., Densification of Si_3N_4–Y_2O_3/Al_2O_3 by a dual N_2 pressure process. *J. Am. Ceram. Soc.*, **64** (1981) C-161–2.
10. Bonnell, D. A., Rühle, M. & Tien, T.-Y., Redistribution of aluminum ions during processing of sialon ceramics. *J. Am. Ceram. Soc.*, **69** (1986) 623–7.
11. Kim, N.-K., Kim, D.-Y., Kranzmann, A., Bischoff, E. & Kang, S.-J. L., Variation of Al concentration in β'-sialon grains formed during liquid phase sintering of Si_3N_4–Al_2O_3–Nd_2O_3. *J. Mater. Sci.*, **28** (1993) 4355–8.
12. Chatfield, C., Ekström, T. & Mikus, M., Microstructural investigation of alpha–beta yttrium sialon materials. *J. Mater. Sci.*, **21** (1986) 2297–307.
13. Ekström, T., Ingelström, N., Brage, R., Hatcher, M. & Johansson, T., α–β sialon ceramics made from different silicon nitride powders. *J. Am. Ceram. Soc.*, **71** (1988) 1164–70.
14. Ingelström, N. & Ekström, T., Relation between composition, microstructure and cutting tool performance of alpha–beta sialons. *J. Phys. (Les Ulis, Fr.)*, **47** (1986) 347–52.
15. Grand, G., Demit, J., Ruste, J. & Torre, J. P., Composition and stability of Y–Si–Al–O–N solid solution based on α-Si_3N_4 structure. *J. Mater. Sci. Lett.*, **14** (1979) 1749–51.
16. Park, S.-Y., Kim, K.-H. & Kang, S.-J. L., Formation of $CaO.6Al_2O_3$ and $MgAl_2O_4$ during dissolution of Al_2O_3 into $CaMgSiO_4$ melt. *J. Mater. Sci. Lett.*, **11** (1992) 315–16.