Journal of the European Ceramic Society 20 (2000) 23–27

Formation and densification of 21R AlN-polytypoid

P.L. Wang*, W.Y. Sun, D.S. Yan

The State Key Lab on High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Shanghai 200050, People's Republic of China

Received 18 January 1999; received in revised form 22 March 1999; accepted 1 April 1999

Abstract

The formation, densification behaviour and mechanical properties of 21R AlN-polytypoid($SiAl_6O_2N_6$) were studied. The results show that 12H($SiAl_5O_2N_5$) is a transitional phase during the formation of 21R. The additives Sm_2O_3 and Nd_2O_3, especially combined with Al_2O_3 can effectively promote the densification of 21R. The hardness(Hv_{10}) of 21R hot-pressed with 2.5 wt% $SmAlO_3$ at 1750°C/1 h is 1443 with a fracture toughness of 4.6 MPa.m$^{1/2}$. The X-ray diffraction pattern of 21R was also determined in the present work. The revised unit cell dimensions of 21R are $a = 3.0461(1)$Å, $c = 56.643(3)$Å. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: AlN polytypoid 21R; Sintering; Mechanical properties; Sialon

1. Introduction

It is well known that sialon ceramics are a family of materials which possess high performance properties. Among the sialon family, β-sialon(β') and α-sialon(α') are the most important phases and have been well developed into engineering ceramics because of their excellent mechanical properties. In the Si–Al–O–N system, at the compositions between β-sialon and AlN, there are five polytypoid phases (15R, 12H, 21R, 27R and $2H^{\delta}$) with wurtzite-type structures having compositions represented as M_mX_{m+1} [1–2]. The crystal structures of AlN-polytypoids have been studied in details [3,4], but studies concerning their fabrication and mechanical properties are scarce [5,6]. Komeya [6] indicated that 27R has an approximately constant strength value at room temperature to 1700°C (380–470 MPa prepared under the special conditions). This high refractoriness of the 27R polytypoid suggests that other polytypoids would be also highly refractory. AlN-polytypoid phases possess needle or elongated platelet morphology. This morphology characteristics is expected to have a strengthening and toughening effect on the matrix phases. The single-phase 12H with small amount of YAG has good high temperature flexural strength (above 500 MPa at 1000–1300°C) although its room temperature strength is only 367 MPa [7]. The phase relationships in the Y–Si–Al–O–N system [8] indicated that AlN-polytypoids (from 12H to $2H^{\delta}$) are compatible with Al_2O_3 -rich α-sialon ($Y_{1/3m}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$, $m = 1.0$, $n = 1.7$). Based on this consideration, an α-sialon-12H composite ceramics [9] has been studied and the results showed that the incorporation of a certain amount of 12H (10wt%) has a great strengthening and toughening effect on the α-sialon ceramics, but does not appreciably impair hardness. These results stimulated us to study the other AlN-polytypoids. On the other hand, recent studies [10] on the morphology of α-sialon indicated that by using β-Si_3N_4 as a starting powder, the Ln-α' formed can develop into aciculate morphology and give a higher fracture toughness. Under general conditions, α-sialon always exhibits equiaxed morphology. Shen et al. observed liquid-rich compositions promoting the formation of elongated α-sialon [11]. We found that α-sialon is more easy to develop into elongated morphology if the compositions locate on or beyond the top limit of the α' region where AlN-polytypoids occur as a second phase. Therefore, the knowledge of AlN-polytypoids seems to be beneficial for developing composite sialon materials with elongated α'. Based on these considerations, we firstly carried out some basic work on 21R, including to inspect the X-ray reflection data. The further studies on flexural strength at high temperature and the fracture mechanism are being carried on and the results will be reported later.

---

* Corresponding author. Fax: + 86-216251-3903.

PII: S0955-2219(99)00090-4

2. Experimental

As indicated in the Si–Al–O–N phase diagram, each AlN-polytypoid phase (M_mX_{m+1}) occurs along a certain line with M:X equal to m:(m + 1). The normal composition of 21R can be taken as $SiAl_6O_2N_6$. Ln_2O_3 (Ln = Sm,Nd) alone and Ln_2O_3 with Al_2O_3 were used as sintering additives. In the Nd(Sm)–Si–Al–O–N system [12], the AIN-polytypoids which are compatible with α-sialon are restricted to the range starting from 21R to $2H^{\delta}$ and $LnAlO_3$ is compatible with all AIN-polytypoids. Therefore, in the present work 21R was studied and the sintering additives Ln_2O_3 (Ln = Nd,Sm) and combined additives Ln_2O_3: Al_2O_3 = 1:1 were selected. The starting materials used were Si_3N_4(UBE), AlN(1.2 wt% oxygen), Al_2O_3(99.99%) and Ln_2O_3(L = Sm, Nd, 99.9%). The oxygen content of the nitride powder was taken into account in the calculation of the compositions. The powders were mixed with absolute alcohol and milled in an agate mortar for 1.5 h, dried and then hot-pressed in a graphite-resistance furnace under 20 MPa in flowing N_2 atmosphere. The bulk density of the specimens was measured by Archimedes' principle. The phase variation in 21R composition with 2.5 wt% $SmAlO_3$ was studied at temperatures ranging from 1500 to 1800°C. For determination of mechanical properties and microstructure observations, the hot pressing temperature was selected to be 1750°C. Phases were identified by X-ray diffraction and patterns of 21R with and without additives were determined using a Guinier-Hägg camera with Cu $K_{\alpha 1}$ radiation and Si as an internal standard. The measurement of X-ray films and refinement of lattice parameters were completed by a computer-linked line scanner (LS-18) system and SCANPI, PIRUM programs [13,14]. Hardness and indentation fracture toughness were measured by using a Vickers diamond indenter under a load of 100N. A polished surface of the samples was observed under SEM(KYKY2000, China).

3. Results and discussion

3.1. Densification and phase formation

It has been well known that all the Si–Al–O–N phases such as β-sialon, O-sialon and AlN-polytypoids can not be densified without additives. Rare earth oxides such as Sm_2O_3 or Nd_2O_3 (generally with Al_2O_3) have been known to be effective sintering additives for α′-β′ or α′. In the present work, Sm_2O_3, Nd_2O_3 either separately combined with Al_2O_3 were used as sintering additives (see Table 1). As indicated, the effect of the additives on densification is obvious. Based on composition and lattice parameter, the theoretical density of 21R is 3.349 g/cm^3(3.385, 3.386g/cm^3 and 3.257 g/cm^3 for 15R, 12H and AlN respectively). For the composition 21R-0 (pure 21R composition without additive), the bulk density of 2.605 g/cm^3 can be easily estimated to be about 80% dense. The addition of small amount of Sm_2O_3 (Nd_2O_3) and Al_2O_3 to the 21R composition would make the theoretical density difficult to be accurately estimated. Based on the bulk density, the type and amount of sintering additives, it seems $SmAlO_3$ is more effective than the other additives for the densification of 21R. Two densification curves of 21R-0 and 21R-3 were determined (see Fig. 1). As indicated in Fig. 1, the composition 21R-0 has very poor densification behavior, but the addition of 2.5 wt% $SmAlO_3$ can effectively promote densification. The density increases to the top value at 1600°C and then nearly keeps constant with increasing temperature. This behavior is very like to 12H, which also needs small amount of additive (2.5 wt%YAG) for full densification [7].

The densification behavior is always reated to the variation in phase compositions. Fig. 2 shows phase variation of the composition 21R-3 during 1500–1800°C.

Table 1
Density and phase compositions after hot-pressed at 1750°C/1 h

Sample	Additives		Density (g/cm^3)	Phases present[a]
	Formula	wt%		
21R-0	None		2.605	21R s; 12H ms; AlN m
21R-1	Sm_2O_3	5.0	3.400	21R s; 27R m; 12H vw; U vw
21R-2	Sm_2O_3	2.5	3.370	21R s; 12H m; U w
21R-3	$SmAlO_3$	2.5	3.396	21R s; U tr
21R-4	Nd_2O_3	2.5	3.391	21R s; U vw
21R-5	$NdAlO_3$	2.5	3.390	21R s

[a] U: U-phase ($Ln_3Si_3Al_3O_{12}N_2$).

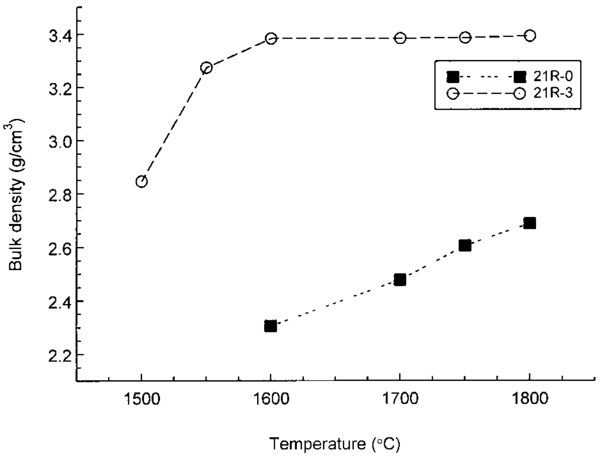

Fig. 1. Effect of additives (2.5 wt%$SmAlO_3$) on densification behaviour of 21R.

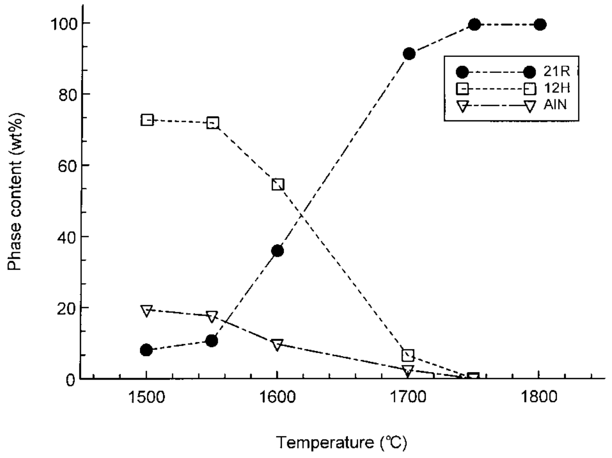

Fig. 2. Variation of phase composition in 21R samples densified with 2.5 wt%SmAlO$_3$ in the temperature range 1500–1800°C.

At the temperatures below 1550°C, the formation of 12H in the composition 21R-3 indicates that 12H has priority over 21R. As a transitional phase, 12H decreases with increasing temperature and finally disappears at 1750°C, at which AlN as a starting powder also completely dissolves. The disappearance of AlN implies the completion of the reaction. The phase analysis for the other compositions hot pressed at 1750 °C/1 h are listed in Table 1. As indicated, to obtain pure single phase 21R, the composition should be strictly controlled. Without additive, the reaction cannot be completed at 1750°C (21R-0). When the composition contains more additives, such as the composition 21R-1 (containing 5 wt% Sm$_2$O$_3$), 27R occurs. In Si–Al–O–N system, 27R (SiAl$_8$O$_2$N$_8$) is located beside 21R (SiAl$_6$O$_2$N$_6$) with more AlN than 21R. At high temperature, the formation of liquid phase which is more SiO$_2$-rich than the matrix phase would make the total solid phase composition shift towards AlN-rich side. Therefore, the occurrence of 27R in 21R composition can balance the total composition. With less additives, 12H is more difficult to remove (as in 21R-2). However, it is also seen from Table 1 that 12H phase does not present in 21R-3, 21R-4 and 21R-5 samples, which use the same amount of additives (2.5 wt%) as 21R-2, and these samples have higher bulk densities than 21R-2. It implies that these compositions are more promotive than 21R-2 for the formation of liquid phase at the same temperature during sintering and the complete dissolution of 12H seems to depend on the amount of liquid phase at sintering temperatures. U-phase (Ln$_3$Si$_3$Al$_3$O$_{12}$N$_2$) [15] is a crystalline phase formed from glasses in Sm(Nd)–Si–Al–O–N systems. Normally, it occurs during heat treatment. In this work, U phase was found in 21R-1 to 21R-4 samples, which may be resulted from the low cooling rate of the furnace. As the amount of U phase in these samples is very limited, the existence of U phase will not play a significant role in influencing mechanical properties.

3.2. The X-ray diffraction data of 21R

As mentioned above, all the AlN-polytypoid phases(15R, 12H, 21R, 27R and 2H$^{\delta}$) possess wurtzite-type structures and their compositions can be represented as M_mX_{m+1} [1,2]. These are built up by MX double layers of metal(M) and non-metal(X) atoms stacked with variants of AB and ABC sequences, as in silicon carbide and with MX_2 layers at periodic intervals to account for the different stoichiometries and structures. Thompson et al. have studied the crystal structures of AlN-polytypoids and gave the complete X-ray diffraction data of AlN-polytypoids (from 8H to 12H$^{\delta}$) [3]. These data have been widely used by the researchers working on sialon ceramics. However, for identification of 21R phase, we got some confusion. A peak at $d=2.697$Å always occurs in 21R compositions which was close to the strongest diffraction peak (100) of AlN, and the strong peak (0021) of 21R, which was reported to be at $d=2.719$Å [3], did not occur. Therefore, in the present study, the work for revision of the X-ray diffraction data of 21R was then carried out. As indicated (see Table 2), the results are good enough because the figures of merit are $M(20)=48$ and $F(20)=41(0.005423, 91)$. The peak occurring at $d=2.697$Å is actually the peak of (0021) of 21R. The revised lattice parameters of 21R are $a=3.0461(1)$Å and $c=56.643(3)$Å ($a=3.048$Å; $c=57.19$Å reported by Thompson [3]). The decrease in c axis of the cell dimension of 21R is consistent with the decrease in d-values for lines of the type (001). According to the Si–Al–O–N behaviour diagram at 1700 °C [16], 21R has a range of composition, from SiAl$_6$O$_2$N$_6$ to around Si$_{0.33}$Al$_{6.67}$O$_{2.67}$N$_{5.33}$, with Si–N by Al–O replacement. Like β sialon, this replacment would also result in the increase of lattice parameters. In order to check if the decrease in c axis of the cell dimension of 21R obtained in this work would be caused by the range of composition, the lattice parameters of two samples with different replacements (Si$_{0.67}$Al$_{6.33}$O$_{2.33}$N$_{5.67}$ and Si$_{0.33}$Al$_{6.67}$O$_{2.67}$N$_{5.33}$) hot-pressed at 1750°C were determined. The lattice parameters of Si$_{0.67}$Al$_{6.33}$O$_{2.33}$N$_{5.67}$ and Si$_{0.33}$Al$_{6.67}$O$_{2.67}$N$_{5.33}$ are $a=3.0486(3)$Å, $c=56.9(1)$Å and $a=3.0513(4)$Å, $c=57.0(1)$Å respectively. The results indicate that the composition (SiAl$_6$O$_2$N$_6$), which is located on the line between SiO$_2$ and AlN in phase diagram of the Si–Al–O–N system, has the smallest cell dimension among the three compositions of 21R and both a and c axes of the cell increase with increase in replacment of Si–N by Al–O for 21R composition.

3.3. Microstructure and mechanical properties

As indicated in Fig. 3(a), pure 21R composition (21R-0) shows much pores and the grains have not well developed. This microstructure coincides with its low density. Fig. 3(b) and (c) represent micrographs of 21R

Table 2
X-ray diffraction data of 21R ($SiAl_6O_2N_6$)[a]

H	K	L	d_{calc}	d_{obs}	$2\theta_{obs}$	I/I_0
0	0	21	2.6973	2.6973	33.187	55.2
1	0	1	2.6351	2.6352	33.993	100.0
1	0	2	2.6265	2.6260	34.115	6.3
1	0	4	2.5934	2.5938	34.552	2.0
1	0	5	2.5692	2.5689	34.897	7.4
1	0	8	2.4719	2.4720	36.313	13.1
1	0	10	2.3913	2.3911	37.587	41.6
0	0	24	2.3601	2.3597	38.105	10.2
1	0	11	2.3478	2.3473	38.315	7.8
1	0	13	2.2566	2.2571	39.910	5.9
1	0	14	2.2097	2.2097	40.803	6.0
0	0	27	2.0979	2.0982	43.077	1.8
1	0	20	1.9303	1.9297	47.053	8.4
1	0	22	1.8425	1.8424	49.429	22.2
1	0	23	1.8002	1.8002	50.668	6.5
1	0	25	1.7188	1.7187	53.253	1.0
1	1	0	1.5230	1.5229	60.771	99.4
1	1	1	1.5225			
1	0	31	1.5020	1.5020	61.708	10.4
1	0	32	1.4699	1.4701	63.201	13.0
1	0	34	1.4086	1.4084	66.315	1.8
1	0	35	1.3794	1.3795	67.890	16.2
1	1	21	1.3262	1.3261	71.023	60.0
2	0	1	1.3186	1.3185	71.497	10.2
2	0	10	1.2846	1.2844	73.701	10.2
2	0	11	1.2777	1.2778	74.147	7.9
1	1	27	1.2325	1.2327	77.350	2.2
2	0	20	1.1957	1.1958	80.204	2.3
2	0	22	1.1739	1.1740	82.014	5.8
2	0	23	1.1627	1.1628	82.974	1.5

[a] Hexagonal $a=3.0461$ (1)Å; $c=56.643(3)$ Å; M (20) = 48; $F(20)=$ 41 (.005423, 91).

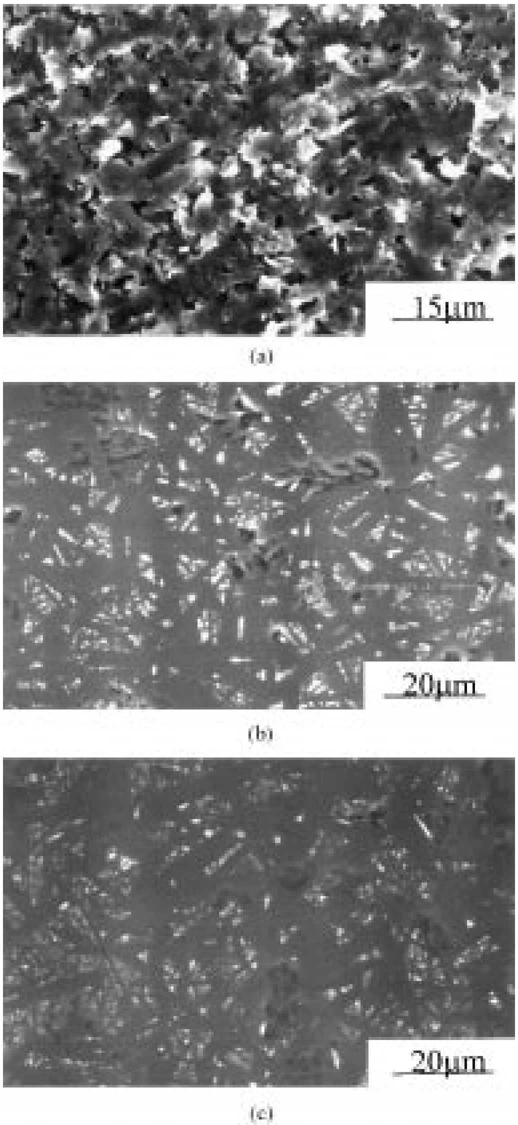

Fig. 3. SEM micrographs of 21R hot-poressed at 1750°C/1 h: (a)21R-0; (b)21R-3 (back scattered) and (c) 21R-5 (back-scattered).

with the addition of 2.5 wt% $SmAlO_3$ and 2.5 wt% $NdAlO_3$ respectively. As expected, in these compositions, 21R grains well developed and exhibited the fiber-like morphology. No obvious difference between Fig. 3(b) and (c) was observed. However, it is noted that some grains of 21R-3 and 21R-5 samples are very large. According to our previous results [7] of 12H, the amount of additive had an effect on the grain size of 12H and the grain size becomes smaller with increasing the additive. The grain size change might be the result of having more nucleation sites being developed because of more liquid phase present during hot pressing. In this work, the amount of additive used in the compositions (21R-2 to 21R-5) are correspondong to the smallest one used in 12H study [7]. Therefore, this may explain the existence of some larger grains in 21R. However, a further study on the factors to affect the grain morphology and how to control the grain growth of 21R are also helpful. The mechanical properties of the compositions (hot pressed at 1750°C/1 h) are listed in Table 3. The hardness(Hv_{10}) and fracture toughness vary with compositions. They are in the range of 1265–1443 for hardness and 4–4.6 MPa.m$^{1/2}$ for fracture toughness. These data are very similar to 12H with 2.5 wt%YAG (1400 and 3.6 MPa.m$^{1/2}$ for hardness and K_{1c}) [7]. Among these five compositions, 21R-3(2.5 wt% $SmAlO_3$) has relatively higher hardness and fracture toughness.

Although the intrinsic nature of 21R is inferior to that of Si_3N_4-based matireals because of its weaker Al–N bond comparing with Si–N bond, the elongated platelet morphology of 21R is expected to have a strengthening and toughening effect on the matrix phases. In fact as mentioned in the introduction section, the incorporation of a certain amount of 12H do has shown a strengthening effect on the α-sialon ceramic [9]. This study is mainly around the basic work of 21R. At this stage, it is difficult to give comment on wether the overall results suggest that 21R material has potential in comparison with sialons. The flexural strength of 21R at high temperature is being carried out and the results will

Table 3
Mechanical properties of 21R hot-pressed at 1750°C/1 h

Sample no.	Hv_{10}	K_{1c} (MPa.m$^{1/2}$)
21R-1	1265	4.0
21R-2	1366	4.0
21R-3	1443	4.6
21R-4	1300	4.0
21R-5	1385	4.4

be reported later. However, the knowledge of 21R would be beneficial to develop composite materials containing α-sialon and AlN-polytypoids. Considering 21R is compatible with α-sialon in the Nd(Sm)-Si–Al–O–N system, a study on Nd(Sm)-α-sialon-21R multiphase ceramic is also worthy to be continued.

4. Conclusion

A dense near single-phase 21R ceramic has been successfully fabricated by hot pressing at 1750 °C for 1 h. In the formation of 21R, 12H occurs as a transitional phase and completely disappears at 1750°C. 21R composition can not be densified without sintering additive. Among the additives used, $SmAlO_3$ is the most effective. The unit cell dimensions of 21R were determined to be $a = 3.0461$ (1)Å, $c = 56.643(3)$ Å. The mechanical properties of 21R vary with the compositions. They are in the range of 1265–1443 for hardness(Hv_{10}) and 4–4.6 MPa.m$^{1/2}$ for fracture toughness. Both the highest hardness and fracture toughness occur in the composition with 2.5 wt% $SmAlO_3$ as sintering additive.

Acknowledgements

This work has received financial support from the National Natural Science Foundation of China, Contract No. 59632100. The technical assistance of Y.X. Jia and J. Zhang are greatly acknowledged.

References

1. Jack, K. H., Nitrogen ceramics. *J. Brit. Ceram. Soc.*, 1973, **72**, 376–386.
2. Gauckler, L. J., Lukas, H. L. and Petzow, G., Contribution to the phase diagram Si_3N_4-SiO_2-AlN-Al_2O_3. *J. Am. Ceram. Soc.*, 1975, **58**, 346–347.
3. Thompson, D. P., Korgul, P. and Hendry, A., The structural characterization of sialon polytypoids. In *Progress in Nitrogen Ceramics*, ed. F. L. Riley Martinus NijhoffIn. The Hague, The Netherlands, 1983, pp. 61–74.
4. Bando, Y., Mitomo, M., Kitami, Y. and Izumi, F., Structural and composition analysis of silicon aluminium oxynitride polytypes by combined use of structure imaging and microanalysis. *J. Microscopy*, 1986, **142**, 235–246.
5. Cannard, P. J., Ekstrom, T. and Tilley, R. J. D., The formation of phases in the AlN-rich corner of the Si–Al–O–N system. *J. Eur. Ceram. Soc.*, 1991, **8**, 375–382.
6. Komeya, K. and Tsuge, A., Formation of AlN polytype ceramics and some of their properties. *Yogyo-kyokai-Shi*, 1981, **89**, 615–620.
7. Li, H. X., Sun, W. Y. and Yan, D. S., Mechanical properties of hot-pressed 12H Ceramics. *J. Eur. Ceram. Soc.*, 1995, **15**, 697–701.
8. Sun, W. Y., Tien, T. Y. and Yan, D. S., Subsolidus phase relationships in part of the system Si,Al,Y/N,O: the system Si_3N_4-AlN-YN-Al_2O_3-Y_2O_3. *J. Am. Ceram. Soc.*, 1991, **74**, 1753–1758.
9. Li, H. X., Sun, W. Y., Yan, D. S. and Tien, T. Y., Mechanical properties of hot-pressed 12H ceramics. In *Proceedings of the 5th International Symposium On Ceramic Materials & Components for Engines*, ed. D.S. Yan et al. World Scientific, Singapore, 1995, pp. 194–197.
10. Chen, I-Wei and Rosenflanz, A., A tough SiAlON ceramic based on α-Si_3N_4 with a whisker-like microstructure. *Nature*, 1997, **389**, 701–704.
11. Shen, Z., Nordberg, L.-O., Nygren, M. and Ekström, T., α-Sialon grains with high aspect ratio-utopia or reality? In *Proc. Nato AST Engineering Ceramics '96 — Higher Reliability through Processing*, ed. G. N. Babini. Kluwer Academic, Dorcrecht, 1977, pp. 169–178.
12. Sun, W. Y., Yan, D. S., Gao, L., Mandal, H., Liddell, K. and Thompson, D. P., Subsolidus phase relationships in the systems Ln_2O3-Si_3N_4-AlN-Al_2O_3(Ln = Nd,Sm). *J. Eur. Ceram. Soc.*, 1995, **15**, 349–355.
13. Johansson, K. E., Palm, T. and Werner, P.-E., An automatic microdensitometer for X-ray powder diffraction photographs. *J. Phys. E.: Sci. Instrum.*, 1980, **13**, 1289–1291.
14. Werner, P.-E., A Fortran program for least-squares refinement of crystal structure cell dimensions. *Arkiv fur Kemi.*, 1969, **31**, 513–516.
15. Thompson, D. P., New grain-boundary phases for nitrogen ceramics. In *Mat. Res. Soc. Symp. Proc.* Vol. 287, 1993; Materials Research Society, eds. I-Wei Chen et al., pp. 79–92.
16. Jack, K. H., Sialon ceramics: retrospect and prospect. In *Mat. Res. Soc. Symp. Proc.* Vol. 287, 1993; Matierals Research Society, eds. I-Wei Chen et al., pp. 15–27.