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Preparation of Y-α-Sialon with Glassy or Crystalline Phases at Grain Boundaries

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Abstract: The phase stability of α-sialon has been investigated on a Y-α-sialon – Y_2O_3–Al_2O_3 plane. Y-α-sialon was stable with YAG liquid composition at 1750°C which could be devitrified to YAG ($3Y_2O_3{\cdot}5Al_2O_3$) by post heat treatment at 1500°C for 4 h. With increase of Al_2O_3 in the liquid composition of YAG, the amount of β-sialon increased. On the other hand, with increase of Y_2O_3 in the liquid composition, the amount of melilite ($Si_3N_4{\cdot}Y_2O_3$) increased. The changes of unit-cell parameters and microstructures with respect to the compositions and amounts of the liquid phase were also discussed.

1 INTRODUCTION

α-sialons are of interest as engineering ceramics because of their high hardness and good thermal shock resistance. However, research of α-sialon ceramics is still in its early stages.[1–4]

The research on α-sialon has been concentrated on the studies of α' monolith[5–11] or recently $\alpha' + \beta'$ composite.[12–16] It seems that there has been little understanding of (α' + glass) or (α' + oxides and/or silicon oxynitrides) systems. Even though sialon ceramics have possibilities to develop as single phase materials, it is very difficult to prepare α' monolithic ceramics without grain boundary phase so that α-sialons were practically prepared with the forms of α-sialon and some amount of glassy phase and/or secondary crystalline phase. So it is important to know the phase stability of α-sialon with grain boundary phases.

In this study, Y-α-sialon composition which is most widely investigated among α-sialon ceramics was prepared with additional Y_2O_3/Al_2O_3 liquid compositions at sintering temperature. The stability of Y-α-sialon and changes of unit-cell parameters and microstructure with respect to the compositions and amounts of Y_2O_3/Al_2O_3 liquid were investigated.

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2 EXPERIMENTAL PROCEDURE

Y-α-sialon can be formed by the following reaction:[5]

$$(4\text{–}3a)Si_3N_4 + a(Y_2O_3 + 9AlN) \rightarrow Y_{2a}(Si_{12-9a}, Al_{9a})(O_{3a}, N_{16-3a}) \quad (1)$$

where the range of solid solubility at 1750°C was reported $2a$ = 0·3–0·8. Various Y_2O_3/Al_2O_3 liquid compositions of 20 wt% were added to a Y-α-sialon composition, $2a$ = 0·45. The Y_2O_3/Al_2O_3 ratio was selected as 0 : 5, 1 : 5, 3 : 5 (YAG), 7 : 5, 10 : 5 (YAM) by molar ratio. Experimental compositions chosen were listed at A–E in Table 1. In the case of YAG compositions (as 3 mol Y_2O_3 + 5 mol Al_2O_3), 0, 10, 20, 30% by weight were added (C, F–H in Table 1).

Si_3N_4 (Ube Industries Co., Tokyo, Japan, SN-E10), AlN (Tokuyama, Tokyo, Japan, Type F), Y_2O_3 (Shin-etsu, Tokyo, Japan, 99·9%), Al_2O_3 (Sumitomo Chemicals Co., Osaka, Japan, AKP-20) powders were used as the starting materials in the preparation of samples. The oxygen impurity in the nitrides was not taken into account. About 15 g of powder and 100 cc hexane were mixed in a Si_3N_4 pot with 100 grams of Si_3N_4 balls for 2 h in a planetary mill. About 3 g of dried powder were hot-pressed at 1750°C for 1 h using a graphite die lined with BN, under a pressure of 20 MPa under static nitrogen of 1 atm pressure. The pressure

Table 1. Experimental compositions (wt%)

	Composition	Si_3N_4	AlN	Y_2O_3	Al_2O_3
A	20A	62·17	11·06	6·77	20·00
B	20Y5A	62·17	11·06	12·77	14·00
C	20YAG	62·17	11·06	18·18	8·59
D	207Y5A	62·17	11·06	21·89	4·88
E	20YAM	62·17	11·06	23·09	3·68
F	YSIALON	77·71	13·83	8·46	—
G	10YAG	69·94	12·45	13·33	4·29
H	30YAG	54·40	9·68	23·04	12·88

was unloaded at 1700°C while temperature was rising. The temperature was raised at a rate of 30°C/min. Cooling rate was about 100°C/min from 1750 to 1300°C. Heat treatment was carried out in an induction heating furnace at 1500°C for 4 h in nitrogen atmosphere.

Bulk densities of sintered and heat treated samples were measured using water immersion. Crystalline phases and unit-cell parameters of specimens were determined using a computerized Philips PW 1700 powder diffractometer. The scan step size and sampling time were set to 0·01° and 1·2 s, respectively. Before investigation, the powder was mixed with 20 wt% of Si powder as an internal standard. Microstructures of sintered bodies were observed using scanning electron microscope.

3 RESULTS AND DISCUSSION

3.1 Phase stabilities of Y-α-sialon with Y_2O_3/Al_2O_3 liquid

Figure 1 shows the area of interest in prismatic representation.[1–3] The experiments were carried out on an α-sialon rich portion of dashed plane. The schematic diagram of experimental compositions is presented in Fig. 2. It should be noted that the composition of α-sialon is restricted as $2a = 0{\cdot}45$ in the general formula (eqn (1)).

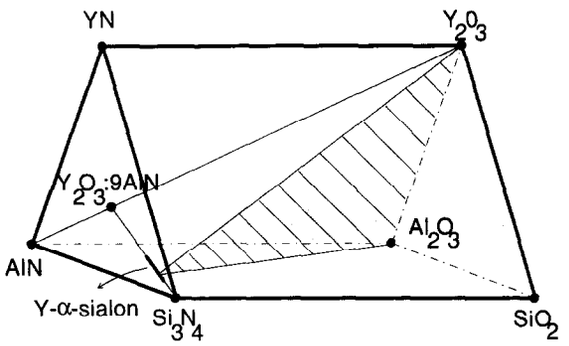

Fig. 1. Schematic representation of research area containing Y-α-sialon.

Table 2 represents crystalline phases in sintered bodies with respect to the liquid compositions in the Y-sialon: (Y_2O_3, Al_2O_3) system. In the samples (20YAG, 207Y5A) with 3 : 5 (Y_2O_3 : Al_2O_3, YAG) and 7 : 5 liquid composition, Y-α-sialon was a major phase, and there was a trace of melilite

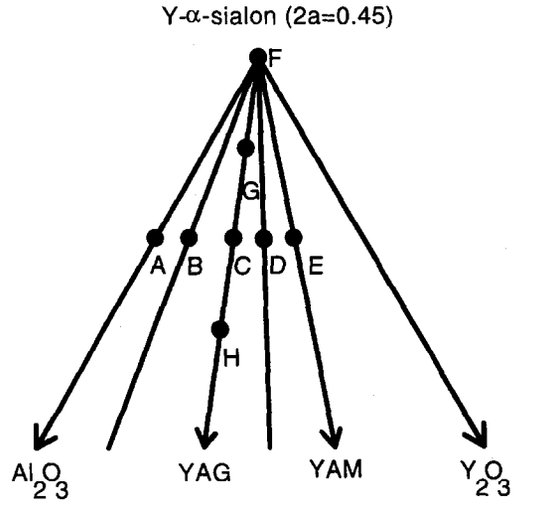

Fig. 2. Schematic diagram of compositions investigated.

Table 2. Crystalline phases and densities of samples sintered with different liquid compositions

Starting composition	Weight loss (%)	Density (g/cm³)	Crystalline phases						
			α'	β'	M	YAG	K	15R	12H
As sintered (1750°C, 1 h)									
20A	1·5	3·24	—	vs	—	—	—	w	—
20Y5A	2·0	3·35	w	vs	—	—	—	—	w
20YAG	2·8	3·42	vs	—	vw	—	—	—	—
207Y5A	2·9	3·46	vs	—	w	—	—	—	—
20YAM	3·6	3·50	vs	—	s	—	—	—	—
After heat treatment (1500°C, 4 h)									
20A	0·3	3·26	—	vs	—	w	—	w	—
20Y5A	0·3	3·37	w	vs	—	m	vw	—	w
20YAG	0·1	3·44	vs	—	—	m	w	—	—
207Y5A	0·1	3·47	vs	—	w	m	w	—	—
20YAM	0·4	3·52	vs	—	s	m	—	—	—

α': Y-α-sialon, β'-: β-sialon, YAG: $3Y_2O_3{\cdot}5Al_2O_3$; M: melilite ($Si_3N_4{\cdot}Y_2O_3$), K: $Y_2O_3{\cdot}Si_2N_2O$; 15R: 15R sialon ($SiAl_4O_2N_4$, AlN polytype); 12H: 12H sialon ($SiAl_5O_2N_5$, AlN polytype); X-ray intensities: s, strong; m, medium; w, weak; v, very.

(Si_3N_4·Y_2O_3). Most of the added Y_2O_3 and Al_2O_3 seems to be present in Y–Si–Al–O–N glass. In the samples (20A, 20Y5A) with higher content of Al_2O_3 than that for α' +YAG, the main phase was β-sialon. A small amount of Y-α-sialon was present in 20Y5A. It is shown that the stability of α-sialon decreases with the increase of Al_2O_3 in the liquid. It suggests that most works on (α' + β')[12–16] are restricted in the composition area of the α'–Al_2O_3–YAG. On the other hand, in the sample (20YAM) with higher content of Y_2O_3 than that for α' + YAG, Y-α-sialon and melilite (Si_3N_4·Y_2O_3) were formed. There were no β-sialon peaks in the specimens which had YAG or YAM liquid compositions. It is noticeable that β-sialon was not formed in the Y-α-sialon–YAG (or–YAM) liquid system. It is known that α-sialon transforms to β-sialon with addition of Al_2O_3.[17,18] But in our experiments, it seems that the simultaneous addition of Y_2O_3 prevents the formation of β-sialon from α-sialon. The stability region of α' + glass is shown to be in α'–3 : 5(Y_2O_3 : Al_2O_3,YAG)–7 : 5(Y_2O_3 : Al_2O_3) as shown by the shaded region in Fig. 3.

After heat treatment of the samples at 1500°C for 4 h, all of the four samples showed YAG phase as a secondary phase. Densities of samples increased slightly. In the samples of 20Y5A, 20YAG and 207Y5A, a small amount of K phase (Y_2O_3·Si_2N_2O) formed. There was no evidence of YAM in the specimen 20YAM. It seemed that YAM is not compatible with Y-α-sialon at that temperature. Thus, α' + YAG materials were prepared by annealing α' + glass (YAG) compositions.

Phases presented in the sintered specimens of the Y-sialon–YAG liquid systems were mainly Y-α-sialon irrespective of the amount of YAG composition as liquid phase (Table 3). There were no peaks of β-sialon in the specimens. With increase of YAG liquid, a small amount of melilite and 12H sialon was formed. In the course of densification of Y-α-sialon, it is known that melilite (Y_2O_3·Si_3N_4) is formed as an intermediate phase which is dissolved into liquid phase at higher temperature and transformed to Y-α-sialon.[2,11] In the composition of Y-α-sialon with the additional 10 or 20 wt% YAG, it seems that melilite persists even above 1750°C. On the other hand, in the case of 30 wt% YAG, 12H AlN polytype ($SiAl_5O_2N_5$) was formed. The preservation of minor phases is supposed to be based on the heterogeneity in the materials.

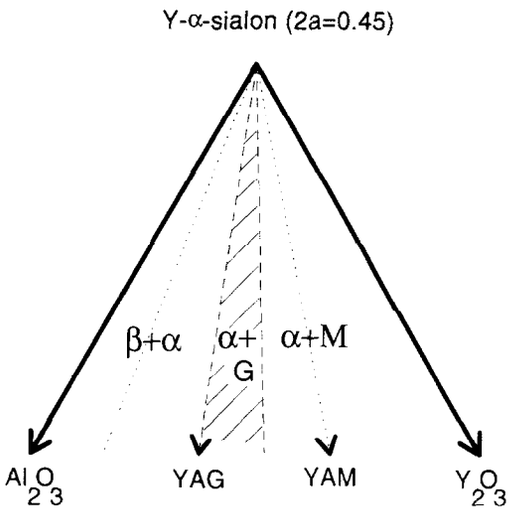

Fig. 3. Schematic phase relation of Y-α-sialon–Y_2O_3–Al_2O_3 at 1750°C. G : glass, M : melilite.

After heat treatment of Y-sialon–YAG liquid specimens at 1500°C for 4 h, glass phase was transformed to YAG and K phase (Y_2O_3·Si_2N_2O), and there was a slight increase in density. Even though in the sample of theoretical Y-α-sialon composition, there was a trace of YAG phase. It suggests that as sintered materials had a glassy phase at grain boundaries even if XRD showed single phase α-sialon. It suggests the difficulty of preparation of single phase α-sialon ceramics.

Table 3. Crystalline phases and densities of samples sintered with different amount of liquid (YAG composition)

Starting composition	Weight loss (%)	Density (g/cm^3)	Crystalline phases				
			α'	YAG	K	M	12H
As sintered (1750°C, 1 h)							
YSIALON	4·4	3·28	vs	—	—	—	—
10YAG	2·6	3·36	vs	—	—	vw	—
20YAG	2·8	3·42	vs	—	—	vw	—
30YAG	3·7	4·47	vs	—	—	—	vw
After heat treatment (1500°C, 4 h)							
YSIALON	0·0	3·29	vs	vw	—	—	—
10YAG	0·0	3·37	vs	w	w	—	—
20YAG	0·1	3·44	vs	m	m	—	—
30YAG	0·0	3·50	vs	s	m	—	—

α': Y-α-sialon, YAG: $3Y_2O_3$·$5Al_2O_3$, K: Y_2O_3·Si_2N_2O; M: melilite (Si_3N_4·Y_2O_3), 12H: 12H sialon ($SiAl_5O_2N_5$, AlN polytype); X-ray intensities: s, strong; m, medium; w, weak; v, very.

Table 4. Unit-cell parameters of sialons with respect to composition of liquid

Starting composition	α-Sialon a(nm)	α-Sialon c(nm)	β-Sialon a(nm)	β-Sialon c(nm)
20A	—	—	0·7655	0·2947
20Y5A	0·7805	0·5686	0·7636	0·2929
20YAG	0·7815	0·5693	—	—
207Y5A	0·7820	0·5692	—	—
20YAM	0·7818	0·5693	—	—

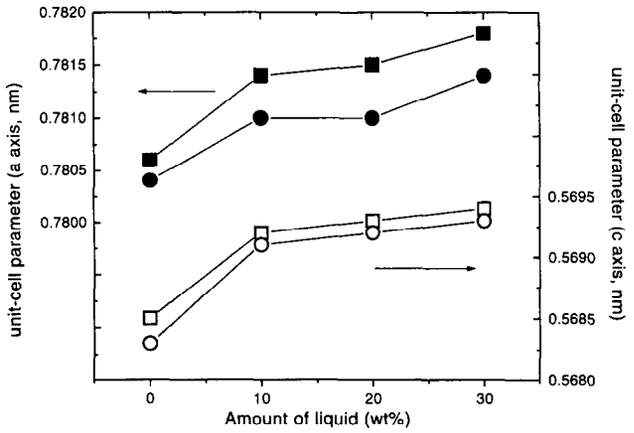

Fig. 4. Change of unit-cell parameter with respect to the amount of liquid (YAG composition); □: as sintered at 1750°C for 1 h , ○: heat treated at 1500°C for 4 h.

3.2 Unit-cell parameter

The dependence of unit-cell parameters of Y-α-sialon and β-sialon on liquid compositions with 20 wt% additional oxides is shown in Table 4. Comparing to data from Y-α-sialon monolithic ceramics,[6] the unit-cell parameters of 20YAG correspond to solubility of about $2a = 0{\cdot}45$ in eqn (1), which is the same with starting composition. In the region of 0:5 (Y_2O_3:Al_2O_3)–3:5, with the increase of amount of Al_2O_3 in the liquid phase, unit-cell parameters of α-sialon decreased and those of β-sialon increased. Whereas, in the region of 3:5–10:5, Y-α-sialons showed similar unit cell dimensions.

Figure 4 represents the change of unit-cell parameters of Y-α-sialon with respect to the amount of liquid in the Y-α-sialon–YAG system. With 10 wt% additional liquid phase, the unit-cell parameters of Y-α-sialon were increased rapidly to the value corresponding to $2a = 0{\cdot}45$. The smaller unit cell size in materials without liquid phase than that calculated might be due to slow solid solution reaction. It is related to the fact that there was a YAG glass in the materials as shown in Table 3, and there was a small increase of unit-cell parameters with the increase of amount of liquid phase. It means that the presence of liquid phase increased the rate of reaction.

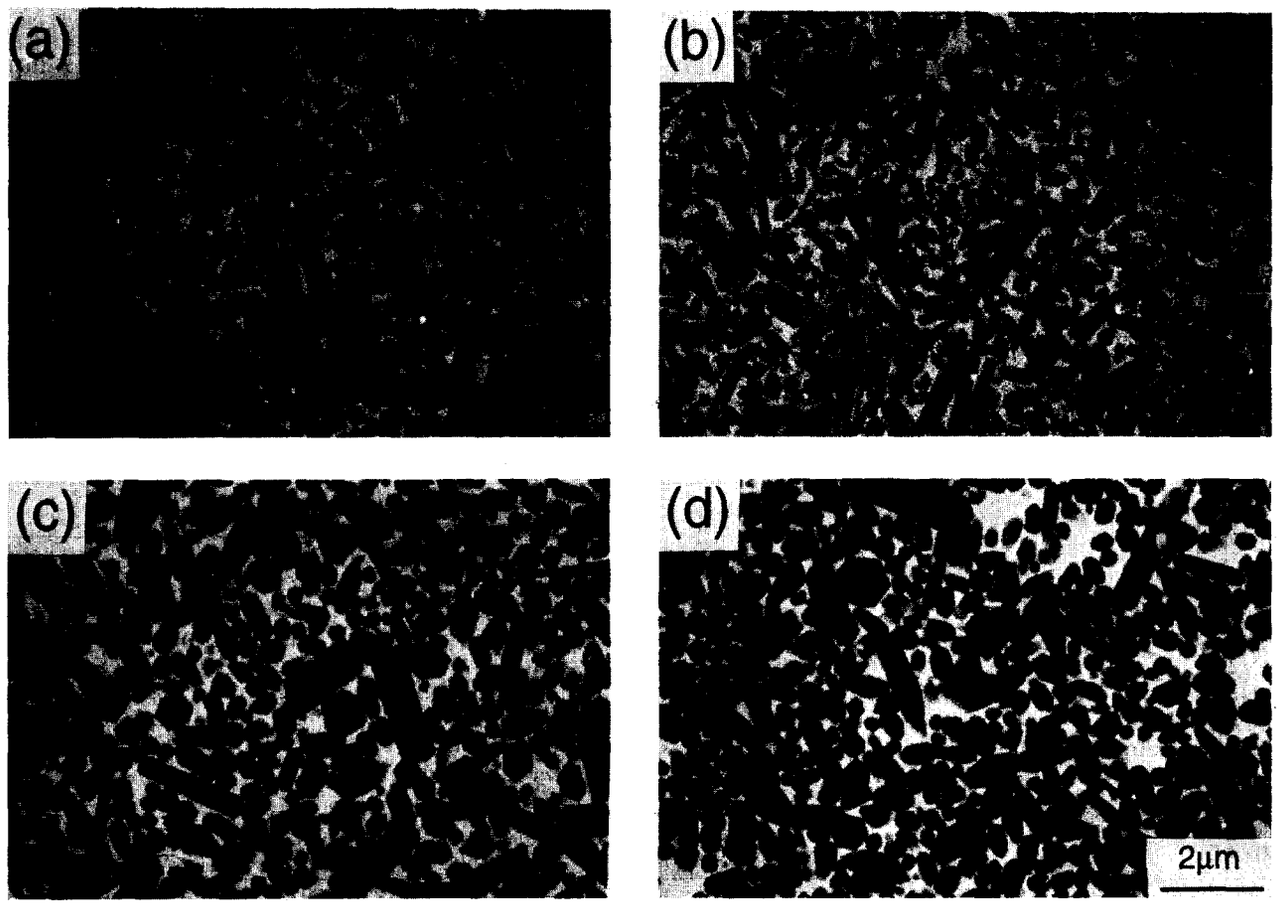

Fig. 5. SEM micrographs of Y-sialon: (Y_2O_3 + Al_2O_3) system sintered at 1750°C for 1 h; (a) 20A, (b) 20Y5A, (c) 20YAG, (d) 20YAM.

In the heat treated samples at 1500°C for 4 h, unit-cell parameters also showed the same tendency, but there were clear decreases of unit-cell parameters for all samples. It might be related to the formation of YAG. The reaction of Y-α-sialon and glass to form YAG took place at low temperature.

3.3 Microstructural characterization

Microstructures of polished surface with respect to the liquid compositions are presented in Fig. 5. All specimens showed sialon grains (gray particles) in Y–Si–Al–O–N glass (white region). In the cases (20A, 20Y5A) of higher Al_2O_3 content, elongated grains of β-sialon were observed. On the other hand, in the cases of 20YAM and 20YAG, faceted Y-α-sialon grains were observed. It is shown that the amount of glassy phase decreased with the increase of β' content because of the dissolution of glassy phase into β-sialon grains.

After heat treatment of the 20YAG specimen at 1500°C for 4 h, Y-α-sialon grains (gray grains) exhibited coalescence (Fig. 6). Grain boundary glass phases which had been connected with each other before heat treatment were isolated. It shows that interface energy between α'-grain and grain boundary phase changed with the temperature as in $\alpha' + \beta' +$ YAG system.[19]

SEM microstructures with respect to the liquid amounts (YAG composition) are presented in Fig. 7. As the amount of liquid increases, well faceted and slightly elongated Y-α-sialon grains were found, even though aspect ratio is not so large. Further study is needed to investigate equilibrium shape of the Y-α-sialon grain in Y–Si–Al–O–N. There was no significant difference in particle size, which seems to be the evidence for reaction-controlled grain growth of α-sialon in the α-sialon–YAG liquid system. In the sample 30YAG, some elongated grains (dark grains in Fig. 7 (d)) which seemed to be 12H grains were developed.

Fig. 6. SEM micrograph of 20YAG after heat treatment at 1500°C for 4 h.

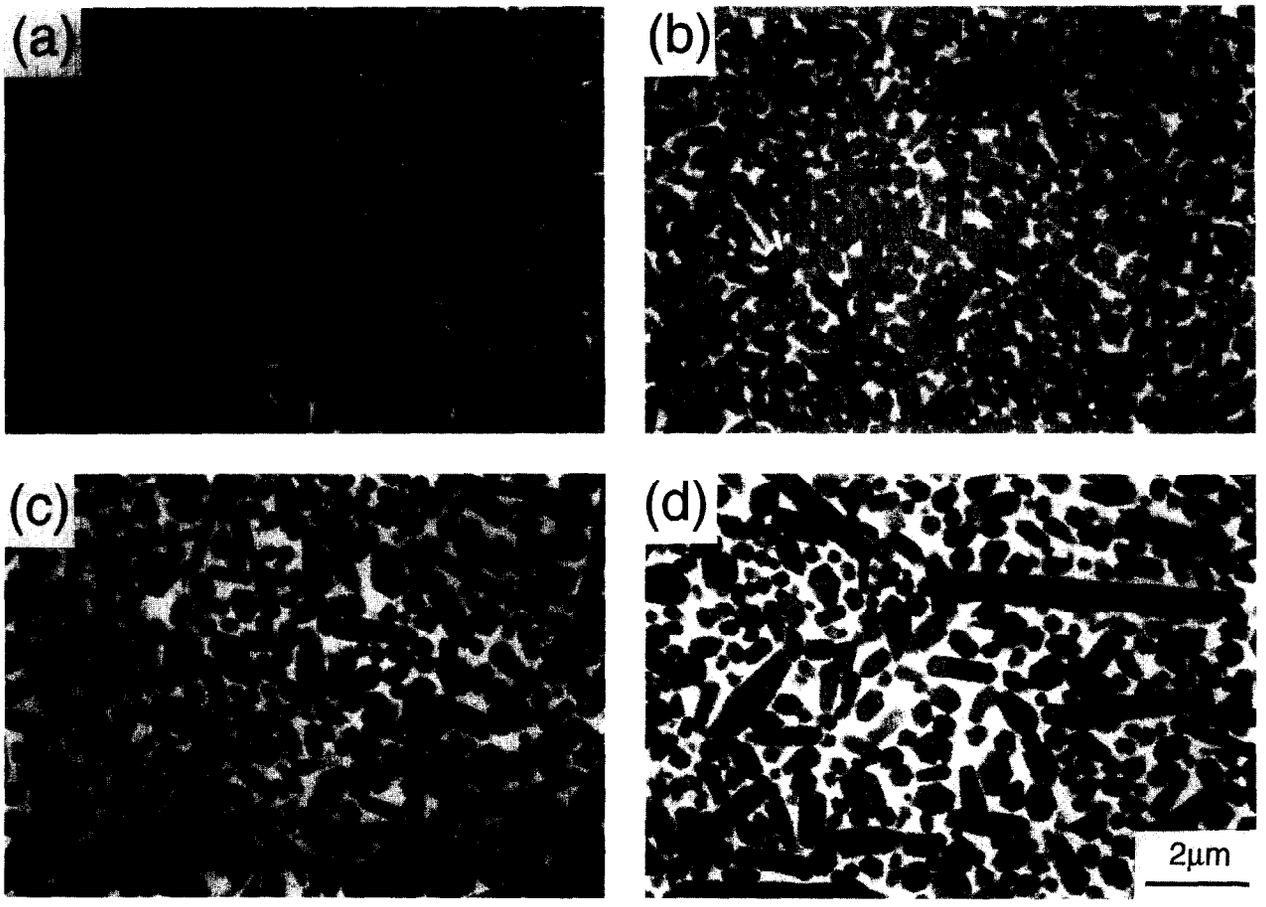

Fig. 7. SEM micrographs of Y-α-sialon: YAG system sintered at 1750°C for 1 h; (a) YSIALON, (b) 10YAG, (c) 20YAG, (d) 30YAG.

4 CONCLUSION

The relationship of Y-α-sialon with Y_2O_3 and Al_2O_3 liquid composition at 1750°C was studied. Y-α-sialon was stable with a liquid in the compositional range of Y_2O_3/Al_2O_3, 3/5–7/5. With increase of Al_2O_3, β-sialon was formed, and with increase of Y_2O_3, Y-α-sialon and melilite were present at sintering temperature. It was possible to fabricate α-sialon with glass or crystalline phase (YAG).

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REFERENCES

1. JACK, K. H., *Progress in Nitrogen Ceramics*, ed. F. L. Riley. Martinus Nijhoff Publishers, Boston, 1983, pp. 45–60.
2. CAO, G. Z. & METSELAAR, R., α-Sialon ceramics: Review. *Chem. Mater.*, **3** (1991) 242–52.
3. MITOMO, M. & TAJIMA, Y., Sintering, properties and applications of silicon nitride and sialon ceramics. *J. Ceram. Soc. Jpn*, **99**(10) (1991) 1014–25.
4. EKSTROM, T. & NYGREN, M., Sialon ceramics. *J. Amer. Ceram. Soc.*, **75**(2) (1992) 259–76.
5. MITOMO, M., TANAKA, H., MURAMATSU, K., LI, N. & FUJII, Y., The strength of α-sialon ceramics. *J. Mater. Sci. Lett.*, **15** (1980) 2661–2.
6. MITOMO, M., IZUMI, F., BANDO, Y. & SEKIKAWA, Y., *Proc. Int. Symp. on Ceram. Comp. for Engine*, ed. S. Somiya, E. Kanai & K. Ando. KTK Science Publishers, Tokyo, 1984, pp. 377–86.
7. CAO, G. Z., METSELAAR, R. & ZIEGLER, G., *Euroceramics*, ed. G. de With, R. A. Terpstra & R. Metselaar. Elsevier Applied Science Publishers, London, Vol. 1, 1989, pp. 346–50.
8. KUANG, S. F., HUANG, Z. K., SUN, W. Y. & YEN, T. S., Phase relationships in the Li_2O–Si_3N_4–AlN system and the formation of lithium-α-sialon. *J. Mater. Sci. Lett.*, **9** (1990) 72–4.
9. REDINGTON, M., O'REILLY, K. & HAMPSHIRE, S., On the relationships between composition and cell dimension in α-sialons. *J. Mater. Sci. Lett.*, **10** (1991) 1228–31.
10. BARTEK, A., EKSTROM, T., HERBERTSSON, H. & JOHANSSON, T., Yttrium α-sialon ceramics by hot isostatic pressing and post-hot isostatic pressing. *J. Amer. Ceram. Soc.*, **75**(2) (1992) 432–9.
11. CHENG, Y. B. & THOMPSON, D. P., Preparation and devitrification of samarium α-sialon ceramics. *J. Eur. Ceram. Soc.*, **14** (1994) 13–21.
12. EKSTROM, T., INGELSTROM, N., BRAGE, R., HATCHER, M. & JOHANSSON, T., α-β sialon ceramics made from different silicon nitride powders. *J. Amer. Ceram. Soc.*, **71**(12) (1988) 1164–70.
13. BOSKOVIC, S. & NICKEL, K. G., *Euro-Ceramics*, ed. G. de With, R. A. Terpstra & R. Metselaar. Elsevier Applied Science Publishers, London, Vol. 1, 1989, pp. 441–5.
14. CAO, G. Z., METSELAAR, R. & ZIEGLER, G., Relations between composition and microstructure of sialons. *J. Eur. Ceram. Soc.*, **11** (1993) 115–22.
15. PERSSON, J., EKSTROM, T., KALL, P. O. & NYGREN, M., Oxidation behavior and mechanical properties of β- and mixed α-β-sialon sintered with additions of Y_2O_3 and Nd_2O_3. *J. Eur. Ceram. Soc.*, **11** (1993) 363–73.
16. WANG, H., SUN, W. Y., ZHUANG, H. R. & YEN, T. S., Preparation of R-α-β-sialons (R = Sm, Gd, Dy, Y and Yb) by pressureless sintering. *J. Eur. Ceram. Soc.*, **13** (1994) 461–5.
17. HAMPSHIRE, S., PARK, S. K., THOMPSON, D. P. & JACK, K. H., α-Sialon ceramics. *Nature*, **274**(31) (1978) 880–2.
18. SUN, W. Y., WALLS, P. A. & THOMSON, D. P., *Non-oxide Technical and Engineering Ceramics*, ed S. Hampshire. Elsevier Applied Science Publishers, London, 1986, pp. 105–17.
19. JASPER, C. A. & LEWIS, M. H., *Proc. 4th Int. Symp. on Ceramic Materials and Components for Engines*, ed. R. Carlsson, T. Johansson, & L. Kahlman. Elsevier Applied Science Publishers, London, 1992, pp. 424–31.