Crystallization and Microstructure Development of $\text{Si}_3\text{N}_4\text{-Ti(C, N)-Y}_2\text{O}_3$ Ceramics Derived from Chemically Modified Perhydropolysilazane

Yuji IWAMOTO†, Koichi KIKUTA* and Shin-ichi HIRANO*

Synergy Ceramics Laboratory, Fine Ceramics Research Association, 2-4-1, Mutsuno, Atsuta-ku, Nagoya-shi 456-8587

*Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya-shi 464-8603

化学修飾パーヒドロポリシラザンより合成した $\text{Si}_3\text{N}_4\text{-Ti(C, N)-Y}_2\text{O}_3$ セラミックスの結晶化と組織形成

岩本雄二†・菊田浩一*・平野眞一*

ファインセラミックス技術研究組合シナジーセラミックス研究所, 456-8587 名古屋市熱田区六野 2-4-1

*名古屋大学大学院工学研究科, 464-8603 名古屋市千種区不老町

[Si-Y-Ti-O-C-N] multicomponent amorphous powders were synthesized by pyrolysis at 1000°C, in NH_3 flow, of chemically modified perhydropolysilazane using $\text{Y(OCH(CH}_3)_2)_3$ and $\text{Ti(N(CH}_3)_2)_4$. The [Si-Y-Ti-O-C-N] powders were fully crystallized to yield Ti(C, N) nano/micro particle-dispersed $\beta\text{-Si}_3\text{N}_4\text{-Y}_2\text{O}_3$ ceramics by hot pressing at 1800°C in N_2 . The resulting ceramics exhibited a uniform and fine-grained microstructure. Titanium in the [Si-Y-Ti-O-C-N] powders could act as a catalyst to accelerate $\alpha/\beta\text{-Si}_3\text{N}_4$ phase transformation as well as an in-situ source for nano/micro Ti(C, N) particles, which lead to microstructural uniformity and grain refinement of $\beta\text{-Si}_3\text{N}_4\text{-Ti(C, N)-Y}_2\text{O}_3$ ceramics.

[Received June 16, 2000; Accepted August 23, 2000]

Key-words : Si_3N_4 , Ti(C, N), Polymeric precursor, Perhydropolysilazane, Crystallization, Microstructure development

1. Introduction

Recently, increasing attention has been directed to the use of silicon-based metal-organic precursors for the manufacture of high-performance ceramics such as Si_3N_4 .^{1)–5)} This chemical processing route has several potential advantages compared with the conventional powder processing methods: control of the purity, compositional homogeneity in the final ceramics and lower processing temperatures in the preparation of refractory ceramics. The solubility and fluidity of metal-organic precursors can also afford potential processing routes for the preparation of ceramic coatings and fibers and the infiltration of porous materials, which are difficult or impossible by the conventional powder processing techniques.

On the other hand, another advantage of this route for the preparation of ceramics is the ability to synthesize silicon-based multicomponent ceramics through chemical modification of silicon-based metal-organic precursors. In this processing route, desired metal elements can be introduced to the precursors. The resulting precursors can be pyrolyzed to yield thermodynamically metastable multicomponent amorphous ceramics. The amorphous ceramics can be processed into polycrystalline ceramics by an additional heat treatment. During this crystallization process, the metastable multicomponent ceramics are partitioned into thermodynamically stable phases. The ratio of thermodynamically stable phases, and the resulting composite microstructure of polycrystalline ceramics can be controlled by controlling chemical composition and structure of precursors at molecular or atomic level. This synthetic route is expected to produce new types of high-performance silicon-based ceramic materials.

In this chemical modification route, oligosilazanes,^{6)–8)}

polysilazanes^{9)–11)} and perhydropolysilazanes^{13)–15)} are often used for fabrication of Si_3N_4 -based ceramics. Among these precursors, perhydropolysilazane (PHPS) has some advantages in high purity and ceramic yields.⁵⁾ Furthermore, PHPS contains many reactive Si-H and N-H groups which can react with various types of chemical modifiers such as metal alkoxides (M(OR)_x , $\text{M}=\text{B},^{12)} \text{Al},^{13)} \text{Y},^{14)} \text{Ti}^{16)}$), metal halides like TiCl_4 ,^{17),18)} and metal amides ($\text{M(NR}_2)_x$, $\text{M}=\text{B},^{15)} \text{Ti}^{16)}$).

The authors have reported that polymeric precursors for [Si-Y-O-C-N] multicomponent ceramics of SiC nanoparticle-dispersed $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3$ ceramics were successfully prepared by chemical modification of commercially available PHPS with yttrium alkoxide and *n*-decyl alcohol,¹⁹⁾ or hydroxypolycarbosilane.²⁰⁾ In our previous work, we also found that a poly-titanosilazane derived from PHPS chemically modified with tetrakis (dimethylamino) titanium had a potential to synthesize TiN or Ti(C, N) nano particle dispersed Si_3N_4 -based ceramics.¹⁶⁾

In this study, [Si-Y-Ti-O-C-N] multicomponent amorphous powders were synthesized from chemically modified PHPS using yttrium triisopropoxide and tetrakis (dimethylamino) titanium. The present paper describes crystallization and microstructural development of $\text{Si}_3\text{N}_4\text{-Ti(C, N)-Y}_2\text{O}_3$ ceramics from the polymeric precursor-derived [Si-Y-Ti-O-C-N] multicomponent powders. The effect of titanium element on the crystallization and microstructure development of $\text{Si}_3\text{N}_4\text{-Ti(C, N)-Y}_2\text{O}_3$ will be also discussed.

2. Experimental procedure

2.1 Precursor synthesis

Figure 1 shows synthetic routes for polymeric precursors investigated in this study. Commercially available PHPS (Tonen Co., N-N610 average molecular weight of 5156, Tokyo) was used as a starting polymer. This polymer mainly consists of structural units of HSiN_3 , H_2SiN_2 , H_3SiN , Si_2NH and also contains some $\text{N(Si(CH}_3)_2)_2$ groups which

† Present address: Japan Fine Ceramics Center, 2-4-1, Mutsuno, Atsuta-ku, Nagoya-shi 456-8587

現在: (財)ファインセラミックスセンター, 456-8587 名古屋市熱田区六野 2-4-1

Fig. 1. Synthetic routes for polymeric precursors.

are introduced to stabilize PHPS toward ambient moisture. Reagents of yttrium triisopropoxide ($\text{Y}(\text{OCH}(\text{CH}_3)_2)_3$, Kojundo Chemical Laboratory Co., Saitama) and tetrakis (dimethylamino) titanium ($\text{Ti}(\text{N}(\text{CH}_3)_2)_4$, Torichemical Co., Yamanashi) were used for the chemical modification of PHPS in this study. The chemical modification reactions of PHPS were carried out under nitrogen. Organic solvents of pyridine and xylene were distilled and dried before use.

Yttrium modified PHPS (Y-PHPS) was synthesized according to a published procedure.¹⁸⁾ As-received PHPS (6.65 g; Si, 63.5; N, 24.8; O, 0.7; C, 2.4 mass%, hence Si = 150 mmol) and $\text{Y}(\text{OCH}(\text{CH}_3)_2)_3$ in given Y/Si atomic ratios of 0.02 (Y2PHPS), 0.03 (Y3PHPS) and 0.04 (Y4PHPS) were mixed with dry pyridine (500 ml). The mixture was refluxed for 2 h with stirring. After cooling down to room temperature, the reaction mixture was concentrated in a rotary evaporator to give a reaction product. Since the product contained large amount of pyridine, dry xylene was added to the product and the mixture was again concentrated in a rotary evaporator to get rid of the residual pyridine, then the residue was dried in vacuum to give Y-PHPS as a pale yellow powder.

Xylene solution of titanium modified PHPS (Ti-PHPS) was prepared according to a published procedure.¹⁶⁾ PHPS (6.65 g, Si = 150 mmol) was dissolved into dry xylene (100 ml) with stirring, then cooled to 0°C. To this solution, $\text{Ti}(\text{N}(\text{CH}_3)_2)_4$ (Ti/Si atomic ratio of 0.10 for Y2Ti10PHPS, and 0.20 for Y2Ti20PHPS) in dry xylene (15 ml) was slowly added by syringe with stirring. After the addition was completed, the reaction mixture was warmed to room temperature, then maintained for 2 h with stirring. To this solution, $\text{Y}(\text{OCH}(\text{CH}_3)_2)_3$ (0.8 g, 3 mmol, Y/Si = 0.02) and dry pyridine (20 ml) were added. The mixture was refluxed at 145°C for 4 h. After cooling down to room temperature, the reaction mixture was concentrated in a rotary evaporator. The residue was dried in vacuum to give yttrium and titanium modified PHPS (Y-Ti-PHPS) as a brown powder.

2.2 Pyrolysis

The polymer sample was ground to a fine powder using a mortar and pestle, then pyrolyzed in a quartz tube furnace (Motoyama, Osaka) under flowing ammonia (NH_3 , 300 ml/min) by heating from room temperature to 1000°C in 5 h, maintaining the temperature at 1000°C for an additional 3 h, and finally furnace cooling down to room temperature to give an amorphous powder. Ceramic yields of Y2PHPS, Y3PHPS, Y4PHPS, Y2Ti10PHPS and Y2Ti20PHPS were 89, 87, 84, 70 and 68 mass%, respectively.

2.3 Heat treatment and hot pressing

The amorphous powder was ground to a fine powder using a mortar and pestle, then sieved through a 250 μm

screen before forming by uniaxial pressing at 150 MPa (10 mm $\times$ 10 mm, 1.5 g). The green compacts were placed on a BN plate within a BN crucible and heat-treated for 1 h in a graphite resistance-heated furnace (Model High Multi 10000, Fujidempa Kogyo, Osaka) at temperatures of 1200, 1400, 1600 and 1800°C. The nitrogen pressures applied in this heat treatment procedure were 196 kPa at 1200°C, 392 kPa at 1400°C and 980 kPa above 1600°C.

Hot pressing was carried out in the same furnace as mentioned above. The green compacts (10 mm $\times$ 10 mm, 1.5 g) were placed in a BN coated graphite die and hot-pressed at 1800°C for 1 h at a stress of 40 MPa under a nitrogen pressure of 980 kPa.

2.4 Characterization

Elemental analyses were performed on the pyrolyzed and 1800°C heat-treated powders for Si, Y and Ti (ICP spectrometry, Model ICAP-757V, Nippon Jarrell-Ash, Kyoto), C (high-temperature combustion method, Model EMGA 110, Horiba, Kyoto), N and O (inert gas fusion method, Model EMGA 650, Horiba, Kyoto). Molar ratio compositions of the 1800°C heat-treated powders were calculated assigning all Y to O as Y_2O_3 ; all O to Si as SiO_2 ; all Ti to N and C as $\text{Ti}(\text{C}_x, \text{N}_{1-x})$; all N to Si as Si_3N_4 . Then, excess C was assigned to be in the elemental state. Based on the molar ratio composition, the total amount of sintering additives was calculated by Eq. (1) using the volume (V) contents of Si_3N_4 , Y_2O_3 and SiO_2 .

$$(V_{\text{Y}_2\text{O}_3} + V_{\text{SiO}_2}) / (V_{\text{Si}_3\text{N}_4} + V_{\text{Y}_2\text{O}_3} + V_{\text{SiO}_2}) \quad (1)$$

X-ray diffraction (XRD) measurements were performed on the pyrolyzed, heat-treated and hot-pressed samples with Cu K α radiation using an automated powder diffractometer equipped with a monochromator (Model RINT 2500, Rigaku, Tokyo). The relative amount of α - and β - Si_3N_4 in the heat-treated powders was calculated using the method reported by Gazzara and Messier.²¹⁾ The $\beta/(\beta + \alpha)$ phase ratio of Si_3N_4 was determined by Eq. (2) using the corrected values for peak intensity of β - Si_3N_4 (210) and α - Si_3N_4 (210).²²⁾

$$I_{\beta(210)c} / (I_{\beta(210)c} + I_{\alpha(210)c}) \quad (2)$$

The lattice parameter of $\text{Ti}(\text{C}_x, \text{N}_{1-x})$ was measured using Si as internal standard. The amount of carbon in the $\text{Ti}(\text{C}_x, \text{N}_{1-x})$ was determined by the Vegard's law using the values of TiN ($c = 0.4242$ nm, JCPDS Card No. 38-1420) and $\text{Ti}(\text{C}_{0.3}, \text{N}_{0.7})$ ($c = 0.4264$ nm, JCPDS Card No. 42-1488).

Apparent densities of the hot-pressed samples were measured by the Archimedes method. Relative densities of the hot-pressed samples were evaluated using theoretical densities (3.242×10^3 kg/m³ for Y2PHPS, 3.400×10^3 kg/m³ for Y2Ti10PHPS and 3.292×10^3 kg/m³ for Y2Ti20PHPS) calculated from the molar ratio compositions of the 1800°C heat-treated powders.

The hot-pressed samples were polished with diamond powder (0.5 μm) and plasma etched using CF_4 for 3 min. Then, the samples were carbon coated and the microstructures were observed using a scanning electron microscopy (SEM; Model S-800, Hitachi, Ltd., Tokyo), and characterized by measuring diameters and lengths of 1000 to 1200 β - Si_3N_4 matrix grains. Microstructures were also studied using a transmission electron microscopy (TEM; Model EM-002B, Topcon Co., Tokyo). Analytical TEM-analysis was performed on the hot-pressed samples using Gatan Imaging Filter mounted on the TEM.

3. Results and discussion

3.1 Polymeric precursor-derived multicomponent powders

Chemical compositions of polymeric precursor-derived multicomponent powders are listed in Table 1. The Y/Si

Table 1. Chemical Composition of Polymeric Precursor-Derived Multicomponent Powders

Polymeric precursor	Composition / mass %						Atomic ratio
	Si	Y	Ti	O	C	N	
Y2PHPS	60.4	4.1	0.0	3.5	1.8	29.2	$\text{Si}_{1.0}\text{Y}_{0.02}\text{Ti}_{0.00}\text{O}_{0.10}\text{C}_{0.07}\text{N}_{0.97}$
Y3PHPS	60.2	5.7	0.0	4.4	1.2	27.5	$\text{Si}_{1.0}\text{Y}_{0.03}\text{Ti}_{0.00}\text{O}_{0.14}\text{C}_{0.05}\text{N}_{0.92}$
Y4PHPS	57.1	7.8	0.0	6.8	1.0	27.2	$\text{Si}_{1.0}\text{Y}_{0.04}\text{Ti}_{0.00}\text{O}_{0.21}\text{C}_{0.04}\text{N}_{0.95}$
Y2Ti10PHPS	47.8	2.9	8.7	8.2	4.2	29.2	$\text{Si}_{1.0}\text{Y}_{0.02}\text{Ti}_{0.11}\text{O}_{0.31}\text{C}_{0.21}\text{N}_{1.28}$
Y2Ti20PHPS	40.7	2.8	16.7	8.3	3.9	26.6	$\text{Si}_{1.0}\text{Y}_{0.02}\text{Ti}_{0.24}\text{O}_{0.36}\text{C}_{0.22}\text{N}_{1.31}$

Fig. 2. XRD patterns of polymeric precursor-derived ceramics.
(a) Y2PHPS, (b) Y2Ti10PHPS and (c) Y2Ti20PHPS.

atomic ratios of these powders are well consistent with the calculated ratios for the chemical modification reactions of PHPS. The Ti/Si atomic ratios of Y2Ti10PHPS and Y2Ti20PHPS are 0.11 and 0.24, respectively. Although, these values are slight larger than the calculated values, yttrium and titanium were successfully doped in the multicomponent powders by two-step chemical modification reaction of PHPS.

XRD measurements were performed on the multicomponent powders. Y2PHPS and Y2Ti10PHPS exhibit broad amorphous diffraction lines (Figs. 2(a) and 2(b)). Y2Ti20PHPS presents broad peaks at around $2\theta(^{\circ})$ of 36.5, 42.5 and 61.7 (Fig. 2(c)). Figure 3 shows typical TEM images of the Y2Ti20PHPS-derived powders. Fine crystallites having a size range of about 10 to 40 nm are dispersed within a large amorphous powder (Figs. 3(a) and 3(b)). The selected area electron diffraction pattern (Fig. 3(c)) is identical to TiN (based on JCPDS Card No. 38-1420).

3.2 Crystallization behavior

Further crystallization behaviors of the multicomponent powders are summarized and shown in Fig. 2. Y2PHPS presents both α - and β - Si_3N_4 peaks at 1400°C, then the α -/ β - Si_3N_4 phase transformation is completed at 1800°C (Fig. 2(a)). According to the XRD analyses, Y3PHPS and

Y4PHPS also presented both α - and β - Si_3N_4 peaks at 1400°C. Then, these powders presented only β - Si_3N_4 peaks at 1800°C.

Y2Ti10PHPS (Fig. 2(b)) presents TiN broad peaks at 1200°C, then presents $\text{Si}_2\text{N}_2\text{O}$ broad peaks at 1400°C. At 1600°C, Y2Ti10PHPS presents both α - and β - Si_3N_4 peaks. The $\text{Si}_2\text{N}_2\text{O}$ peaks disappear and the α -/ β - Si_3N_4 phase transformation is completed at 1800°C. Upon heating to 1800°C, the TiN peaks become sharp. However, these peaks are slightly shifted to lower angles, which indicates the solid solution formation of titanium carbonitride ($\text{Ti}(\text{C}_x, \text{N}_{1-x})$). The lattice parameter of $\text{Ti}(\text{C}_x, \text{N}_{1-x})$ in the 1800°C heat-treated Y2Ti10PHPS is 0.4249 nm and the composition can be determined following the Vegard's law as $\text{Ti}(\text{C}_{0.10}, \text{N}_{0.90})$. The crystallization behavior of Y2Ti20PHPS is similar to that of Y2Ti10PHPS. Finally at 1800°C, Y2Ti20PHPS presents β - Si_3N_4 and $\text{Ti}(\text{C}_{0.11}, \text{N}_{0.89})$ peaks (Fig. 2(c)). The relative peak intensity to β - Si_3N_4 of $\text{Ti}(\text{C}_x, \text{N}_{1-x})$ is higher than that of 1800°C heat-treated Y2Ti10PHPS (Fig. 2(b)), which is well consistent with the difference in Ti content of these powders as shown in Table 1.

The formation of $\text{Si}_2\text{N}_2\text{O}$ from 1400 to 1600°C in the Y-Ti-PHPS-derived powders is due to the large amount oxygen introduced together with yttrium and titanium (Table 1).

Fig. 3. TEM observation of 1000°C-pyrolyzed Y2Ti20PHPS. (a) bright-field TEM image, (b) dark-field TEM image and (c) selected-area electron diffraction pattern.

Table 2. Chemical Composition of 1800°C Heat-Treated Powders

Polymeric precursor	Composition / mass %						Calculated molar ratio				
	Si	Y	Ti	O	C	N	Si ₃ N ₄	Y ₂ O ₃	SiO ₂	Ti(C _x N _{1-x}) ₃	Free C
Y2PHPS	56.5	4.1	0.0	2.2	0.04	37.2	1.0	0.035	0.054	0.0	0.005
Y3PHPS	54.4	6.4	0.0	3.6	0.02	35.6	1.0	0.057	0.093	0.0	0.003
Y4PHPS	52.9	8.7	0.0	4.6	0.01	33.8	1.0	0.080	0.118	0.0	0.001
Y2Ti10PHPS	49.2	3.4	10.1	2.8	0.30	34.3	1.0	0.034	0.101	0.374 [0.10]	0.007
Y2Ti20PHPS	41.8	3.1	19.6	3.0	0.61	31.6	1.0	0.036	0.141	0.856 [0.11]	0.005

Y-Ti-PHPS and amorphous [Si-Y-Ti-O-C-N] powders may be highly reactive towards ambient moisture, which leads to the increase of oxygen content. During heat treatment above 1600°C, Si₂N₂O decomposed to Si₃N₄ with volatile SiO and O₂ (Eq. (3)).

Chemical compositions and calculated molar ratio compositions of the 1800°C heat-treated powders are listed in Table 2. Compared with the initial composition (Table 1), Y-PHPS-derived [Si-Y-O-C-N] powders show decrease in carbon and oxygen contents, and increase in nitrogen content. These chemical composition changes are due to some reactions such as carbothermal nitridation of SiO₂ (Eq. (4)),¹⁹ and the carbon in these powders was almost spent out for the reactions.

Y-Ti-PHPS-derived [Si-Y-Ti-O-C-N] powders also show the same changes in chemical composition. However, the carbon contents of Y2Ti10PHPS and Y2Ti20PHPS are 0.3 and 0.6 mass%, respectively (Table 2). These carbon contents are due to the Ti(C_xN_{1-x})₃ solid solution formation between TiN and carbon in the [Si-Y-Ti-O-C-N] powders, and the rest of free carbon in the Ti-Y-PHPS-derived powders is almost the same level as that in the Y-PHPS-derived powders.

Figure 4 shows the change of $\beta/(\beta + \alpha)$ phase ratio of Si₃N₄ in the polymeric precursor-derived powders during heat treatment up to 1800°C. As reference data, the ratios of as-received PHPS-derived amorphous [Si-N] powder¹⁶ are also plotted in Fig. 4. Both α - and β -Si₃N₄ crystallization of the [Si-N] powder started at 1200°C. Then, the β -Si₃N₄ contents are below 15% at temperatures from 1400 to 1800°C.

Amorphous Si₃N₄ in the multicomponent powders investigated in this study is rather stable up to 1200°C. After Si₃N₄ crystallization started above 1400°C, the β -Si₃N₄ content increases consistently with heat treatment temperature. Then, the transformation is completed at 1800°C, and the β -Si₃N₄ content at 1600°C is much different in each powder.

Fig. 4. $\beta/(\beta + \alpha)$ phase ratio of Si₃N₄ in polymeric precursor-derived powders as a function of heat treatment temperature in N₂.

Figure 5 shows the relation between total amount of sintering additives and $\beta/(\beta + \alpha)$ Si₃N₄ phase ratio after heat treatment at 1600°C. Y-PHPS-derived powders show that the β -Si₃N₄ content increases with increasing total amount of sintering additives and the ratio reaches 63.9% at 12.8 vol% (Y4PHPS). Although the total amount of sintering additives in the Y-Ti-PHPS-derived powders is below 11 vol%, the ratios of Y2Ti10PHPS and Y2Ti20PHPS reach 70.5 and 100%, respectively.

According to our previous study, polymeric precursor-derived [Si-Y-O-C-N] multicomponent powders produced Si-Y-O-N liquid phase at 1600°C.¹⁹ Thus, the Si-Y-O-N liquid phase could promote the α/β -Si₃N₄ phase transformation above 1600°C of Y-PHPS-derived powders, and the transformation was enhanced consistently with amount of

liquid phase.

The rapid $\alpha/\beta\text{-Si}_3\text{N}_4$ phase transformation observed in the Y-Ti-PHPS-derived powders is due to the existence of Ti. The Si-Ti-O system can produce a liquid phase above 1550°C^{23} and the amount of the liquid phase increases with increasing Ti content. Accordingly, the formation of Si-Ti-Y-O-N liquid phase accelerated the $\alpha/\beta\text{-Si}_3\text{N}_4$ phase transformation, and the transformation was accelerated consistently with Ti content in the Y-Ti-PHPS-derived powders.

3.3 Microstructure of hot-pressed samples

The polymeric precursor-derived powders were also fully crystallized during hot pressing up to 1800°C for 1 h (Fig. 2), and relative densities of Y2PHPS-, Y2Ti10PHPS- and Y2Ti20PHPS-derived ceramics reached 99.0, 99.5 and 99.2 %, respectively.

Figure 6 shows polished and plasma etched sections of the hot-pressed samples, and the $\beta\text{-Si}_3\text{N}_4$ matrix grain size distributions of these samples are shown in Fig. 7. Y2PHPS yielded an extremely bimodal microstructure composed of large rod-like grains and fine needle-like grains (Fig. 6(a)). The large rod-like grains are in a size range of about 2 to 4 μm in diameter and 4 to 20 μm in length. The fine needle-like grains are submicron in diameter and smaller than 3.5 μm in length (Fig. 7(a)). Compared with Y2PHPS, Y2Ti10PHPS yielded a uniform microstructure composed of fine rod-like $\beta\text{-Si}_3\text{N}_4$ matrix grains of submicron in diameter and smaller than 3.5 μm in length (Figs. 6(b) and 7(b)). Y2Ti20PHPS yielded a uniform and extremely fine microstructure composed of $\beta\text{-Si}_3\text{N}_4$ matrix grains of sub-

micron in diameter and smaller than 2.5 μm in length (Figs. 6(c) and 7(c)).

The bimodal microstructure development observed in the

Fig. 5. Relation between total amount of sintering additives and $\beta/(\beta+\alpha)$ phase ratio of Si_3N_4 after heat treatment at 1600°C .

Fig. 6. Polished and plasma etched sections of hot-pressed samples.

(a) Y2PHPS, (b) Y2Ti10PHPS and (c) Y2Ti20PHPS.

Fig. 7. $\beta\text{-Si}_3\text{N}_4$ matrix grain size distributions of hot-pressed samples. (a) Y2PHPS, (b) Y2Ti10PHPS and (c) Y2Ti20PHPS.

Fig. 8. TEM images of Y2Ti10PHPS-derived ceramics showing (a) fine particles located within a β -Si₃N₄ matrix grain and (b) a submicron particle (marked by an arrow), (c) EDS spectrum obtained from the particle marked by the arrow.

Y2PHPS-derived ceramics can be explained by relating to the slow α -/ β -Si₃N₄ phase transformation as shown in Figs. 4 and 5. As formerly discussed, the α -/ β -Si₃N₄ phase transformation through liquid phase involved the dissolution of α -Si₃N₄ into liquid phase, saturation of the liquid phase with dissolved Si and N atoms/ions and the nucleation of β -Si₃N₄ on the nucleation site. As nucleation sites, preexisting β -Si₃N₄ in the starting Si₃N₄ powder and liquid matrix were first suggested.²⁴⁾ Recently, core structures of small β -Si₃N₄ grains within β -SiAlON and small α -Si₃N₄ grains within α - or β -SiAlON were also reported as nucleating sites.^{25)–27)} As shown in Fig. 2(a), Y2PHPS-derived amorphous powders were free from preexisting β -Si₃N₄. Among other possible nucleation sites, in-situ produced β -Si₃N₄ in the Y2PHPS-derived powders is thought to be the most favorable one due to its same crystal structure. The β -Si₃N₄ contents at 1400°C of Y2PHPS-derived powders was 12.5%. Even at 1600°C,

Fig. 9. TEM image and elemental ratio map of Y2Ti10PHPS-derived ceramics. (a) bright-field TEM image and (b) elemental Ti-L ratio map of titanium from the same field as shown in (a).

the ratio was as low as 32.2%. During hot pressing from 1400 to 1800°C, the small amount of β -Si₃N₄ could act as selected nucleation sites to grow as large rod-like grains with consumption of α -Si₃N₄. Consequently, Y2PHPS yielded the extremely bimodal microstructure.

On the other hand, the β -Si₃N₄ contents at 1600°C of Y-Ti-PHPS-derived powders were above 70%. Accordingly, higher number of β -Si₃N₄ grains could grow through Ostwald ripening during hot pressing from 1600 to 1800°C, which lead to the microstructure uniformity observed in the Y-Ti-PHPS-derived ceramics.

To study the dispersion behavior of Ti(C, N) phase, microstructures of Y-Ti-PHPS-derived ceramics were observed by TEM. As typical observation results, TEM images of Y2Ti10PHPS-derived ceramics are shown in Fig. 8. Fine particles with diameters of about 10–100 nm are observed within a β -Si₃N₄ matrix grain (Fig. 8(a)). These particles are identified as Ti(C, N) phase by the elemental ratio map shown in Fig. 9. A large particle with a diameter of about 0.6 μ m, which can be easily distinguished from β -Si₃N₄ matrix grains, is also observed (Fig. 8(b), marked by an arrow). The large particle can be assigned as Ti(C, N) by the EDS analysis (Fig. 8(c)). Further TEM observation confirmed that Ti(C, N) phase was dispersed as particles having a size range of about 10 nm to 1.6 μ m and the Ti(C, N) particles with diameters larger than 0.5 μ m were located at β -Si₃N₄ matrix grain boundaries.

The large Ti(C, N) particles located at β -Si₃N₄ matrix grain boundaries were thought to suppress β -Si₃N₄ matrix grain growth in the Y-Ti-PHPS-derived ceramics, which could especially contribute the microstructure refinement observed in the Y2Ti20PHPS-derived ceramics.

According to these results, titanium in the [Si-Y-Ti-O-C-N] powders could act as a catalyst to accelerate α -/ β -

Si_3N_4 phase transformation as well as an in-situ source for nano/micro Ti(C, N) particles, which lead to microstructure uniformity and refinement of $\beta\text{-Si}_3\text{N}_4\text{-Ti(C, N)-Y}_2\text{O}_3$ ceramics.

4. Summary

[Si-Y-Ti-O-C-N] multicomponent amorphous powders were synthesized by pyrolysis at 1000°C , in NH_3 flow, of chemically modified PHPS using $\text{Y}(\text{OCH}(\text{CH}_3)_2)_3$ and $\text{Ti}(\text{N}(\text{CH}_3)_2)_4$. The crystallization and microstructure development were studied by comparison with [Si-Y-O-C-N] amorphous powders derived from PHPS chemically modified with $\text{Y}(\text{OCH}(\text{CH}_3)_2)_3$.

(1) Amorphous Si_3N_4 in the [Si-Y-Ti-O-C-N] powders was rather stable below 1400°C in N_2 . Above 1600°C , Si-Ti-Y-O-N liquid phase accelerated the α/β -phase transformation of Si_3N_4 and the [Si-Y-Ti-O-C-N] powders yielded $\beta\text{-Si}_3\text{N}_4\text{-Ti(C, N)-Y}_2\text{O}_3$ ceramics at 1800°C .

(2) Fully dense $\beta\text{-Si}_3\text{N}_4\text{-Ti(C, N)-Y}_2\text{O}_3$ ceramics were also synthesized by hot pressing at 1800°C in N_2 . The resulting ceramics exhibited a uniform and fine-grained microstructure.

(3) Ti(C, N) phase was dispersed as particles having a size range of 10 nm to $1.6\text{ }\mu\text{m}$ and the large Ti(C, N) particles with diameters larger than $0.5\text{ }\mu\text{m}$ were located at the $\beta\text{-Si}_3\text{N}_4$ matrix boundaries.

(4) Titanium in the [Si-Y-Ti-O-C-N] powders could act as a catalyst to accelerate $\alpha/\beta\text{-Si}_3\text{N}_4$ phase transformation as well as an in-situ source for nano/micro Ti(C, N) particles, which lead to microstructure uniformity and refinement of $\beta\text{-Si}_3\text{N}_4\text{-Ti(C, N)-Y}_2\text{O}_3$ ceramics.

Acknowledgments This work has been entrusted by NEDO as part of the Synergy Ceramics Project under the Industrial Science and Technology Frontier (ISTF) Program promoted by AIST, MITI, Japan. The authors are members of the Joint Research Consortium of Synergy Ceramics. The authors also would like to acknowledge Mr. Tomoharu Saitoh for the analytical TEM analysis at Japan Fine Ceramics Center (JFCC).

References

- 1) K. J. Wynne and R. W. Rice, *Annu. Rev. Mater. Sci.*, **14**, 297-334 (1984).
- 2) D. Seyferth and G. H. Wiseman, "Ultrastructure Processing of Ceramics, Glasses and Composites," Ed. by L. L. Hench and D. R. Ulrich, Wiley Interscience, New York (1984) pp. 2656-71.
- 3) K. B. Schwartz, D. J. Rowcliffe, Y. D. Blum and R. M. Raine, *Mater. Res. Soc. Symp. Proc.*, **73**, 265-71 (1986).
- 4) W. R. Schmit, V. Sukumar, W. J. Hurley, Jr., R. Garcia, R. H. Doremus and L. V. Interrante, *J. Am. Ceram. Soc.*, **73**, 2412-18 (1990).
- 5) O. Funayama, M. Arai, Y. Tashiro, H. Aoki, T. Suzuki, K. Tamura, H. Kaya, H. Nishii and T. Isoda, *J. Ceram. Soc. Japan (Seramikusu Ronbunshi)*, **98**, 104-07 (1990).
- 6) D. Seyferth, G. Brodt and B. Boury, *J. Am. Ceram. Soc.*, **73**, 2131-33 (1990).
- 7) W. R. Schmit, W. J. Hurley, Jr., R. H. Doremus, L. V. Interrante and P. S. Marchetti, "Ceramic Transactions, Vol. 19," Ed. by M. D. Sacks, Am. Ceram. Soc., Westerville, OH (1991) pp. 19-25.
- 8) D. Seyferth and H. Plenio, *J. Mater. Sci. Lett.*, **15**, 348-49 (1996).
- 9) J. Bill, M. Friess, F. Aldinger and R. Riedel, *Mater. Res. Soc. Symp. Proc.*, **346**, 605-15 (1994).
- 10) J. Bill and F. Aldinger, *Adv. Mater.*, **7**, 775-87 (1995).
- 11) R. Riedel and W. Dressler, *Ceram. Int.*, **22**, 233-39 (1996).
- 12) O. Funayama, T. Kato, Y. Tashiro and T. Isoda, *J. Am. Ceram. Soc.*, **76**, 717-23 (1993).
- 13) O. Funayama, Y. Tashiro, T. Aoki and T. Isoda, *J. Ceram. Soc. Japan*, **102**, 908-12 (1994).
- 14) Y. Iwamoto, H. Matsubara and R. J. Brook, "Ceramic Transactions, Vol. 51," Ed. by H. Hausner, G. L. Messing and S. Hirano, Am. Ceram. Soc., Westerville, OH (1995) pp. 193-97.
- 15) O. Funayama, T. Aoki and T. Isoda, *J. Ceram. Soc. Japan*, **104**, 355-60 (1996).
- 16) Y. Iwamoto, K. Kikuta and S. Hirano, *J. Ceram. Soc. Japan*, **108**, 350-56 (2000).
- 17) Y. Iwamoto, K. Kikuta and S. Hirano, "Ceramic Transactions, Vol. 83," Ed. by G. L. Messing, S. Hirano and F. F. Lange, Am. Ceram. Soc., Westerville, OH (1998) pp. 63-70.
- 18) Y. Iwamoto, K. Kikuta and S. Hirano, *J. Mater. Res.*, **14**, 4294-301 (1999).
- 19) Y. Iwamoto, K. Kikuta and S. Hirano, *J. Mater. Res.*, **13**, 353-61 (1998).
- 20) Y. Iwamoto, K. Kikuta and S. Hirano, *J. Mater. Res.*, **14**, 1886-95 (1999).
- 21) C. P. Gazzara and D. R. Messier, *Am. Ceram. Soc. Bull.*, **56**, 777-80 (1977).
- 22) C. R. Blanchard and S. T. Schwab, *J. Am. Ceram. Soc.*, **77**, 1729-39 (1994).
- 23) R. C. DeVries, R. Roy and E. F. Osborn, *Trans. Brit. Ceram. Soc.*, **53**, 531-35 (1954).
- 24) J. Wess and W. A. Kaysser, "Progress in Nitrogen Ceramics," Ed. by F. L. Riley, Martinus Nijhoff Publisher, The Hague (1983) p. 169.
- 25) M. Kramer, M. J. Hoffman and G. Petzow, *J. Am. Ceram. Soc.*, **76**, 2778-84 (1993).
- 26) S.-L. Hwang and I.-W. Chen, *J. Am. Ceram. Soc.*, **77**, 1711-18 (1994).
- 27) S.-L. Hwang and I.-W. Chen, *J. Am. Ceram. Soc.*, **77**, 1719-28 (1994).