

High Temperature Properties of Si_3N_4 -Re Silicon Oxynitride (Re=Y, Yb, Er, La) Ceramics

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Four different β - Si_3N_4 ceramics with silicon oxynitrides [$\text{Y}_{10}(\text{SiO}_4)_6\text{N}_2$, $\text{Yb}_4\text{Si}_2\text{N}_2\text{O}_7$, $\text{Er}_9\text{Si}_3\text{N}_4\text{O}_3$, and $\text{La}_{10}(\text{SiO}_4)_6\text{N}_2$, respectively] as secondary phases have been fabricated by hot-pressing the Si_3N_4 - $\text{Re}_4\text{Si}_2\text{N}_2\text{O}_7$ (Re=Y, Yb, Er, and La) compositions at 1820°C for 2 h under a pressure of 25 MPa. The high temperature strength and oxidation behavior of the hot-pressed ceramics were characterized and compared with those of the ceramics fabricated from Si_3N_4 - $\text{Re}_2\text{Si}_2\text{O}_7$ compositions. The Si_3N_4 - $\text{Re}_4\text{Si}_2\text{N}_2\text{O}_7$ compositions investigated herein showed comparable high temperature strength to those from Si_3N_4 - $\text{Re}_2\text{Si}_2\text{O}_7$ compositions. Si_3N_4 ceramics from a Si_3N_4 - $\text{Y}_4\text{Si}_2\text{N}_2\text{O}_7$ composition showed the highest strength of 877 MPa at 1200°C among the compositions. All Si_3N_4 ceramics investigated herein showed a parabolic weight gain with oxidation time at 1400°C and the oxidation products of the ceramics were SiO_2 and $\text{Re}_2\text{Si}_2\text{O}_7$. The Si_3N_4 - $\text{Re}_4\text{Si}_2\text{N}_2\text{O}_7$ compositions showed inferior oxidation resistance to those from Si_3N_4 - $\text{Re}_2\text{Si}_2\text{O}_7$ compositions, owing to the incompatibility of the secondary crystalline phases of those ceramics with SiO_2 , the oxidation product of Si_3N_4 . Si_3N_4 ceramics from a Si_3N_4 - $\text{Er}_4\text{Si}_2\text{N}_2\text{O}_7$ composition showed the best oxidation resistance of 0.375 mg/cm² after oxidation at 1400°C for 192 h in air among the compositions.

Key Words : Si_3N_4 , Rare-earth Oxide Additives, High Temperature Strength, Oxidation Behavior

I. Introduction

Many properties of Si_3N_4 ceramics are degraded at high temperatures due to the residual grain boundary glassy phase^{1,2)} that is inevitably present in liquid-phase sintered Si_3N_4 . Several attempts to optimize high temperature properties have been investigated, including the crystallization of the amorphous grain boundary phase by a postsintering heat treatment,³⁾ the formation of a transient liquid phase,⁴⁾ and the reduction of the overall additive content in combination with the use of refractive additives.^{5,6)}

Work performed by Lange *et al.*⁷⁾ on the Si_3N_4 - SiO_2 - Y_2O_3 system has shown that the high temperature properties of Si_3N_4 can be improved by choosing compositions in the Si_3N_4 - $\text{Si}_2\text{N}_2\text{O}_7$ - $\text{Y}_2\text{Si}_2\text{O}_7$ compatibility triangle, since the $\text{Si}_2\text{N}_2\text{O}_7$ and $\text{Y}_2\text{Si}_2\text{O}_7$ phases are in equilibrium with SiO_2 (the oxidation product of Si_3N_4). Lange⁸⁾ also proposed similar behavior for compositions in the Si_3N_4 - SiO_2 - CeO_2 system. On this basis, various rare-earth oxides have been studied as potential sintering additives, since it is expected that Si_3N_4 - SiO_2 -rare-earth oxide systems would also exhibit this type of behavior. It has been shown that rare-earth oxides are as effective as Y_2O_3 in the densification of Si_3N_4 .^{3,9,10)} Furthermore, refractory disilicate, $\text{Re}_2\text{Si}_2\text{O}_7$ (Re refers to the cation of a rare earth oxide), can be crystal-

lized at grain boundaries, thereby resulting in improved high temperature properties.^{3,11-13)} These results make the Si_3N_4 - $\text{Re}_2\text{Si}_2\text{O}_7$ composition attractive for the high temperature applications of Si_3N_4 .

Recently, a Si_3N_4 - $\text{Yb}_4\text{Si}_2\text{N}_2\text{O}_7$ composition has also been investigated due to the superior high temperature stability (i.e., high melting temperature) of $\text{Yb}_4\text{Si}_2\text{N}_2\text{O}_7$ phase.¹⁴⁾ As expected, the Si_3N_4 from the composition showed superior high temperature strength to that of Si_3N_4 from Si_3N_4 - $\text{Yb}_2\text{Si}_2\text{O}_7$ composition.¹⁵⁾ Other rare-earth oxides would have similar phase relationships with Si_3N_4 - SiO_2 - Yb_2O_3 system^{3,7,8,16,17)} and, therefore, the Si_3N_4 - $\text{Re}_4\text{Si}_2\text{N}_2\text{O}_7$ compositions could be considered as candidates for high temperature application of Si_3N_4 . Although many studies have investigated the effect of rare-earth oxide as sintering additives on the high temperature properties of Si_3N_4 , the Si_3N_4 - $\text{Re}_4\text{Si}_2\text{N}_2\text{O}_7$ compositions have not been studied except Si_3N_4 - $\text{Yb}_4\text{Si}_2\text{N}_2\text{O}_7$ composition.

In the previous studies,^{18,19)} we characterized the high temperature flexural strength and oxidation behavior of Si_3N_4 ceramics prepared from the Si_3N_4 - $\text{Re}_2\text{Si}_2\text{O}_7$ compositions. In this study, we characterized the high temperature flexural strength and oxidation behavior of four different Si_3N_4 ceramics prepared from the Si_3N_4 - $\text{Re}_4\text{Si}_2\text{N}_2\text{O}_7$ (Re=Y, Yb, Er, and La) compositions by hot-pressing and compared with those of Si_3N_4 prepared from the Si_3N_4 -

Table 1. $\text{Si}_3\text{N}_4\text{-Re}_4\text{Si}_2\text{N}_2\text{O}_7$ Compositions (w%)

Material	Si_3N_4	SiO_2	Re_2O_3
SNY	85.93	0.87	13.20
SNYb	77.52	0.80	21.60
SNEr	78.48	0.81	20.70
SNLa	82.23	0.78	16.97

$\text{Re}_2\text{Si}_2\text{O}_7$ compositions.

II. Experimental Procedure

Commercially available Si_3N_4 (SN E-10, Ube Industries, Tokyo, Japan), Y_2O_3 , Yb_2O_3 , Er_2O_3 , La_2O_3 (99.9%, Johnson Matthey, Seabrook, NH, U. S. A.) and SiO_2 (99.9%, Aerosil 200, Degussa Co., NJ, U. S. A.) powders were used as starting materials. Four different mixtures correspond to the $\text{Si}_3\text{N}_4\text{-Re}_4\text{Si}_2\text{N}_2\text{O}_7$ composition, as shown in Table 1, were prepared. The total amount of the sintering additives was fixed at 12 vol%. The mixtures were milled in methanol for 24 h using Si_3N_4 balls. The milled slurry was dried, sieved, and hot-pressed at 1820°C for 2 h under a pressure of 25 MPa in a nitrogen atmosphere.

Densities of hot-pressed specimens (designated as SNRe) were measured using Archimedes method. The theoretical densities of the specimens were calculated according to the rule of mixtures based on the theoretical densities of starting materials. X-ray diffractometry (XRD) was used to determine the crystalline phases. The hot-pressed specimens were cut, polished, and then plasma-etched by CF_4 containing 7.8% O_2 . The microstructures were observed by scanning electron microscopy (SEM). Flexural strength test specimens were cut into $2 \times 1.5 \times 20$ mm bars from hot-pressed disc samples, and their surfaces and edges polished with an 800-grit diamond wheel. The flexural strength value was measured at room temperature and 1200°C by a three-point bending method with a span of 15 mm and a cross head speed of 0.5 mm/min. The heating rate upto the testing temperature was 5°C/min and ten minutes were hold before testing for a thermal equilibrium. Average value obtained from the five specimens was used as a data. To test for oxidation resistance $18 \times 18 \times 2.5$ mm specimens were cut and polished, placed on platinum wire in a box furnace, heated to 1400°C at a heating rate of 450°C/h, and held at the temperature for 192 h. The furnace was cooled and heated between 12-72 h intervals in order to measure weight changes in the specimens. The materials were characterized by X-ray diffraction to identify crystalline phases present on the surface of the oxidized ceramics. The oxidized surface then was characterized by scanning electron microscopy and energy-dispersive X-ray spectroscopy (EDX).

III. Results

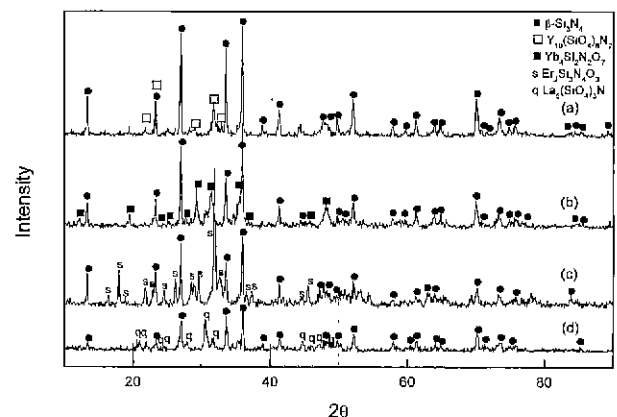
Relative densities of SNRe are listed in Table 2. The rel-

Table 2. Relative Density, Weight Gain, and Rate Constant (k) of Parabolic Oxidation for SNRe. For Comparison, Weight Gain and Rate Constant of the Si_3N_4 Fabricated from $\text{Si}_3\text{N}_4\text{-Re}_4\text{Si}_2\text{O}_7$ Compositions¹⁸⁾ were Included

Material	$\text{Si}_3\text{N}_4\text{-Re}_4\text{Si}_2\text{N}_2\text{O}_7$			
	Y	Yb	Er	La
Relative density(%)	99.9	98.6	99.1	98.7
Flexural strength(MPa)				
Room temperature	982	778	992	1.58
1200°C	877	624	752	876
Weight gain (1400°C, air, 192 h, mg/cm ²)	0.471	0.635	0.375	0.856
$k[\text{mg}^2/(\text{cm}^4 \times \text{h}) \times 10^{-4}]$	11.2	12.5	6.0	36.2
Material	$\text{Si}_3\text{N}_4\text{-Re}_4\text{Si}_2\text{O}_7$			
	Y	Yb	Er	La
Flexural strength(MPa)				
1200°C	893	754	762	663
Weight gain (1400°C, air, 192 h, mg/cm ²)	0.280	0.413	0.134	0.305
$k[\text{mg}^2/(\text{cm}^4 \times \text{h}) \times 10^{-4}]$	3.9	8.1	1.0	4.8

ative densities of $\geq 98.6\%$ were achieved by hot-pressing with a holding time of 2 h at 1820°C. The highest density was obtained for SNY and the lowest density of 98.6% for SNYb. XRD of the specimens (SNRe) showed $\beta\text{-Si}_3\text{N}_4$ as the major phase and various Re-silicon oxynitrides, $\text{Y}_{10}(\text{SiO}_4)_6\text{N}_2$, $\text{Yb}_4\text{Si}_2\text{N}_2\text{O}_7$, $\text{Er}_2\text{Si}_3\text{N}_4\text{O}_3$, and $\text{La}_{10}(\text{SiO}_4)_6\text{N}_2$, respectively, as the minor phases (Fig. 1). It is well known that $\text{Y}_4\text{Si}_2\text{N}_2\text{O}_7$ phase cannot coexist with Si_3N_4 ,⁷⁾ and therefore, $\text{Y}_{10}(\text{SiO}_4)_6\text{N}_2$ phase was crystallized for SNY. On the other hand, as reported in previous study,¹⁶⁾ $\text{Yb}_4\text{Si}_2\text{N}_2\text{O}_7$ phase was easily crystallized for SNYb. Although it is expected that rare-earth oxides would have similar phase relationships with $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-Yb}_2\text{O}_3$ system, $\text{Er}_4\text{Si}_2\text{N}_2\text{O}_7$ and $\text{La}_4\text{Si}_2\text{N}_2\text{O}_7$ phases were not crystallized for SNEr and SNLa, respectively.

As shown in Fig. 2, the microstructures of SNRe were

**Fig. 1.** XRD patterns of SNRe: (a) SNY, (b) SNYb, (c) SNEr and (d) SNLa.

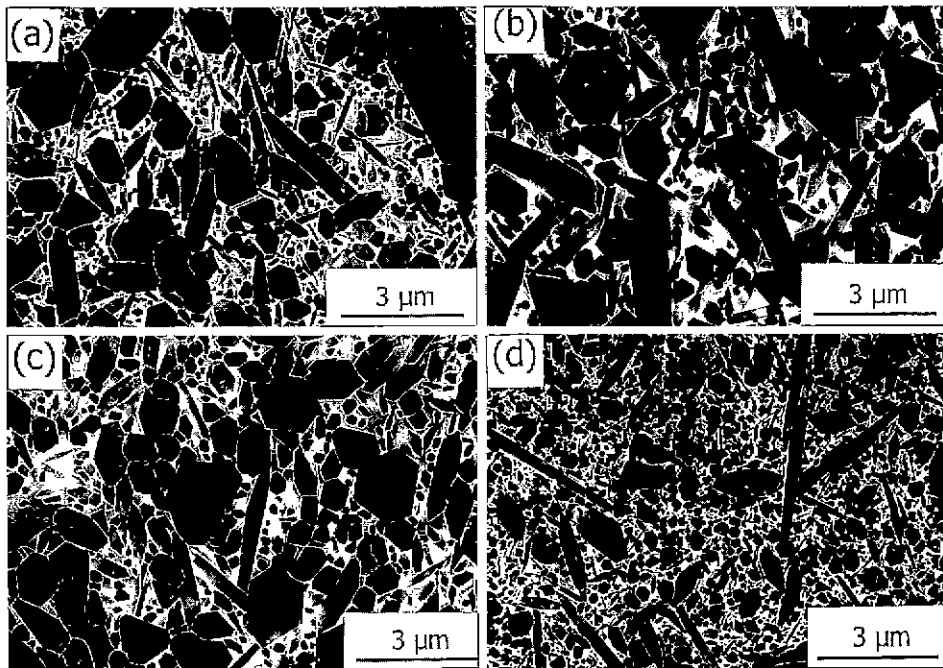


Fig. 2. Microstructures of SNRe: (a) SNY, (b) SNYb, (c) SNEr and (d) SNLa.

similar with each other except SNLa, which showed finer microstructure than others. It has been reported that the growth rate of the prismatic plane of Si_3N_4 grains in a glass containing rare-earth oxides decreases with increasing the cationic radius of the rare-earth oxide due to the higher degree of the adsorption of cations on the surface of Si_3N_4 grains.²⁰ Adsorption of cations on the surface of Si_3N_4 grains restricts the adsorption of Si^{+4} and N^{-3} from the glass phase. The cationic radius of La^{+3} (1.160×10^{-1} nm) is larger than those of Y^{+3} (1.011×10^{-1} nm), Yb^{+3} (0.985×10^{-1} nm), and Er^{+3} (1.004×10^{-1} nm). Therefore, the high degree of adsorption of La^{+3} ion on the surface of Si_3N_4 grains may result in the finer microstructure for SNLa.

The flexural strengths of SNRe measured at room temperature and 1200°C are listed in Table 2. For comparison, the flexural strength at 1200°C of Si_3N_4 ceramics fabricated from Si_3N_4 - $\text{Re}_2\text{Si}_2\text{O}_7$ compositions by hot-pressing under the same conditions¹⁸⁾ were included. At room temperature, the flexural strengths of SNRe show similar values of ~1 GPa with each other except SNYb. It showed the value of 778 MPa that could be contributed to the low density. The highest strength of SNLa could be contributed to the finer microstructure. At 1200°C, the flexural strength of SNY showed the highest value of 877 MPa. The results of this and previous study¹⁸⁾ showed that Si_3N_4 sintered with Y_2O_3 showed the highest high temperature strength among the compositions investigated herein. It also showed that the high temperature strength of SNRe fabricated from the Si_3N_4 - $\text{Re}_2\text{Si}_2\text{O}_7$ compositions were comparable to that of the Si_3N_4 from Si_3N_4 - $\text{Re}_2\text{Si}_2\text{O}_7$ compositions.

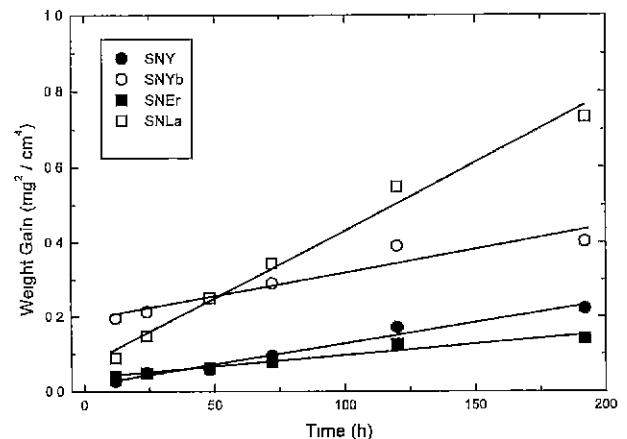


Fig. 3. Parabolic plot of specific weight gains as a function of time at 1400°C.

Fig. 3 shows the relation between the square of the weight gain and the oxidation time at 1400°C. The oxidation behavior of SNRe follows a parabolic rate law of the type;

$$W^2 = kt \quad (1)$$

where W is the weight gain per unit surface area, k is the rate constant of parabolic oxidation, and t is the exposure time. The parabolic oxidation behavior of these ceramics indicates that the rate-determining step in an oxidation process is a diffusional process associated with the migration of additive cations and anions along the grain boundary phases to the interface between the ceramic and the surface oxide.²⁾ The fast oxidation rate of SNYb and SNLa in the initial stage of oxidation (<12 h) may be due to the open porosity of the specimens, which showed relatively

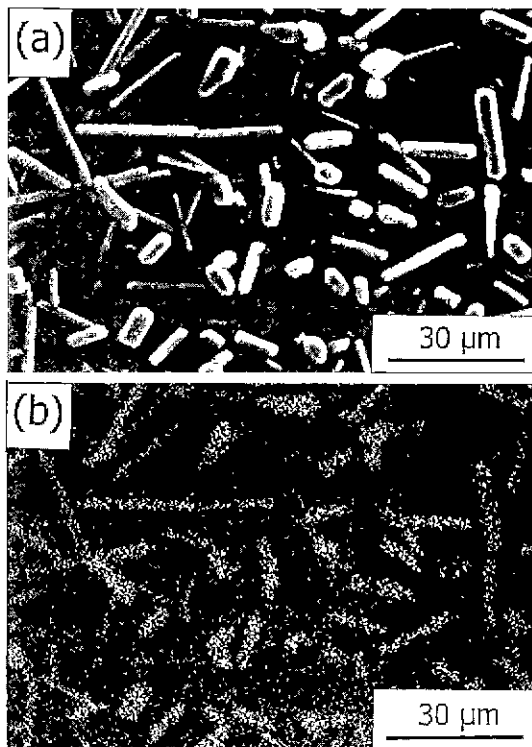


Fig. 4. SEM micrograph of (a) the oxidized surface of SNY and (b) Y mapping of the surface.

low densities. The observed weight gains of SNRe after oxidation at 1400°C for 192 h and the rate constants of parabolic oxidation, k , are listed in Table 2. For comparison, the weight gains and rate constants of Si_3N_4 ceramics fabricated from $\text{Si}_3\text{N}_4\text{-Re}_2\text{Si}_2\text{O}_7$ compositions by hot-pressing under the same conditions¹⁹ were included. The results shown in Table 2 indicate that the oxidation resistance, which was estimated indirectly from the weight gain during oxidation, of SNEr, SNY, and SNYb is better than that of SNLa and Si_3N_4 sintered with Er_2O_3 showed the best oxidation resistance among the compositions investigated herein.

As shown in Table 2, SNRe fabricated from the $\text{Si}_3\text{N}_4\text{-}$

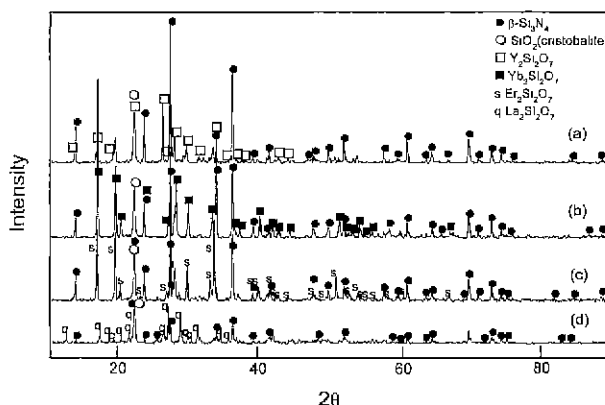


Fig. 5. XRD patterns of the oxidized surfaces of SNRe: (a) SNY, (b) SNYb, (c) SNEr and (d) SNLa

$\text{Re}_4\text{Si}_2\text{N}_2\text{O}_7$ compositions showed inferior oxidation resistance to the Si_3N_4 from $\text{Si}_3\text{N}_4\text{-Re}_2\text{Si}_2\text{O}_7$ compositions. Fig. 4 shows the SEM and EDX image of oxidized surface of SNY, as a typical example of SNRe. Fig 4 (b) indicates that the oxide on the surface contains Y. XRD of the oxidized surfaces of SNRe only show $\text{Re}_2\text{Si}_2\text{O}_7$ and SiO_2 (Fig. 5). Present results indicate that the oxidation products of SNRe fabricated from $\text{Si}_3\text{N}_4\text{-Re}_2\text{Si}_2\text{O}_7$ compositions are $\text{Re}_2\text{Si}_2\text{O}_7$ and SiO_2 .

IV. Discussion

The refractoriness of grain boundary glassy phase predominantly determines the high temperature properties of Si_3N_4 since it dominates the viscosity of glassy phase at high temperature. Low viscosity of glassy phase at high temperature easily induces the grain boundary sliding under stress and results the degradation of strength. It also accelerates the diffusion rate of cations and anions along the residual grain boundary glassy phases under an oxidation condition and results the poor oxidation resistance of Si_3N_4 .^{2,12} The refractoriness of grain boundary glassy phase strongly depends on the chemistry of the glassy phase. According to the high resolution transmission electron microscopy works²⁰ the glassy phase is not a pure SiO_2 but the SiO_2 phase containing cations of sintering additives. It is why the refractoriness of glassy phase depends on the kind of sintering additives. Cinibulk *et al.*^{11,12} reported that the high temperature strength and oxidation behavior of Si_3N_4 fabricated from the $\text{Si}_3\text{N}_4\text{-Re}_2\text{Si}_2\text{O}_7$ (Re=Y, Yb, Er, Dy, Gd, and Sm) compositions were roughly correlated to the eutectic temperature of $\text{SiO}_2\text{-Re}_2\text{O}_3$ system since the refractoriness of grain boundary glassy phase correlates to the eutectic temperature of the system. Choi *et al.*¹³ reported that the high temperature properties of Si_3N_4 fabricated from the $\text{Si}_3\text{N}_4\text{-Re}_2\text{Si}_2\text{O}_7$ (Re=Y, Yb, Ho, Dy, Er, Sm, Ce, Lu, La, Pr, Gd, and Sc) were roughly correlated to the cationic radius of Re_2O_3 . It is due to the bond strength between cation and anion in the glassy phase. The bond strength is characterized as a field strength which is proportional to the ionic charge and the reciprocal of the ion size. Therefore, it increases with a decreasing cationic radius of the Re_2O_3 and, consequently, a greater refractory nature of glassy phase could be expected.

The stability of grain boundary crystalline phase is also important to the high temperature properties of Si_3N_4 . Previous studies have shown that the high temperature properties of Si_3N_4 can be improved by forming the stable second crystalline phase at high temperature (e.g., $\text{Re}_2\text{Si}_2\text{O}_7$ ^{7,8,11,12} and $\text{Yb}_4\text{Si}_2\text{N}_2\text{O}_7$ ¹⁵).

The high temperature strength of SNRe studied herein show somewhat different behavior from those of the previously reported $\text{Si}_3\text{N}_4\text{-Re}_2\text{Si}_2\text{O}_7$ composition. SNYb showed the lowest strength at 1200°C even though the $\text{Yb}_4\text{Si}_2\text{N}_2\text{O}_7$ phase is stable at high temperature,¹⁴ the eutectic temperatures of $\text{Yb}_2\text{O}_3\text{-SiO}_2$ system (1660°C) is relatively high,

and the cationic radius of Yb^{+3} is small (0.985×10^{-1} nm). On the contrary, SNLa showed relatively high strength at 1200°C even though the eutectic temperature the La_2O_3 - SiO_2 system (1625°C) is low and the cationic radius is large (1.160×10^{-1} nm). Furthermore, SNY containing the $\text{Y}_{10}(\text{SiO}_4)_6\text{N}_2$ phase, which is unstable at high temperature,⁷ showed the highest strength at 1200°C .

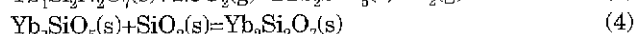
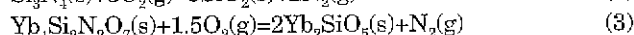
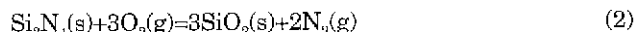
The high temperature strength of SNRe cannot be explained on the basis of eutectic temperature,¹¹ cationic radius,¹⁸ and the stability of secondary crystalline phase.⁷ The fast crystallization of glassy phase of SNRe may attribute to the strength behavior. The XRD result shown in Fig. 1 indicates that the fast crystallization of secondary phase after sintering was occurred in SNRe. As reported previously,²¹ the fast crystallization of secondary phase could reduce the effect of glassy phase on the high temperature properties of Si_3N_4 . The time dependency of high temperature properties of Si_3N_4 may also attribute to the strength behavior. The refractoriness of glassy phase and stability of crystalline phase are important to the high temperature properties, however, they can play a critical role when the diffusional process of cation and anion are involved.¹² It means that they are critical to the long-term measured high temperature properties, e.g., oxidation resistance and creep, but not to the short-term measured high temperature property, e.g., high temperature strength.

When the glassy phase and secondary crystalline phase do not play a critical role, other factors such as microstructure and density can play a greater role in determining the high temperature strength. Therefore, as in the room temperature strength, the lower strength of SNYb at 1200°C could be attributed to the low density and the higher strength of SNLa could be attributed to the finer microstructure.

The oxidation behavior of SNRe is similar to that of the Si_3N_4 - $\text{Re}_2\text{Si}_2\text{O}_7$ composition. The weight gains of SNRe are roughly correlated to the eutectic temperatures of the Re_2O_3 - SiO_2 system, i.e., lower weight gains with increasing the eutectic temperature. Furthermore, the weight gains also roughly correlated to the cationic radius of Re_2O_3 , i.e., lower weight gains with decreasing the cationic radius of Re_2O_3 . It is attributed to the greater refractory nature of grain boundary glassy phases with increasing the Re_2O_3 - SiO_2 system and decreasing the cationic radius. The contribution of both small cationic radius of Er^{+3} ion and high eutectic temperature of Er_2O_3 - SiO_2 system to the refractoriness of the grain boundary glassy phase can explain the superior oxidation resistance of the SNEr and Si_3N_4 from Si_3N_4 - $\text{Re}_2\text{Si}_2\text{O}_7$ composition, indicating that Er_2O_3 is a suitable sintering additive for oxidation-resistant Si_3N_4 ceramics.

The results shown in Table 2 also indicate that the secondary crystalline phase is important to the oxidation behavior of Si_3N_4 . The oxidation resistance of SNRe, which contains various Re-silicon oxynitrides as secondary crys-

talline phase is inferior to the oxidation resistance of Si_3N_4 fabricated from the Si_3N_4 - $\text{Re}_2\text{Si}_2\text{O}_7$ compositions and containing Re-disilicate as secondary crystalline phase.¹⁸ It has been reported that $\text{Y}_{10}(\text{SiO}_4)_6\text{N}_2$ phase is incompatible with SiO_2 and unstable in an oxidizing condition.⁷ It has also been reported that the Si_3N_4 containing Yb_4 - $\text{Si}_2\text{N}_2\text{O}_7$ is oxidized to form SiO_2 and $\text{Yb}_2\text{Si}_2\text{O}_7$ by the following reactions^{14,22}:



Reactions (3) and (4) occur due to the incompatibility of $\text{Yb}_4\text{Si}_2\text{N}_2\text{O}_7$ and Yb_2SiO_5 phases with SiO_2 and induce migration of Yb^{+3} ions from the bulk to the oxidized surface. It means that the reactions (3) and (4) enhance the oxidation of Si_3N_4 ceramics. The properties of $\text{Er}_2\text{Si}_3\text{N}_4\text{O}_3$ and $\text{La}_{10}(\text{SiO}_4)_6\text{N}_2$ phases have not been clearly identified. However, from the facts that (1) $\text{Y}_9\text{Si}_3\text{N}_4\text{O}_3$ and $\text{Y}_{10}(\text{SiO}_4)_6\text{N}_2$ phases are incompatible to SiO_2 and unstable in an oxidizing condition⁷ and (2) the oxidation products of Si_3N_4 ceramics containing $\text{Er}_2\text{Si}_3\text{N}_4\text{O}_3$ or $\text{La}_{10}(\text{SiO}_4)_6\text{N}_2$ phase are $\text{Re}_2\text{Si}_2\text{O}_7$ and SiO_2 , $\text{Er}_2\text{Si}_3\text{N}_4\text{O}_3$ and $\text{La}_{10}(\text{SiO}_4)_6\text{N}_2$ phases are expected to be incompatible with SiO_2 and unstable in the oxidizing conditions. The $\text{Re}_2\text{Si}_2\text{O}_7$ is also oxidation product of Si_3N_4 ceramics fabricated from the Si_3N_4 - $\text{Re}_2\text{Si}_2\text{O}_7$ compositions.^{4,18} In Si_3N_4 ceramics containing $\text{Re}_2\text{Si}_2\text{O}_7$ as a secondary phase, compositional gradient of Re^{+3} ions is the driving force of the migration of Re^{+3} ions from the bulk to the surface since $\text{Re}_2\text{Si}_2\text{O}_7$ phase is compatible to SiO_2 .⁷ Therefore, the compositional gradient of Re^{+3} ions as well as the incompatibility of Re-silicon oxynitride phases [$\text{Y}_{10}(\text{SiO}_4)_6\text{N}_2$, $\text{Yb}_4\text{Si}_2\text{N}_2\text{O}_7$, $\text{Er}_2\text{Si}_3\text{N}_4\text{O}_3$, and $\text{La}_{10}(\text{SiO}_4)_6\text{N}_2$] with SiO_2 act as the driving force of the oxidation of SNRe and result in the inferior oxidation resistance of the ceramics, comparing to the Si_3N_4 from the Si_3N_4 - $\text{Re}_2\text{Si}_2\text{O}_7$ compositions.

V. Conclusion

The high temperature strength of Si_3N_4 fabricated by hot-pressing the Si_3N_4 - $\text{Re}_4\text{Si}_2\text{N}_2\text{O}_7$ (Re=Y, Yb, Er, and La) compositions was affected by the microstructure and density due to the fast crystallization of Re-silicon oxynitrides [$\text{Y}_{10}(\text{SiO}_4)_6\text{N}_2$, $\text{Yb}_4\text{Si}_2\text{N}_2\text{O}_7$, $\text{Er}_2\text{Si}_3\text{N}_4\text{O}_3$, and $\text{La}_{10}(\text{SiO}_4)_6\text{N}_2$, respectively] as secondary phases. However, the oxidation resistance of Si_3N_4 was dominated by the refractoriness of grain boundary glassy phase, which can be assumed by the dependency of it to the eutectic temperature of Re_2O_3 - SiO_2 system and cationic radius of Re_2O_3 . The oxidation resistance of Si_3N_4 was also affected by the stability of secondary crystalline phase at high temperature. The Re-silicon oxynitrides secondary phase is incompatible to SiO_2 and contributes to the inferior oxidation resistance of Si_3N_4 , as compared with the silicon disilicate secondary phase.

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