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Effect of oxide addition on the sintering and high-temperature strength of Si_3N_4 containing Y_2O_3

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The effect of oxide addition on the sintering behaviour and high-temperature strength of Si_3N_4 containing Y_2O_3 was studied at 0.1 to 30 MPa N_2 at 1600 to 2000° C. The addition of oxide, i.e. MgO, Al_2O_3, La_2O_3, or Nd_2O_3, was found to lower the densification temperature and increase the densification rate. The addition of Al_2O_3 or MgO reduced the strength of sintered materials at $>1350°$ C. The addition of La_2O_3 or Nd_2O_3, on the other hand, did not affect high-temperature strength which remained equivalent to that of the material containing only Y_2O_3. These results indicate that the glassy phases in these systems are as refractory as that in the Si_3N_4–Y_2O_3.

1. Introduction

The evaluation of silicon nitride for heat engine applications has led to successful results such as the turbocharger rotor. This material is now, however, used only at temperatures below 1000° C because its strength is reduced at higher temperatures. Thus, the mechanical properties at elevated temperatures must be improved for use in higher temperature engines such as the gas turbine engine.

The degradation of high-temperature mechanical properties in Si_3N_4 is generally caused by the grain-boundary phase. For the fabrication of dense, high-strength silicon nitride, oxide additives such as MgO [1], Y_2O_3–Al_2O_3 [2], Y_2O_3–MgO [3], and Y_2O_3–Nd_2O_3 [4] are used to promote densification through a liquid-phase sintering mechanism [5]. After densification, however, these additives remain as grain-boundary glassy phases, which deteriorate the high-temperature properties of the ceramics such as the creep and the high-temperature strength [6, 7].

Silicon nitride containing Y_2O_3 is known to have excellent mechanical properties at elevated temperatures [8]. Sintering with this additive is usually performed by hot pressing or hot isostatic pressing because of poor sinterability.

This paper reports the effect of a second additive on the sinterability of the Si_3N_4–Y_2O_3 system. The effect of a second additive on high-temperature strength of sintered materials will be discussed in relation to the composition and refractoriness of the grain-boundary glassy phase.

2. Experimental procedure

2.1. Starting materials

The Si_3N_4 powder (oxygen content 1.2%, particle size 1.2 μm; Grade H1, H. C. Stark, Berlin), 5 mol % Y_2O_3 (purity 99.9%, particle size 4 μm; Shinetsu Chemical, Tokyo, Japan), and 5 mol % of the second oxide (M_2O_x) were ground together in ethanol for 94 h using a ball mill. The second oxide was chosen from La_2O_3, Nd_2O_3 (both 99.5% purity, particle size 4 μm, Shinetsu Chemical, Tokyo, Japan), Al_2O_3 (99.5% pure, particle size −325 mesh; grade A16, Alcoa, Pittsburgh, Pennsylvania), or MgO (99.1% pure, particle size 0.23 μm; Grade HP-10, Konoshima Chemical, Japan). The amount of magnesium oxide additive was calculated assuming that its molecular form was Mg_2O_2. Silicon nitride containing only Y_2O_3 (Si_3N_4–10 mol % Y_2O_3) was also examined. After drying, the mixed powders were sieved through a 60 mesh screen.

2.2. Sintering

The powder mixtures were die-pressed under 20 MPa and then isostatically pressed under 200 MPa. The size of the pressed specimens was about 5 mm × 6 mm × 50 mm. The compacts were placed in a reaction-bonded silicon nitride crucible, which was put into the hot zone of a furnace. The specimens were fired at a constant heating rate of $500° C h^{-1}$ and maintained at the soak temperature (1600 to 2000° C) for 1 h.

Sintering was performed in a 0.1, 10, or 30 MPa N_2 gas pressure. Pressureless sintering was carried out at 1600 to 1700° C. Gas-pressure sintering (GPS) under 10 MPa N_2 was carried out at 1800 to 1900° C; gas-pressure sintering under 30 MPa N_2 was performed at 2000° C. The gas-pressure sintering method was employed for firing at higher temperatures without thermal decomposition of silicon nitride [9].

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2.3. Characterization

The densities of the sintered specimens were measured using Archimedes method.

The samples prepared were polished using a diamond paste and then coated with a thin layer of evaporated carbon for observation by scanning electron microscopy (SEM). The microstructures of the specimens were then observed using the secondary electron image.

The specimens for bending tests, which were prepared by firing at 2000° C under 30 MPa N_2 for 1 h, were ground to size 3 mm × 4 mm × 40 mm using an 800-grit diamond wheel. Flexural strength data were measured at temperatures from 1100 to 1500° C in 0.1 MPa N_2 by a three-point bending test with a 30 mm span at a cross-head speed of 0.5 mm min^{-1}.

2.4. Dilatometric study

The specimens for dilatometric study were fabricated to a size of 10 mm diameter and 12 mm high. The compact was placed in a boron nitride crucible with a power bed of Si_3N_4. The crucible was put into a carbon container serving as the susceptor for induction heating. The specimens were fired at a constant heating rate of 25° C min^{-1} and maintained at 1800 or 2000° C in 1 MPa N_2. The densification curve of the specimen during heating was measured using a dilatometer [10].

3. Results

3.1. Sintering of Si_3N_4-Y_2O_3-M_2O_x

The weight loss of silicon nitride with the additions of Y_2O_3 and a second oxide (M_2O_x) during sintering was less than 5 wt % for all compositions. This indicates that thermal decomposition reactions were depressed under the selected sintering conditions.

Fig. 1 presents the relationship between the sintering temperature and bulk density of silicon nitride containing Y_2O_3 and M_2O_x. When the single oxide of 10 mol % Y_2O_3 (SN10Y) was employed to densify the silicon nitride, shrinkage was not apparent below 1700° C. The density increased with increasing temperature and reached 93% theoretical density at 2000° C. When a second oxide was added (Si_3N_4–5 mol % Y_2O_3–5 mol % M_2O_x: SN5Y5M), higher densities were achieved than in SN10Y. The maximum density was achieved at 1900° C for SN5Y5M.

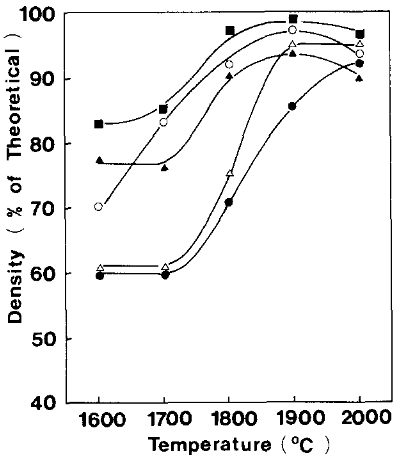

Figure 1 Density of Si_3N_4 containing 5 mol % Y_2O_3 and 5 mol % M_2O_x where M = (▲) Mg, (■) Al, (○) La, (△) Nd, (●) Y, as a function of heating temperature. The specimens were heated at 1600 to 2000° C for 1 h in 0.1 to 30 MPa N_2.

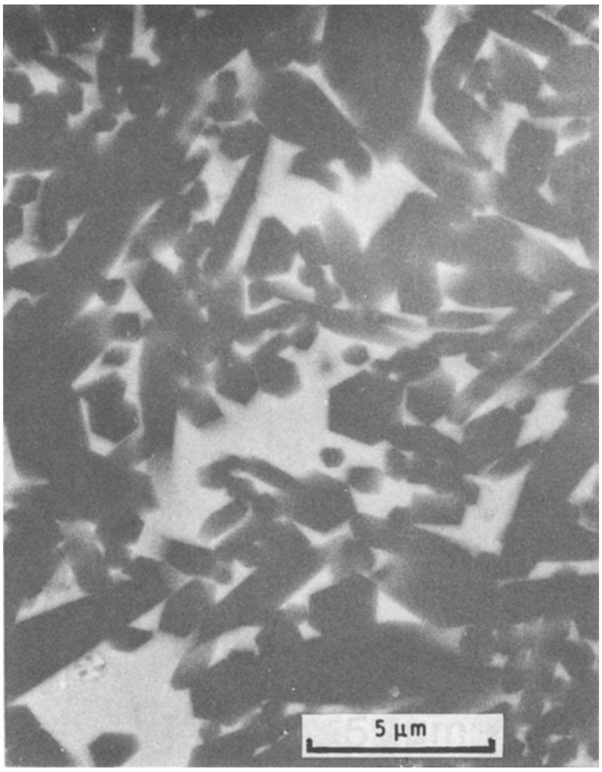

Figure 2 Scanning electron micrograph of Si_3N_4 with 5 mol % Y_2O_3 and 5 mol % Nd_2O_3 sintered at 1900° C.

Fig. 2 indicates the microstructure of Si_3N_4 containing Y_2O_3 and Nd_2O_3 sintered at 1900° C. Development of fibrous Si_3N_4 grains in a secondary phase was observed.

3.2. High-temperature flexural strength

Fig. 3 shows three-point flexural strength of SN10Y at temperatures from 1100 to 1500° C. In the temperature range from 1100 to 1300° C the flexural strength of SN10Y maintained a constant level of about 400 MPa. The strength, however, decreased with increasing temperature above 1300° C.

Fig. 4 illustrates the three-point flexural strength of SN10Y and SN5Y5M (M = Mg, Al, La, Nd) at 1200,

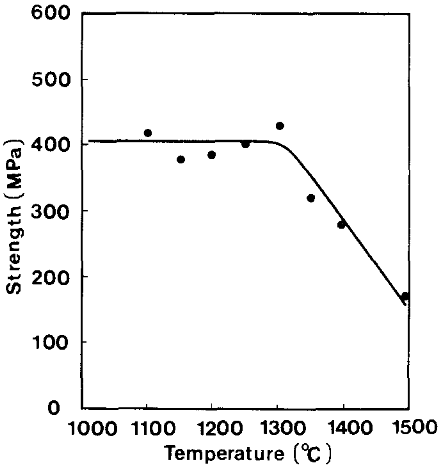

Figure 3 Three-point flexural strength of Si_3N_4 with 10 mol % Y_2O_3 as a function of temperature (1100 to 1500° C).

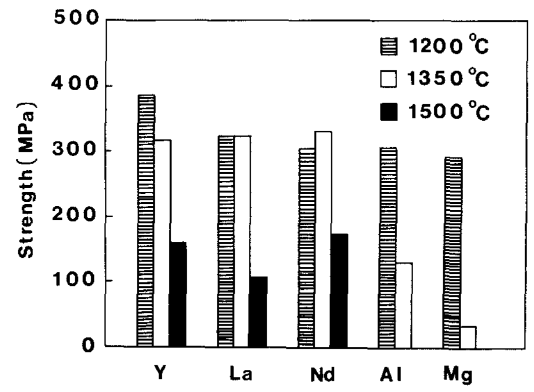

Figure 4 Three-point flexural strength of Si_3N_4 with 5 mol % Y_2O_3 and 5 mol % M_2O_x (M = Mg, Al, La, Nd, Y) at 1200, 1350 and 1500° C.

1350 and 1500° C. The strength for SN5Y5La and SN5Y5Nd at 1350° C remained as high as that at 1200° C; this tendency was similar to SNY10. The strength for SN5Y5Mg and SN5Y5Al at 1350° C, however, decreased below 150 MPa.

Fig. 5 shows the load-deflection curves recorded during the bending tests for SN5Y5Mg, SN5Y5Al and SN5Y5Nd. The curves at 1200° C were typical for brittle fractures. At 1350° C the curves of SN5Y5Mg and SN5Y5Al featured a ductile behaviour, whereas that of SN5Y5Nd still presented a brittle behaviour. The curve of SN5Y5Nd showed ductile behaviour at 1500° C. The curves for SN10Y and SN5Y5La were similar to that for SN5Y5Nd.

3.3. Sintering behaviour

Fig. 6 presents the sintering behaviour for SN10Y, SN5Y5Al and SN5Y5Nd during firing at 1800 and 2000° C. The densification rates are also plotted in the figures. Shrinkage of SN10Y, which was not apparent below 1600° C, started at about 1650° C and achieved 3% at 1800° C and 7% at 2000° C when the temperature was rising. After maintaining at the soak temperature for 1 h, a 5% shrinkage was achieved at 1800° C and a 14% shrinkage was achieved at 2000° C. Only one densification process (Process I), which started at 1650° C, was observed when sintered at 1800° C. In the case of sintering at 2000° C, however, another densification process (Process II), which started at 1900° C, was also observed.

The partial substitution of the second oxide for Y_2O_3 promoted densification of silicon nitride. The shrinkage for SN5Y5Al started at 1400° C, a temperature which was 250° C lower than that in SN10Y. Nearly fully dense materials were fabricated only by Process I. The shrinkage curve for SN5Y5Mg also featured a similar tendency. SN5Y5Nd, on the other hand, started to shrink at 1600° C. This temperature was a little lower than that in SN10Y. The second densification process was also observed at > 1900° C as in SN10Y. SN5Y5La showed a similar tendency.

4. Discussion

4.1. Effect of a second oxide on the sintering of Si_3N_4-Y_2O_3

The present work confirms that the addition of a second oxide is effective in promoting the sintering of silicon nitride containing Y_2O_3. A mixed rare-earth oxide additive (Y_2O_3-Ln_2O_3: Ln = Ce, Nd, La, Sm) has been reported to be effective for the sintering of silicon nitride because it lowers the liquid-formation temperature [4]. In the present work, MgO and Al_2O_3 were also found to be effective.

Sintering of SN10Y would take place by the following mechanism. An SiO_2-rich liquid is generated by the reaction between native SiO_2 and part of the Y_2O_3 at a temperature near 1660° C [11]. The shrinkage of Process I shown in Fig. 6 would take place through the dissolution-precipitation mechanism in this liquid. With increasing temperature, the residual Y_2O_3 reacts with the SiO_2-rich liquid and then an Y_2O_3-rich liquid is generated at > 1800° C ([11], Fig. 2388). The formation of Y_2O_3-rich liquid results in an increase in the amount of liquid phase. Process II observed at > 1900° C is attributed to the increased amount of liquid phase.

In the case of SN5Y5Al, the phase relation ([11], Fig. 2586) predicts that the reaction between native SiO_2, Y_2O_3, and Al_2O_3 produces the liquid phase in the Y_2O_3-Al_2O_3-SiO_2 system at 1400° C; this liquid leads to the shrinkage of Process I. The residual Y_2O_3 and Al_2O_3 also dissolve to the liquid phase gradually with increasing temperature. This brings about an increase in the amount of liquid so that sintering can take place over a wide temperature range. Then the composition of the grain boundary changes to near the Y_2O_3 corner in the Y_2O_3-Al_2O_3-SiO_2 system

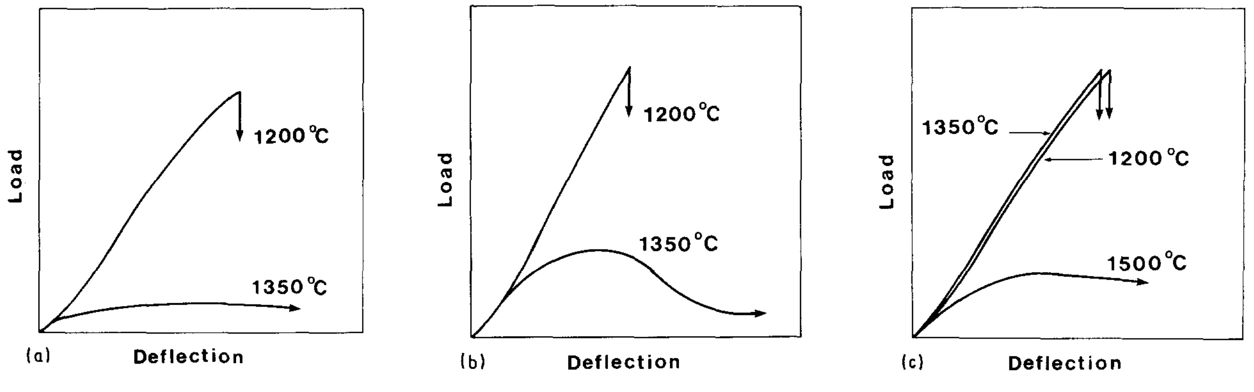

Figure 5 Load-deflection curves for (a) Si_3N_4-5 mol % Y_2O_3-5 mol % Mg_2O_2, (b) Si_3N_4-5 mol % Y_2O_3-5 mol % Al_2O_3, and (c) Si_3N_4-5 mol % Y_2O_3-5 mol % Nd_2O_3.

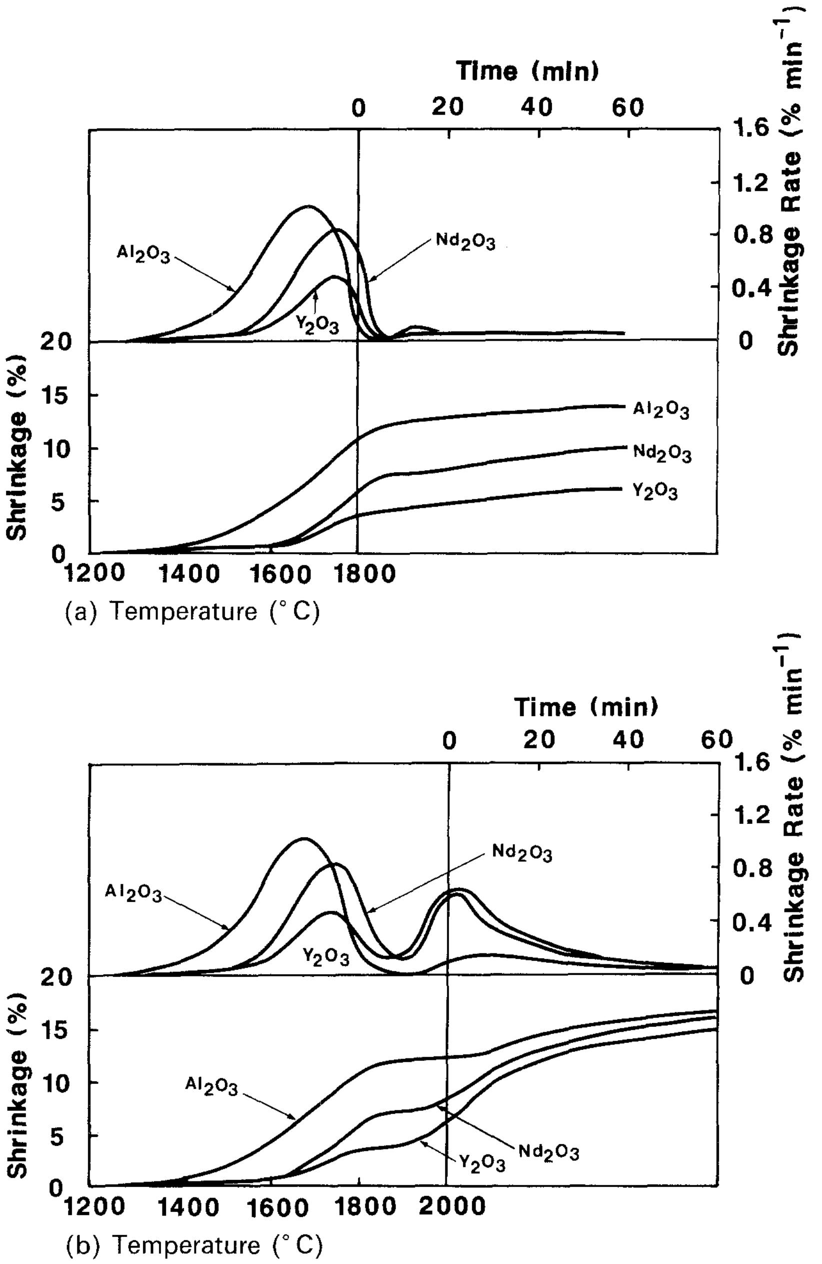

Figure 6 Sintering behaviour for Si_3N_4 containing 5 mol% Y_2O_3 and 5 mol% M_2O_x (M = Al, Nd, Y) during firing at (a) 1800° C and (b) 2000° C.

because some Al_2O_3 dissolves in the silicon nitride grains. In the case of SN5Y5Mg, sintering would take place by a similar mechanism although MgO cannot make a solid solution with silicon nitride.

In SN5Y5Nd and SN5Y5La, the first shrinkage was observed at 1600° C, which is about 50° C lower than in SN10Y. The contribution of Process I in this system is smaller than in Y_2O_3–Al_2O_3 or Y_2O_3–MgO systems because the amount of liquid is smaller at lower temperatures. Shrinkage during Process II was observed at almost the same temperature as in SN10Y. This shrinkage should take place throughout the liquid whose melting point is higher than SN5Y5Al or SN5Y5Mg and nearly the same as SN10Y.

SN5Y5Mg and SN5Y5Al achieved sufficient shrinkage to give full densification below 1800° C. SN5Y5La or SN5Y5Nd, however, did not achieve sufficient shrinkage at 1800° C. The contribution of Process II is necessary for SN5Y5La or SN5Y5Nd to achieve further shrinkage; thus a temperature higher than 1900° C is required.

The densities of SN5Y5M (M = Mg, Al, La) sintered at 2000° C were lower than those sintered at 1900° C. This is attributed to the effect of gas pressure on the sintering. Although high nitrogen pressure is effective for minimizing the thermal decomposition of Si_3N_4 during sintering [9], the sintering under > 10 MPa lowered the densities of sintered materials because of the inhibition of the final stage of densification [12]. In this study, the nitrogen gas pressure adopted for sintering at 2000° C is too high to promote the final stage of sintering.

4.2. Effect of a second oxide on high-temperature strength

The strength of sintered silicon nitride with an oxide additive is often reduced at high temperatures. Although the liquid phase promotes sintering, it forms a glassy phase at grain boundaries and degrades high-temperature strength. The degree of strength decrease at high temperature is related to the viscosity of the grain-boundary glassy phase. The observed load–deflection curves suggest that this mechanism is reasonable for the reduction of high-temperature strength. Consequently, the composition of liquid phase strongly affects the high-temperature strength of sintered silicon nitride.

In the present study, the high-temperature strength of SN5Y5Al and SN5Y5Mg was reduced, although that of SN5Y5La and SN5Y5Nd remained equivalent to that of SN10Y. This might be due to lower melting temperature and lower viscosity of the grain-boundary phases for SN5Y5Al and SN5Y5Mg. In these materials, sintering occurs through a liquid generated at < 1900° C. In SN5Y5La and SN5Y5Nd, on the other hand, liquid phase generated at > 1900° C promotes sintering for Process II. This indicates that the glassy phase in SN5Y5Al and SN5Y5Mg is less refractory than in the other systems. As a result, sintered materials in these systems have a higher strength at elevated temperatures.

Silicon nitride containing Al_2O_3 forms sialon through a solid solution of Al_2O_3 into grains [13]. Compositional-controlled sialon has been reported to have excellent mechanical properties at elevated temperatures [14]. Although the SN5Y5Al composition may produce sialon, it revealed a strength reduction at elevated temperatures. This strength reduction would be caused by the formation of grain-boundary glassy phase of Y_2O_3–Al_2O_3–SiO_2 system with low melting temperature due to the partial dissolution of Al_2O_3 into grains.

Increasing the liquid formation temperature in the sintering of Si_3N_4 is an effective method for improving the high-temperature mechanical properties of Si_3N_4. Hence, the sintering additive should be selected on the basis of poor sinterability at low temperatures and sufficient sinterability at high temperatures. A dilatometer study is effective for this purpose. We assume that the material which does not shrink at lower temperatures and achieves full-densification at higher temperatures is favourable for improving the high-temperature properties of Si_3N_4. In the present study Y_2O_3–La_2O_3 and Y_2O_3–Nd_2O_3 additive are effective for improving sinterability with high-temperature strength, similar to Y_2O_3.

5. Conclusions

The effect of a second oxide on the densification and high-temperature strength of Si_3N_4 containing Y_2O_3 was studied and the following results were obtained.

1. The addition of a second oxide, such as MgO, Al_2O_3, La_2O_3 and Nd_2O_3, to the Si_3N_4–Y_2O_3 system promotes sintering.
2. In the Y_2O_3–Al_2O_3 and Y_2O_3–MgO systems sinterability was remarkably improved at temperatures higher than 1400° C, but strength reduction was observed at 1350° C. The dilatometric study indicated that the lowest liquid formation temperatures in these systems are lower than those in other systems. The reduction of high-temperature strength in these systems is caused by a glassy phase with a low softening temperature.
3. In the Y_2O_3–La_2O_3 and Y_2O_3–Nd_2O_3 systems, sinterability was improved more than in Y_2O_3 system and the strength at elevated temperature remained as high as that in the Y_2O_3 system. This is because the glassy phase in these systems is as refractory as that in the Si_3N_4–Y_2O_3 system.

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