Properties of Oxynitride Glasses in the Ln-Si-Al-O-N Systems (Ln=Rare-Earth)

Yuichiro MURAKAMI and Hirokazu YAMAMOTO

Advanced Technology Research Center, Mitsubishi Heavy Industries Ltd., 1-8-1, Sachiura, Kanazawa-ku, Yokohama-shi 236

Ln-Si-Al-O-N 系オキシナイトライドガラスの性質 (Ln=希土類)

村上勇一郎・山本博一

三菱重工業(株)基盤技術研究所, 236 横浜市金沢区幸浦 1-8-1

[Received September 8, 1993; Accepted December 15, 1993]

Effect of radius of rare-earth ions on the characteristics of oxynitride glasses in the Ln-Si-Al-O-N systems (Ln=Dy, Er, Gd, La, Nd, Sm, Y, Yb) was studied. The glass transition temperature and the softening temperature of these glasses were determined, but their correlation with the radius of rare-earth ions was found to be weak. Oxidation behavior of these glasses was analyzed by assuming that the weight change is proportional to the n -th power of the oxidation time, and it was found that the oxidation exponent, n , tends to decrease and that the oxidation resistance tends to increase with decreasing radius of rare-earth ions. Yb-Si-Al-O-N glass had the best oxidation resistance in these rare-earth-containing oxynitride glasses. The oxidation mechanism of the oxynitride glasses was also discussed.

Key-words: Oxynitride glass, Rare-earth, Glass transition, Oxidation, Crystallization, Solubility, Self-repairing

1. Introduction

The oxynitride glasses containing rare-earth elements (Ln) of the Ln-Si-Al-O-N systems (hereafter abbreviated as Ln-Si-Al-O-N glass) have excellent properties such as high elastic modulus and high chemical durability¹⁾⁻⁹⁾ and have attracted attention as a practical application to glass fiber for fiber-reinforcement, nuclear waste glass, neutron-absorbent glass, joining agent for ceramics, etc.¹⁾⁻⁴⁾

In the oxynitride glasses, the structure of glass has been studied by molecular orbital calculation, ²⁹Si NMR, neutron diffraction, etc.,⁷⁾⁻⁹⁾ and the physical properties such as density, glass transition temperature, viscosity and Vickers hardness have been reported to have a tendency of increasing with increase in the concentration of nitrogen.¹⁾⁻⁶⁾ Because the Si-N bond is more covalent than the Si-O bond and the nitrogen atom has more bridging bonds than the oxygen atom, it is considered that the network of glass becomes more resistant against bending and the packing density of glass increases, as the oxygen atoms, which are the negative elements constituting the glass, are substituted partly by the nitrogen atoms.⁷⁾⁻⁹⁾ However, the application of oxynitride

glasses at high temperatures is limited, because they tend to be oxidized in air at temperatures above about 800°C.¹⁰⁾⁻¹³⁾ Then, regarding the oxynitride glasses, the oxidation resistance should also be examined.

On the other hand, in the oxide glasses, the glass transition temperature and the softening temperature of the rare-earth-containing aluminosilicate glasses have been reported to rise with decrease in the radius of rare-earth ion.^{14),15)} As an origin of this phenomenon, it is considered that the field strength of rare-earth ion increases and the bonds between rare-earth ion and the surrounding oxygen become stronger as the radius of rare-earth ion decreases. However, in the oxynitride glasses, effect of the radius of rare-earth ion on the properties of glasses has not been studied particularly.

In this study, the glass transition temperature, the softening temperature and the oxidation behaviors of oxynitride glasses in the Ln-Si-Al-O-N systems (Ln=Dy, Er, Gd, La, Nd, Sm, Y, Yb) were clarified and the effect of radius of rare-earth ion on the characteristics of oxynitride glasses was investigated. In addition, the oxidation mechanism of the oxynitride glass was also discussed.

2. Experimental procedure

The starting powders were Al₂O₃ (purity : 99.9%, averaged particle size : 0.96 μ m), SiO₂ (99.99%, 0.94 μ m), Si₃N₄ (99.9%, 0.3 μ m) and Ln₂O₃ (99.9%, about 1 μ m, Ln=Dy, Er, Gd, La, Nd, Sm, Y, Yb). These powders were mixed in the presence of ethanol as the solvent to prepare specimens with the given composition. The mixture was dried and pressed at 1 MPa into a disc shape with dimensions of about 30 mm ϕ $\times$ 10 mm. This green product was melted at 1550°C for 1h in a BN crucible under the nitrogen atmosphere of 0.8 MPa and was then quenched to prepare the oxynitride glasses.

The oxynitride glasses were heated at 5°C/min up to a maximum of 1200°C in a nitrogen atmosphere in order to determine the glass transition temperature, using a differential thermal analyzer (DTA), and to determine the softening temperature, using a ther-

mechanical analyzer (TMA). The oxidation behaviors of the oxynitride glasses in air at a temperature range from 1000 to 1100°C were assessed by monitoring the weight changes of specimens, using a thermogravimetric analyzer (TGA); the specimen with about $4 \times 4 \times 4$ mm in dimension was set quickly into a furnace kept at a given temperature and treated in air to follow the weight changes.

The surfaces and the cross-sections of the oxidized specimens were observed by a scanning electron microscope (SEM) to clarify the change of microstructure during oxidation. The structures of the oxide scales and the crystalline phases were analyzed by using an X-ray diffractometer (XRD) and an X-ray microanalyzer (EPMA).

3. Results and discussion

3.1 Properties of rare-earth-containing oxynitride glasses

In the previous paper,¹⁶⁾ the present authors have shown that the solidus temperatures of the $\text{Ln}_2\text{Si}_2\text{O}_7$ - $\text{Al}_6\text{Si}_2\text{O}_{13}$ - SiO_2 compatibility systems (Ln=Dy, Er, Gd, La, Nd, Sm, Y, Yb), i.e. the ternary eutectic temperatures of these systems, are in a range of 1305–1500°C. In order to prepare glasses, specimens should be melted at a temperature above eutectic temperatures. Thereby, the temperature for preparing the various Ln-Si-Al-O-N glasses was selected to 1550°C.

The glass-forming regions of the Al_2O_3 - Ln_2O_3 - SiO_2 systems have been already reported in the systems with Ln=Gd, La, Nd, Sm, Y, Yb.^{2),16)–18)} In the previous paper,¹⁶⁾ the present authors have shown that the solubility of Si_3N_4 into the Al_2O_3 - Y_2O_3 - SiO_2 glass is about 6 mol% at 1550°C. If the concentration of the Si_3N_4 additives is kept to 5 mol%, it is expected that Si_3N_4 might be soluble into every kind of Al_2O_3 - Ln_2O_3 - SiO_2 glass at 1550°C and that the oxynitride glasses can be obtained without the precipitation of Si_3N_4 particles. Then, the $(\text{Al}_2\text{O}_3)_{28}(\text{Ln}_2\text{O}_3)_{10}(\text{SiO}_2)_{57}(\text{Si}_3\text{N}_4)_5$ composition was selected for the preparation of Ln-Si-Al-O-N glasses.

The softening temperature, T_d , and the glass transition temperature, T_g , of the Ln-Si-Al-O-N glasses with $(\text{Al}_2\text{O}_3)_{28}(\text{Ln}_2\text{O}_3)_{10}(\text{SiO}_2)_{57}(\text{Si}_3\text{N}_4)_5$ composition (Ln=Dy, Er, Gd, La, Nd, Sm, Y, Yb) are given as a function of the radius of rare-earth ion in Fig. 1. Although T_d and T_g seem to have a weak tendency of rising with decrease in the radius of rare-earth ion, the strong correlation between them as reported in the Al_2O_3 - Ln_2O_3 - SiO_2 glasses¹⁴⁾ has not been observed in the present Ln-Si-Al-O-N glasses. Because the density of oxynitride glass has been already increased by the incorporation of nitrogen atoms, the effect of the radius of rare-earth ion on the properties of the oxynitride glasses might be small compared with that of the oxide glasses. Since T_g and T_d of glasses are generally dependent on composition, details should also be investigated in the

Fig. 1. (a) Softening temperature, T_d , and (b) glass transition temperature, T_g , of the oxynitride glasses with $(\text{Al}_2\text{O}_3)_{28}(\text{Ln}_2\text{O}_3)_{10}(\text{SiO}_2)_{57}(\text{Si}_3\text{N}_4)_5$ composition (Ln=Dy, Er, Gd, La, Nd, Sm, Y, Yb) as a function of the radius of rare-earth ion.

other composition. T_g and T_d of the Ln-Si-Al-O-N glasses obtained in this work are in the range of 915–950°C and 960–1020°C, respectively.

In the previous paper,¹³⁾ the present authors have studied the oxidation behavior of the Y-Si-Al-O-N glass and shown that the activation energy for oxidation has different values at temperatures below and above T_d . Then, to clarify the effect of the rare-earth ion on the oxidation behaviors of the Ln-Si-Al-O-N glasses, the weight changes of glasses during oxidation were monitored by TGA in air at 1037°C, which is higher than T_d of these glasses. The relationships between relative weight change, $\Delta W/\Delta W_{\max}$, and holding time, t , in these glasses are shown in Fig. 2. These relations are generally represented by the following formula:

$$\log(\Delta W/\Delta W_{\max}) = \log C + n \log t \quad (1)$$

where ΔW is the weight change during oxidation, $\Delta W_{\max}$ is the theoretical weight change assuming that Si_3N_4 is completely oxidized into SiO_2 , C is the rate constant for oxidation and n is the oxidation exponent dependent on the oxidation mechanism. The observed $\log(\Delta W/\Delta W_{\max})$ - $\log t$ relation becomes nearly straight line with a slope, n , in the special range of holding time. In the Sm-Si-Al-O-N

Fig. 2. Relative weight change, $\Delta W/\Delta W_{\max}$, of the oxynitride glasses with $(\text{Al}_2\text{O}_3)_{28}(\text{Ln}_2\text{O}_3)_{10}(\text{SiO}_2)_{57}(\text{Si}_3\text{N}_4)_5$ composition (Ln=Dy, Er, Gd, La, Nd, Sm, Y, Yb) during oxidation at 1037°C in air as a function of the oxidation time, t (h).

glass, n equals 1.0 at the initial stage of oxidation and 2.0 at the final stage of oxidation. On the contrary, in the Yb-Si-Al-O-N glass, n equals 1.0 at the initial stage, 1/2 at the middle stage and 1/6 at the final stage of oxidation. From these results, it is clarified that the Y-Si-Al-O-N glass has the poorest oxidation resistance and the Yb-Si-Al-O-N glass has the best oxidation resistance in these glasses. The weight gains at the initial stage of oxidation in the glasses with Ln=Dy, Gd and Er are smaller than that of the glass with Ln=Yb. This is ascribed to the fact that the weight gain appears gradually after the appearance of the initial weight loss, which is probably due to the partial decomposition of oxynitride glass before the initiation of oxidation. The initial weight loss has also been reported for the oxidation of the Ca-Si-Al-O-N glass.¹¹⁾

As the oxidation mechanism of nitride, it is generally accepted that the oxidation rate is controlled by the interface reaction when $n=1.0$, by the diffusion in the oxide scale when $n=1/2$ and by the autocatalytic reaction when $n>1$.^{13),19)} It is also generally known that the thermal decomposition of the various kinds of inorganic compounds occurs by the autocatalytic reaction.²⁰⁾

The oxidation process of the oxynitride glass at the initial stage seems to be complicated, because the initial weight loss occurs in some glasses. Then, the effect of the radius of rare-earth ion on the oxidation behaviors of the Ln-Si-Al-O-N glasses was studied at the final stage of oxidation. The relation between the oxidation exponent, n , and the radius of rare-earth ion in the Ln-Si-Al-O-N glasses is shown in Fig. 3. From this result, it is found that the oxidation exponent, n , tends to decrease and, accordingly, that the oxidation resistance tends to increase as the radius of rare-earth ion decreases. Especially, in the glasses containing rare-earth with large ionic radius such as Nd, La, Sm and Gd, n is larger than 1 and the glasses are oxidized severely accompanied with frothing at high temperature in air. On the contrary, in the glasses containing rare-earth with small ionic radius such as Dy, Er and Yb, n is smaller than 1, i.e.

Fig. 3. Oxidation exponent, n , of the oxynitride glasses with $(\text{Al}_2\text{O}_3)_{28}(\text{Ln}_2\text{O}_3)_{10}(\text{SiO}_2)_{57}(\text{Si}_3\text{N}_4)_5$ composition (Ln=Dy, Er, Gd, La, Nd, Sm, Y, Yb) at the final stage of oxidation as a function of the radius of rare-earth ion.

the oxidation rate is smaller than that of the linear law, ($n=1$).

The SEM micrographs (back-scattered electron image) of the surfaces of the Ln-Si-Al-O-N glasses oxidized at 1040°C for 24h in air and the X-ray diffraction patterns of the oxide scales in these glasses are shown, respectively, in Fig. 4 and Fig. 5. In Figs. 4(a) and (b), large and black areas are the open

Fig. 4. SEM micrographs (back-scattered electron image) of the surfaces of oxynitride glasses with $(\text{Al}_2\text{O}_3)_{28}(\text{Ln}_2\text{O}_3)_{10}(\text{SiO}_2)_{57}(\text{Si}_3\text{N}_4)_5$ composition oxidized at 1040°C for 24h, where Ln shows (a) La, (b) Nd, (c) Gd, (d) Dy, (e) Er and (f) Yb.

Fig. 5. X-ray diffraction patterns of the oxynitride glasses with $(\text{Al}_2\text{O}_3)_{28}(\text{Ln}_2\text{O}_3)_{10}(\text{SiO}_2)_{57}(\text{Si}_3\text{N}_4)_5$ composition oxidized at 1040°C for 24h, where Ln shows (a) La, (b) Nd, (c) Gd, (d) Dy, (e) Er and (f) Yb. ○ : $\text{Al}_6\text{Si}_2\text{O}_{13}$, ▽ : $\text{Ln}_2\text{Si}_2\text{O}_7$, □ : SiO_2 .

pore. In the glasses containing rare-earth with large ionic radius such as La and Nd, the oxide scales have many open pore as shown in Figs. 4(a) and (b). From the X-ray diffraction patterns shown in Figs. 5(a) and (b), the oxide scales are found to be mainly amorphous, although they contain small amount of $\text{Al}_6\text{Si}_2\text{O}_{13}$; the black needle-like particles observed in Figs. 4(a) and (b) are considered to be $\text{Al}_6\text{Si}_2\text{O}_{13}$.

On the contrary, in the glasses containing rare-earth with small ionic radius such as Er and Yb, the oxide scales seem to be very fine and dense, having less open pore, as shown in Figs. 4(e) and (f). From the X-ray diffraction patterns shown in Figs. 5(e) and (f), the oxide scales are found to be crystalline. Of the crystalline phase existed in these scales, the amount of $\text{Ln}_2\text{Si}_2\text{O}_7$ (rare-earth disilicate) seems to be much larger than those of $\text{Al}_6\text{Si}_2\text{O}_{13}$ and SiO_2 . In the back-scattered electron images of Figs. 4(e) and (f), white portion is considered to be the position where the crystallites of $\text{Ln}_2\text{Si}_2\text{O}_7$ exist.

In addition, in the oxide scales of the glasses containing Gd and Dy, the amounts of the open pore and the crystals in them seem to be intermediate between those of the Nd and Er-containing glasses as shown in Figs. 4 and 5.

As revealed in Fig. 5, in the Ln-Si-Al-O-N glasses, nature of the oxide scales tends to become more crystalline and the amount of $\text{Ln}_2\text{Si}_2\text{O}_7$ in the oxide scales tends to increase as the radius of rare-earth ion decreases. In the previous paper, the present authors have shown that the eutectic temperature of the $\text{Ln}_2\text{Si}_2\text{O}_7$ - $\text{Al}_6\text{Si}_2\text{O}_{13}$ - SiO_2 compatibility system has a tendency of rising with decrease in the radius of rare-earth ion.¹⁶⁾ Because this eutectic temperature is the lowest temperature for the coexistence of the solid ($\text{Ln}_2\text{Si}_2\text{O}_7$, $\text{Al}_6\text{Si}_2\text{O}_{13}$, SiO_2) and the liquid phases, it is suggested that the enthalpy of formation (ΔH) for $\text{Ln}_2\text{Si}_2\text{O}_7$ tends to increase with decrease in the radius of rare-earth ion. This may cause the increasing tendency of becoming crystalline and growing crystals of $\text{Ln}_2\text{Si}_2\text{O}_7$ in the oxide scales with decrease in the radius of rare-earth ion. It is considered, moreover, that the viscosity of glasses tends to increase in the systems with higher eutectic temperature and with smaller radius of the rare-earth ion.²¹⁾

As revealed in Figs. 2 and 3, the oxidation resistance of the Ln-Si-Al-O-N glasses is considered to increase as the radius of rare-earth ion decreases. As an origin of this phenomenon, it is considered that the viscosity of glass increases and that the oxide scale becomes more crystalline as the radius of rare-earth ion decreases. Then, in the Ln-Si-Al-O-N glasses containing rare-earth ion with large ionic radius, because the glass is suggested to have low viscosity and the amorphous oxide scale, the simultaneous decomposition and oxidation occur at high temperature in air accompanied with the formation of bubbles and the frothing, which may ac-

celerate the decomposition and oxidation of the oxynitride glass and, accordingly, may cause the autocatalytic oxidation in these glasses.

On the other hand, in the Ln-Si-Al-O-N glasses containing rare-earth ion with small ionic radius, because the glass is suggested to have high viscosity and the dense and crystalline oxide scale, the frothing may be suppressed and the diffusion rate of mobile species in the oxide scale is considered to have a large effect on the oxidation rate of the oxynitride glass. This may cause the oxidation rate becoming smaller than that of the linear law.

From these results, it is concluded that the Yb-Si-Al-O-N glass, forming the dense and crystalline oxide scale, has the best oxidation resistance in the Ln-Si-Al-O-N glasses obtained in this work.

3.2 Oxidation behavior of Yb-Si-Al-O-N glass

The $\log(\Delta W/\Delta W_{\max})-\log t$ relation of the Yb-Si-Al-O-N glass shown in Fig. 2 consists of three straight lines, suggesting that there are three types of the oxidation stage. Then, as another composition located in the glass-forming region of the Al_2O_3 - Yb_2O_3 - SiO_2 system,¹⁶⁾ the $(\text{Al}_2\text{O}_3)_{20}(\text{Yb}_2\text{O}_3)_{12}(\text{SiO}_2)_{68}$ composition was selected and the Yb-Si-Al-O-N glass was prepared by adding Si_3N_4 into this glass in order to clarify the details of the property of Yb-Si-Al-O-N glass.

The effects of Si_3N_4 concentration on T_g and T_d of the oxynitride glasses in the quasi-binary $(\text{Al}_2\text{O}_3)_{20}(\text{Yb}_2\text{O}_3)_{12}(\text{SiO}_2)_{68}-\text{Si}_3\text{N}_4$ system are shown in Fig. 6. T_g and T_d tend to rise as the Si_3N_4 concentration increases until they become to the almost constant values in the region of Si_3N_4 concentration above about 6 mol%, where the coexistence of two phases (β - Si_3N_4 precipitates in the glassy phase) has been confirmed by XRD and SEM. From these results, the solubility of Si_3N_4 into this Al_2O_3 - Yb_2O_3 - SiO_2 glass is found to be about 6 mol% at 1550°C.

The relative weight change of the Yb-Si-Al-O-N glass with $(\text{Al}_2\text{O}_3)_{18.9}(\text{Yb}_2\text{O}_3)_{11.3}(\text{SiO}_2)_{64.3}(\text{Si}_3\text{N}_4)_{5.5}$ composition, which is the highest concentration of

Fig. 6. Composition dependence of the glass transition temperature, T_g , and the softening temperature, T_d , of the oxynitride glasses in the quasi-binary $(\text{Al}_2\text{O}_3)_{20}(\text{Yb}_2\text{O}_3)_{12}(\text{SiO}_2)_{68}-\text{Si}_3\text{N}_4$ system which were prepared by quenching the liquid phase at 1550°C.

Si_3N_4 obtained in Fig. 6, was monitored by TGA in air at the temperature range of 1038–1089°C (1311–1362 K). The results are given in Fig. 7. In this glass, n equals 1 at the initial stage, 1/2 at the middle stage and 1/6 at the final stage of oxidation. Then, as the oxidation mechanism, it is considered that the interface reaction controlled oxidation occurs at the initial stage and that the diffusion controlled oxidation occurs at the middle stage. At the final stage, n equals 1/6, which is lower than that ($n=1/2$) of the parabolic law.

When the oxidation temperature is changed, the $\log(\Delta W/\Delta W_{\max})-\log t$ line is shifted in parallel, suggesting that the rate constant for oxidation, C , is a function of temperature. In each oxidation stage, $\ln C$ is plotted against $1/T$ (Arrhenius plot) in order to determine the activation energy ΔE for oxidation, as shown in Fig. 8. The ΔE values in the present Yb-Si-Al-O-N glass are smaller than those (760–1340 kJ/mol) of the Y-Si-Al-O-N glass.¹³⁾ This implies that the temperature dependence of the oxidation rate in the former is milder than that of the latter.

To clarify the difference of oxidation mechanism between the stages of $n=1/2$ and $n=1/6$, the SEM

Fig. 7. Relative weight change, $\Delta W/\Delta W_{\max}$, of the oxynitride glasses with $(\text{Al}_2\text{O}_3)_{18.9}(\text{Yb}_2\text{O}_3)_{11.3}(\text{SiO}_2)_{64.3}(\text{Si}_3\text{N}_4)_{5.5}$ composition during oxidation at each temperature in air as a function of the oxidation time, t (h). n represents the oxidation exponent.

Fig. 8. $\ln C$ vs. $1/T$ plot showing a relation between rate constant for oxidation, C , and reciprocal temperature, $1/T$, for the $(\text{Al}_2\text{O}_3)_{18.9}(\text{Yb}_2\text{O}_3)_{11.3}(\text{SiO}_2)_{64.3}(\text{Si}_3\text{N}_4)_{5.5}$ glass. ΔE shows the activation energy for oxidation. n represents the oxidation exponent.

micrographs of the cross-sections of the Yb-Si-Al-O-N glasses, which were oxidized at 1069°C for 12h and at 1089°C for 20h, respectively, are shown in Figs. 9(a) and (b). In the stage of $n=1/2$, as shown in Fig. 9(a), the dense and crystalline oxide scale has been formed and any crystal has not been grown at the interface between the oxide scale and the glass, although some crystallites have been already grown locally in the inner parts of the glass, suggesting the partial occurrence of the crystallization. In the stage of $n=1/6$, as shown in Fig. 9(b), many crystals have been grown from the interface to the inner part of the glass, although some crystals have been already grown locally in the inner parts of the glass also at this stage. The white crystals in Fig. 9(b) were confirmed to be $\text{Yb}_2\text{Si}_2\text{O}_7$ and the black ones to be $\text{Al}_6\text{Si}_2\text{O}_{13}$ by EPMA. From these results, at the stage of $n=1/6$, the crystals such as $\text{Yb}_2\text{Si}_2\text{O}_7$ are suggested to be nucleated at the interface and to grow from the interface to the inner part of the glass; this may decrease the amount of glassy phase at the vicinity of interface and decrease the diffusion rate of mobile species, and as a result, the oxidation rate may become smaller than that of the parabolic law.

In addition, in the temperature range above about 1100°C, because the glass has a strong tendency of being crystallized, the oxidation rate decreases and the $\ln C-1/T$ relation shown in Fig. 8 deviates from the straight line, although details are omitted in this paper. Moreover, the formation of $\text{Yb}_2\text{Si}_2\text{O}_7$ in the oxide scale and the growth of $\text{Yb}_2\text{Si}_2\text{O}_7$ at the inter-

Fig. 9. SEM micrographs (back-scattered electron image) of the cross sections of oxynitride glasses with $(\text{Al}_2\text{O}_3)_{18.9}(\text{Yb}_2\text{O}_3)_{11.3}(\text{SiO}_2)_{64.3}(\text{Si}_3\text{N}_4)_{5.5}$ composition. (a) oxidized at 1069°C for 12h and (b) oxidized at 1089°C for 20h.

face, as observed in Fig. 5(f) and Fig. 9, suggest that there is a possibility of the outward migration of Yb ions during oxidation of the Yb-Si-Al-O-N glass.

From these results, the Yb-Si-Al-O-N glass is considered to have a good oxidation resistance and to become a candidate of the new functional material having self-repairing-type oxidation inhibition, because its oxidation rate is reduced as the crystallization is initiated at the interface when the surface is oxidized.

4. Summary

The properties of rare-earth-containing oxynitride glasses in the Ln-Si-Al-O-N systems (Ln=Dy, Er, Gd, La, Nd, Sm, Y, Yb) were investigated and the following results were obtained.

(1) The glass transition temperature and the softening temperature in these glasses are in a range of 915–950°C and 960–1020°C, respectively.

(2) The correlation between the glass transition and softening temperatures of glasses and the radius of rare-earth ion is weak in these oxynitride glasses.

(3) The oxidation behaviors of the Ln-Si-Al-O-N glasses were analyzed by assuming that the weight change was proportional to the n -th power of oxidation time, and it was found that the oxidation exponent, n , tends to decrease and that the oxidation resistance tends to increase as the radius of rare-earth ion decreases.

(4) The Yb-Si-Al-O-N glass has the best oxidation resistance in the Ln-Si-Al-O-N glasses obtained in this work.

(5) In the oxidation process of the Yb-Si-Al-O-N glass, n equals 1 at the initial stage (interface reaction controlled oxidation), 1/2 at the middle stage (diffusion controlled oxidation) and 1/6 at the final stage of oxidation. In the stage of $n=1/6$, the oxidation rate is decelerated than that of the parabolic

law, because many crystals grow from the interface to the inner parts of glass and the amount of glassy phase at the vicinity of interface are contracted during oxidation.

References

- 1) R. E. Loehman, *J. Non-Cryst. Solids*, **42**, 433–45 (1980).
- 2) J. Rocherulle, P. Verdier and Y. Laurent, *Mater. Sci. Eng.*, **82**, 265–68 (1989).
- 3) B. Steffestun and G. H. Frischat, *J. Am. Ceram. Soc.*, **76**, 699–704 (1993).
- 4) P. A. Walls, S. Asada and M. Ueki, Proc. Annual Meeting Ceram. Soc. Japan (1990) p. 109.
- 5) A. Makishima, M. Mitomo, N. Ii and M. Tsutsumi, *J. Am. Ceram. Soc.*, **66**, C55–56 (1983).
- 6) S. Sakka, K. Kamiya and T. Yoko, *J. Non-Cryst. Solids*, **56**, 147–52 (1983).
- 7) M. Murakami and S. Sakka, *J. Non-Cryst. Solids*, **101**, 271–79 (1988).
- 8) H. Unuma, H. Maekawa, H. Kiyono, K. Kawamura, T. Maekawa and T. Yokokawa, *J. Ceram. Soc. Japan*, **100**, 1292–96 (1992).
- 9) J. Jin, T. Yoko, S. Sakka, T. Fukunaga and M. Misawa, *J. Am. Ceram. Soc.*, **76**, 630–34 (1993).
- 10) R. R. Wusirika, *J. Am. Ceram. Soc.*, **68**, C294–97 (1985).
- 11) M. Desmaison-Brut, J. Desmaison and P. Verdier, *J. Non-Cryst. Solids*, **105**, 323–29 (1988).
- 12) C. O'Meara and G. L. Dunlop, *J. Eur. Ceram. Soc.*, **8**, 161–70 (1991).
- 13) Y. Murakami and H. Yamamoto, *J. Ceram. Soc. Japan*, **100**, 708–13 (1992).
- 14) J. E. Shelby and J. T. Kohli, *J. Am. Ceram. Soc.*, **73**, 39–42 (1990).
- 15) S. Tanabe, K. Hirao and N. Soga, *J. Am. Ceram. Soc.*, **75**, 503–06 (1992).
- 16) Y. Murakami and H. Yamamoto, *J. Ceram. Soc. Japan*, **101**, 1101–06 (1993).
- 17) A. Makishima, Y. Tamura and T. Sakaino, *J. Am. Ceram. Soc.*, **61**, 247–49 (1978).
- 18) E. M. Erbe and D. E. Day, *J. Am. Ceram. Soc.*, **73**, 2703–13 (1990).
- 19) M. Billy, *Sci. Ceram.*, **14**, 45–60 (1988).
- 20) S. Hashimoto, "Kagaku Sosetsu No. 9", Chem. Soc. Japan (1975) pp. 209–36.
- 21) M. K. Cinibulk, G. Thomas and S. M. Johnson, *J. Am. Ceram. Soc.*, **75**, 2044–49 (1992).