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Oxidation Behaviour of Yttrium and Neodymium Oxynitride Glasses

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Abstract

The oxidation behaviour of oxynitride glasses in M–Si–Al–O–N system (M = Nd, Y) has been studied in air and under various oxygen pressures. The influence of glass composition on the oxidation resistance was studied at 1075°C by varying Y/Al or Si/Al ratios and also by substituting Y by Nd and by varying the nitrogen content. The reactivities in air of the YSiAlON system is studied in the temperature range of 1000–1150°C. The oxidation resistance of YSiAlON glasses is better than for glasses containing Nd. A pressure law is determined for the YSiAlON system based upon data from oxidation at 1050 and 1075°C at oxygen pressures in the range of 15–100 kPa. The nature and morphology of oxidised samples were characterised by optical microscopy, XRD and SEM. These investigations reveal that the oxidation of the studied oxynitride glasses is governed by a reaction process where the progress of the internal interface is the limiting step.

1 Introduction

It is well established that oxidation and high temperature mechanical properties of silicon nitride ceramics are strongly dependent on the residual secondary phases. These can be glass or crystalline phases and are formed as a result of sintering additives or impurities in the material powders used in the synthesis of the ceramics. This has aroused a considerable interest in oxynitride glasses both as bulk materials and as grain boundary secondary phases in the nitride ceramics. Jack[1] was the first to report the existence of oxynitride glasses in the YSiAlON system. Additional information on the preparation and characterisation of glasses in this system has been given by Shillito *et al.*[2] and Loehman.[3,4] Subsequently, considerable investigations were carried out to determine the extent of vitreous regions in a wide range of M–Si–O–N and M–Si–Al–O–N systems[5-21] (M = either Ba, Ce, Ca, La, Li, Mg, Mn, Na, Nd or Y) including the effects of increasing nitrogen content on the properties of these glasses. The first systematic investigation of the effects of nitrogen on properties of alumino-silicate glasses was carried out by Drew *et al.*[11-13] who found that glass transition temperature, viscosity, microhardness and refractive index all increased as nitrogen was substituted for oxygen in the glass network. Another interest in oxynitride glasses is their ability to form glass-ceramics for potential thermomechanical applications. However, the mechanisms governing their transformation are still unknown. The products of glass crystallisation are also sensitive to nitrogen content and the results obtained by different authors vary.[22-26] The high temperature use of oxynitride glasses, in air, is limited by their oxidation resistance but relatively little data on their oxidation resistance are available in the literature[26-29] for a limited number of glass systems.

The present work is part of a European collaboration between four partners on the preparation and characterisation of a wide range of compositions of oxynitride glasses in various systems. This study has been undertaken to investigate the oxidation behaviour of some glasses in order to define their use under isothermal conditions and to explain the degradation mechanisms of sintered silicon nitride materials at high temperatures. In this paper some data on the influence of glass composition, heat treatment conditions and oxygen pressure on the oxidation resistance and the morphology of glasses are reported. In contrast to CaSiAlON and MnSiAlON systems studied[27–28] the exploitation of the results was facilitated by the fact that samples preserve their geometry under oxidation. A second paper is devoted to explaining the mechanisms governing the oxidation of oxynitride glasses in the YSiAlON system.

2 Materials and Procedure

2.1 Glass preparation

The Jänecke triangular prism representation is used to represent glass composition within these M-sialon systems with concentrations of components expressed in equivalents (as shown in Fig. 1). Constant oxygen:nitrogen ratios can be represented by vertical triangular planes within the prism parallel to the oxide and nitride faces. $4N^{3-}$ are replaced by $6O^{2-}$ on moving from left to right and the distance x represents the concentration of nitrogen and the distance y represents the concentration of oxygen, in equivalents, such that $x/(x + y) = (3[N])/(2[O] + 3[N])$ where [O] and [N] are, respectively, the atomic concentration of oxygen and nitrogen within any composition. For any plane, the O : N ratio is fixed and the concentrations of the cations are calculated in equivalents in the normal way for a 3-component system. The compositions used for this study are shown in Table 1.

Glasses were prepared using the melting procedure described by Hampshire *et al.*[16] from mixtures of 99.99% pure silicon nitride powder with high purity oxides (Al_2O_3, Nd_2O_3, SiO_2 and Y_2O_3). They were mixed in isopropanol, dried, and pressed into pellets. Large batches of 40–70 g were melted in a boron nitride lined graphite crucible under 100 kPa nitrogen at 1700°C for 1 h. The glass was poured into a pre-heated graphite mould and annealed at 850–900°C for 1 h and allowed to cool slowly.

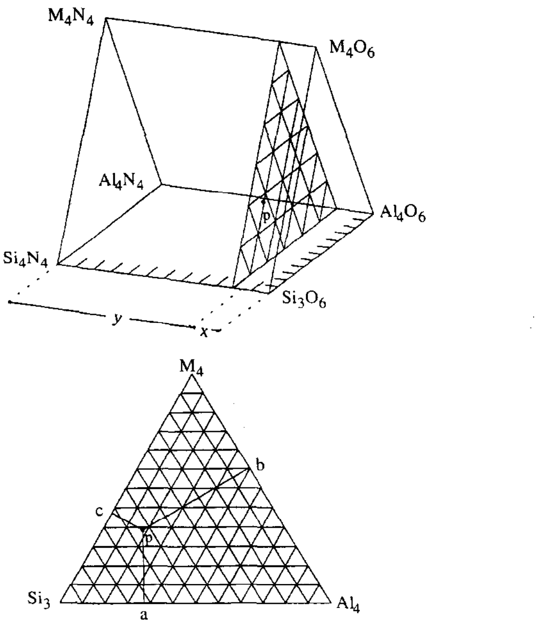

Fig. 1.. Jänecke prism representation of the M–Si–Al–O–N system.

2.2 Glass characterisation

Specimens were examined by optical microscopy (Olympus PMG3) and subjected to X-ray diffraction using a diffractometer (Philips PW1130) and a Guinier camera to confirm their amorphous nature, while chemical analysis of the nitrogen content was performed by a gas chromatographic analyser (Carlo Erba 1106). The oxidised samples were also characterised using X-ray diffraction, optical microscopy, SEM (Philips XL30) with integrated EDAX. Bulk glass densities were measured by an archimedean displacement using water as the immersion liquid, the accuracy of the measurement is ±0·05.

The nominal compositions in equivalent percent (e/o) cations/anions, glass densities and the values of nitrogen content found by analysis of the prepared glasses are detailed in Table 1.

Table 1. Glass compositions

	Composition (e.o)					*N (weight %)*		*Density*
Glasses	*Y*	*Si*	*Al*	*O*	*N*	*Cal.*	*Exp.*	
YSi17G4	40	56	4	83	17	3·377	3·32 ± 0·08	4·13
YSi17G8	36	56	8	83	17	3·502	3·415 ± 0·1	4·03
YSi17G12	32	56	12	83	17	3·638	3·59 ± 0·11	3·87
YSi1G16	28	56	16	83	17	3·775	3·43 ± 0·19	3·75
YSi10G16	28	56	16	90	10	2·22	2·19 ± 0·09	3·69
YY17G12	28	60	12	83	17	3·76	3·53 ± 0·10	3·71
YY17G20	28	52	20	83	17	3·78	3·59 ± 0·1	3·73
YY17G22	28	50	22	83	17	3·78	3·61 ± 0·12	3·74
Glass	*Nd*	*Si*	*Al*	*O*	*N*	*cal*	*exp*	*Density*
NdSi17G16	28	56	16	83	17	3·03	3·08 ± 0·05	4·56

2.3 Oxidation experiments

Cubic samples ($4 \times 4 \times 4$ mm^3) were cut from the pellets using a low-speed diamond saw and then carefully polished with diamond pastes and cleaned in an ultrasonic bath. The oxidation resistance of glasses in air and under controlled atmosphere was carried out using a thermobalance (Ugine Eyraud B60).

While the furnace was heated at a constant rate of 20°C min^{-1} to the oxidation temperature, the sample was kept in a cold zone then lowered quickly into the hot zone where it was kept only during the isothermal oxidation treatment.

3 Results

The oxidation reaction of oxynitride glasses, in the quinary systems, is very complicated due to the formation of a number of crystalline phases in the oxide layer. The nature and morphology of the oxidation products will be explained later. The crystalline phases are formed according to the following general reactions:

$$\mathrm{YSiAlON} + a\mathrm{O_2} \rightarrow b\mathrm{Y_2Si^2O^7} + c\mathrm{Y_2SiO_5} + d\mathrm{Al_2O_3} + e\mathrm{Al_6Si_2O_{13}} + \text{amorphous oxide} + \mathrm{N_2}\nearrow$$

From weight changes it is possible to determine the fractional weight gain according to the equation:

$$\alpha = {}^{\Delta W_t}/_{\Delta W_\infty}$$

where ΔW_t is the weight gain for a given time t and ΔW_∞ is the weight gain which corresponds to a complete oxidation of the oxynitride glass. In this case ΔW_∞ corresponds to the experimental values of nitrogen content seeing that we obtain a complete oxidation when all nitrogen is substituted by oxygen in the glass network.

3.1 Influence of the glass composition

The behaviour at high temperature of oxynitride glasses is closely linked to the total composition. The nature and the concentration of each element are important parameters which influence the structure of the glass network. Oxidation resistance varies from one system to another[27–29] but the role of the different elements in the oxidation resistance of these glasses remains unknown. Considering that the structure controls the viscosity, the physical properties and the degradation of oxynitride glasses, systematic investigations were carried out to study the influence of glass composition on their oxidation resistance and to explain the contribution of each constituent. The experiments were carried out using the following series of samples:

(a) constant ratio Y/Si/Al and varying O/N ratio in order to evaluate the influence of nitrogen content;

(b) constant ratio M/Si/Al/O/N and varying the type of metallic cation;

(c) constant ratio Y/O/N and varying Si/Al to explain the role of silicon and aluminium in the network;

(d) constant ratio Si/O/N and varying Y/Al to explain the role of yttrium and aluminium as network modifiers.

The oxidised samples at 1075°C preserve their geometry. After oxidation of glasses we have seen no changes in the morphology of samples or the plasticity of the substrates.

The oxidation behaviour of oxynitride glasses is strongly dependent on the glass composition as shown in Fig. 2. The incorporation of nitrogen increases the oxidation resistance (Fig. 2(a)). As it will be shown later the oxidation starts above the glass transition temperature. When oxygen is replaced by nitrogen in silicon co-ordination tetrahedra, the increase of the degree of reticulation and the individual negative charge leads to an increase in the coulombic forces between these tetrahedra and the cations, thus enabling a higher refractoriness and compactness of the network.

The same effect is observed on the substitution of neodymium by yttrium (Fig. 2(b)). This could imply that the size of the cation alone is responsible for the behaviour changes at high temperatures; it can be explained by the fact that the strength of the bond between the metallic ion and the surrounding oxygen ions in the glass structure (M–O) where (M = Nd, Y) increases with increasing field strength of the metallic ion. It is known that the field strength varies with the reciprocal of the ionic radius which means that the Y–O bonds are stronger than Nd–O ones. As the M–O bonds are weaker than the Al–O and Si–O bonds, a more compact glass network is obtained with the stronger M–O bonds. The same results were observed by Shelby *et al.*[31] on the properties of oxide alumino-silicate glasses and by Persson *et al.*[30] while oxidising silicon nitride with $\mathrm{Y_2O_3}$ and $\mathrm{Nd_2O_3}$ additives.

Results for glasses that are oxidised at 1075°C for 20 h are shown in Figs 2(c) and (d). The role played by aluminium in the glass structure depends strongly on its concentration. For the low concentrations, aluminium is expected to exist in fourfold coordination with oxygen where the presence of ($\mathrm{AlO_4}$) tetrahedra confers to aluminium the role of network former. As the aluminium content increases, it seems that the glass structure becomes more disordered[32–34] which could explain the decrease of the oxidation resistance. A negative effect of aluminium on the oxidation resistance of silicon nitride is also revealed by Gogotsi *et al.*[35]

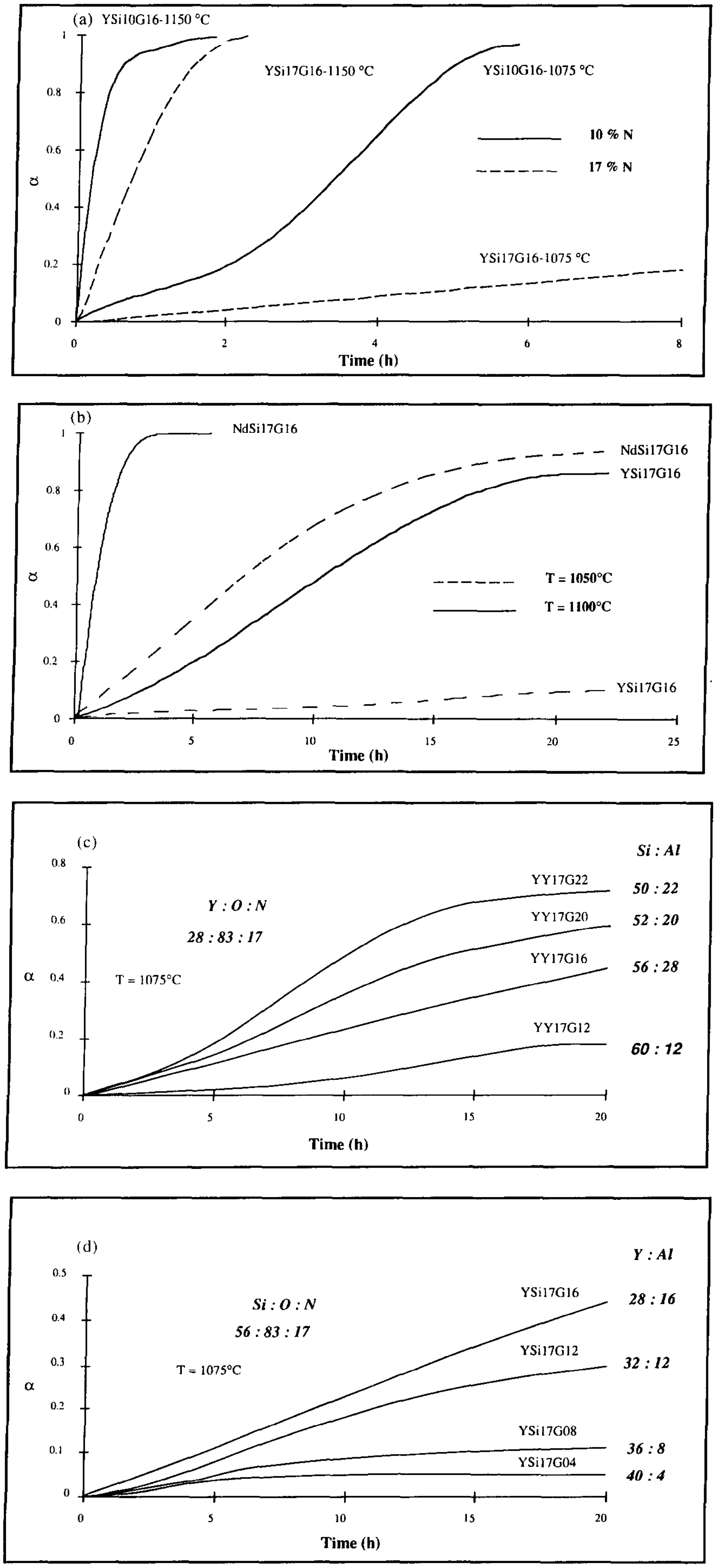

Fig. 2. Oxidation kinetics in air of oxynitride glasses: (a) with a constant ratio Y/Si/Al = 28/56/16 and various nitrogen contents; (b) with a constant ratio Si/Al/O/N=56/16/83/17 and changing rare earth element; (c) with a constant ratio Y/O/N=28/83/17 and varying Si/Al; (d) with a constant ratio Si/O/N=56/83/17 and varying Y/Al.

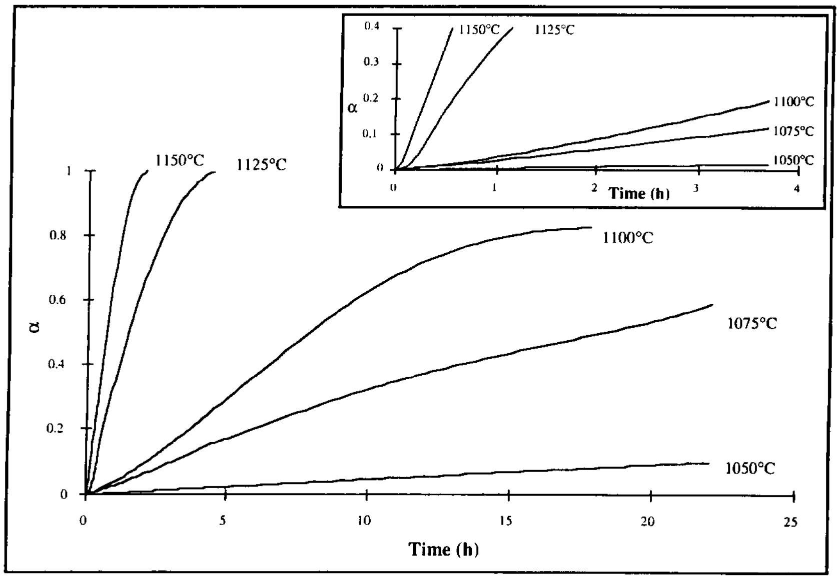

Fig. 3. Oxidation kinetics in air of YSi17G16 oxynitride glasses.

If we compare the oxidation curves of YSi17G12 and YY17G12 specimens which are characterised by a constant ratio Al/O/N and a varying Y/Si ratio, we observe that the oxidation resistance of the glasses decreases when yttrium replaces silicon. This is due to the fact that the substitution of silicon (network forming) by yttrium (network modifying) tends to make the glass structure more random. The other explanation is that, for glasses with a constant ratio Al/O/N, the increase of Y/Si ratio is followed by a slight increase in the concentration of aluminium in five-fold coordination.[33] Thus, oxynitride glasses containing more nitrogen and silicon and less aluminium are characterised by higher oxidation resistance.

3.2 Influence of the oxidation temperature

Oxidation of oxynitride glasses was investigated in air between 1000 and 1150°C for YSi17G16.

(a) Oxidation kinetics

The reactivity of YSiAlON glasses with oxygen starts around 1000°C with a weak weight gain (Fig. 3). For higher temperatures, the oxidation rate increases significantly and the oxidation is almost complete in a few hours at 1150°C. The oxidation curves of the studied glasses exhibit a sigmoïdal shape and the latent period of the reaction decreases with the increase of the oxidation temperature. For each isotherm, the oxidation rate has a maximum and the time of appearance of this maximum changes with the temperature. No initial weight loss was observed in the lower temperature range, which is not in agreement with results reported by Desmaison-Brut *et al.*[27–28] for the CaSiAlON and MnSiAlON systems.

(b) Nature and morphology of the reaction products

In order to explain the mechanisms governing the oxidation of oxynitride glasses, we have studied the nature and the morphology of the reaction products.

The oxide scale changes continuously with oxidation conditions (temperature and time). The reaction of the glasses with oxygen leads to the release of nitrogen and the formation of voids at the internal interface, which is followed by the growth of a white oxide layer.

At low temperatures, samples are covered by a thick oxide layer which increases with the oxidation time and temperature (Figs 4 and 5). The oxide layer thicknesses, measured from the micrographs (Figs 5(a), (b) and (c)) are 15, 360 and 760 μm for samples oxidised for 22 h respectively at 1000, 1050 and 1075°C. The increase of temperature favours the formation of nitrogen bubbles and the creation of porosity in the oxide scale and at the internal interface, as seen in Figs 5 (b) and (c). The presence of the bubbles leads to the formation of an irregular interface and favours the access of oxygen. The continuous changes in the morphology of oxidised samples is accompanied by the formation of a number of crystalline phases in the oxide layer. For the first oxidation temperatures, a crystalline phase transformation is observed as a function of time or temperature (Table 2). This successive change in the nature of the oxidation products indicates the non-recovering character of the formed oxide layer. The difference in mechanical properties between the oxide layer and the substrate favours the relaxation of stresses at the internal interface which leads to cracking at the edges of the samples to induce a maltese cross symmetry (Fig. 4(b)).

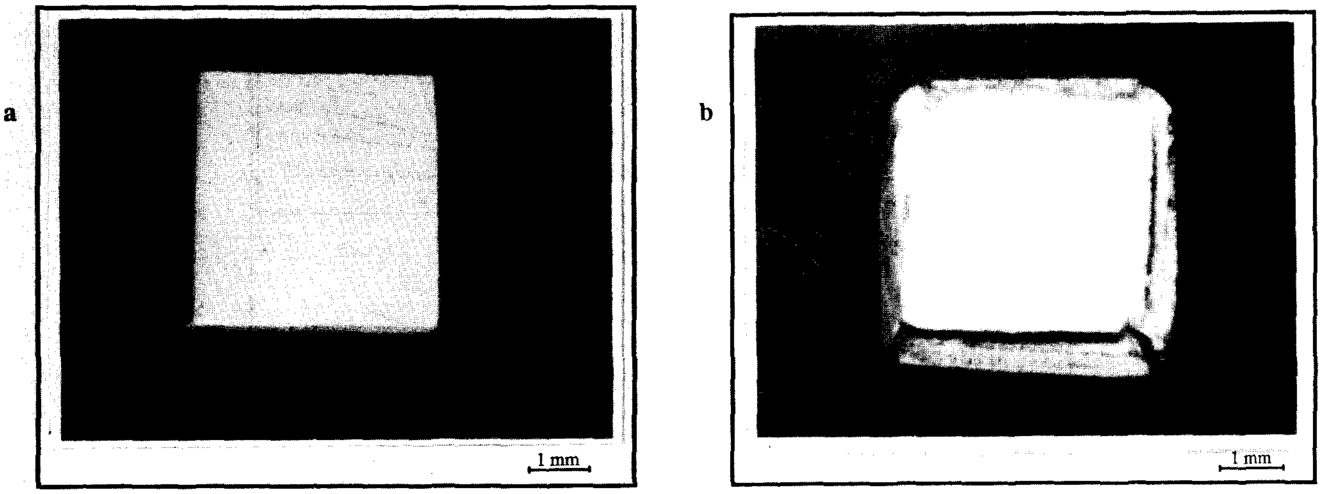

Fig. 4. Optical micrographs of oxidised glasses: (a) YSi17G16 at 1000°C (22 h); (b) YSi17G16 at 1075°C (22 h).

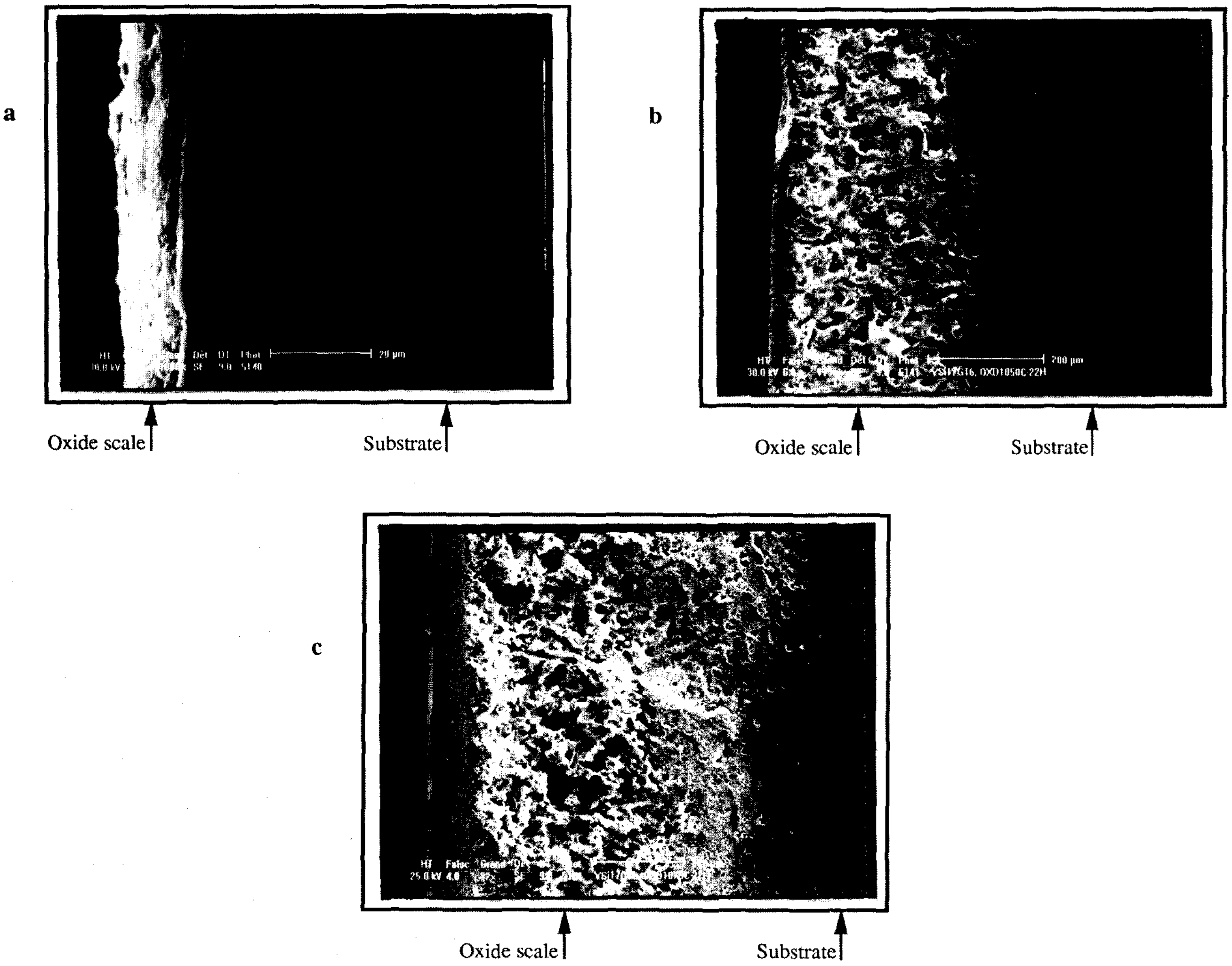

Fig. 5. Cross-section SEM photomicrographs of oxidised glasses: (a) YSi17G16 at 1000°C (22 h); (b) YSi17G16 at 1050°C (22 h); (c) YSi17G16 at 1075°C (22 h).

At high temperatures, oxidation occurs very quickly with the formation of very large bubbles and extensive porosity in the oxide layer and the substrate. The presence of this porosity in the oxide layer increases the volume of oxide scales (Fig. 6) and facilitates the rapid access of oxygen to the centre of samples.

The crystalline phases present in the oxide scales, detected by X-ray diffraction, are given in Table 2.

At 1000°C and for 22 h of heat treatment, the oxide layer contains $\alpha Y_2Si_2O_7$ and a small amount of yttriallite ($yY_2Si_2O_7$) and corundum. With the increase of oxidation time a gradual substitution of $\alpha Y_2Si_2O_7$ by yttriallite occurs. After 100 h of

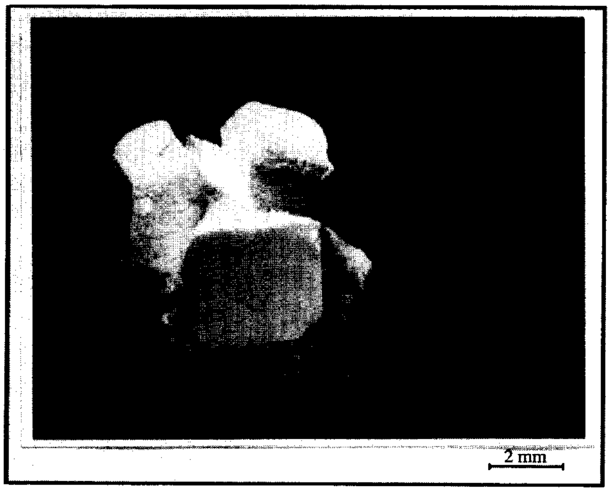

Fig. 6. Optical micrographs of YSi17G16 oxidised at 1150°C (18 h).

heat treatment the oxide layer is formed by yttriallite as the main oxide, with the presence of small quantities of mullite, corundum, cristoballite and $\alpha Y_2Si_2O_7$. The simultaneous presence of α and $yY_2Si_2O_7$ is in agreement with the crystallisation results of Hampshire *et al.*[16] and Dinger *et al.*[25] where they observe the presence of yttrium dissilicates for glasses heat treated with the same conditions. For the higher oxidation temperatures, X-ray diffraction data of oxidised samples, reveal no change in the nature of crystalline phases present in the oxide layer and confirm the absence of any transformation in the oxide layer.

A small amount of crystallisation of the substrates is detected above 1050°C ($yY_2Si_2O_7$).

(c) Kinetics modelling

For cubic samples the oxidation reaction rate is calculated up to the edge *a* of the cube using the following equations:

$-da/dt = 2k$

where, $a = a_0 - 2kt$

and a_0 is the initial cube edge, k is the rate constant which corresponds to the growth of the oxide layer along the time (mm.s^{-1}) and t the time.

α can be expressed by: $\alpha = 1 - a^3/a_0^3$)

$a = a_0 - (1 - \alpha)^{1/3}$

and we obtain the following kinetics equation:

$$F(\alpha) = 1-(1-\alpha)^{1/3} = 2kt/a_0 \qquad (1)$$

The sigmoïdal shape of the oxidation curves, the texture and the morphology of the porous oxide scale which show a direct access of oxygen to the internal interface and the growth of the maltese cross symmetry imply that the oxidation of YSi17G16 is governed by a reaction process where the progress of the internal interface is the limiting step. This assumption is confirmed by the determination of $F(\alpha).a_0/2t$ which increases from the beginning of the reaction to become constant after a few minutes or by the linearity of the transformations as a function of time as shown in Fig. 7. The

Table 2. Crystalline phases in the oxide layer after a heat treatment in air at various temperatures

Temperature	*Time (h)*	*Crystalline phases*
1000°C	22	$\alpha Y_2Si_2O_7$, $yY_2Si_2O_7$, Al_2O_3
1000°C	100	$yY_2Si_2O_7$, $\alpha Y_2Si_2O_7$, $Al_6Si_2O_{13}$, Al_2O_3, SiO_2
1050°C	22	$yY_2Si_2O_7$, $Al_6Si_2O_{13}$, Al_2O_3, SiO_2
1075°C	22	$yY_2Si_2O_7$, $Al_6Si_2O_{13}$, SiO_2
1100°C	22	$yY_2Si_2O_7$, $Al_6Si_2O_{13}$, SiO_2
1125°C	5	$yY_2Si_2O_7$, $Al_6Si_2O_{13}$, SiO_2
1150°C	18	$yY_2Si_2O_7$, $Al_6Si_2O_{13}$, SiO_2

$Al_6Si_2O_{13}$ (mullite); SiO_2 (α-cristoballite); Al_2O_3 (corundum).

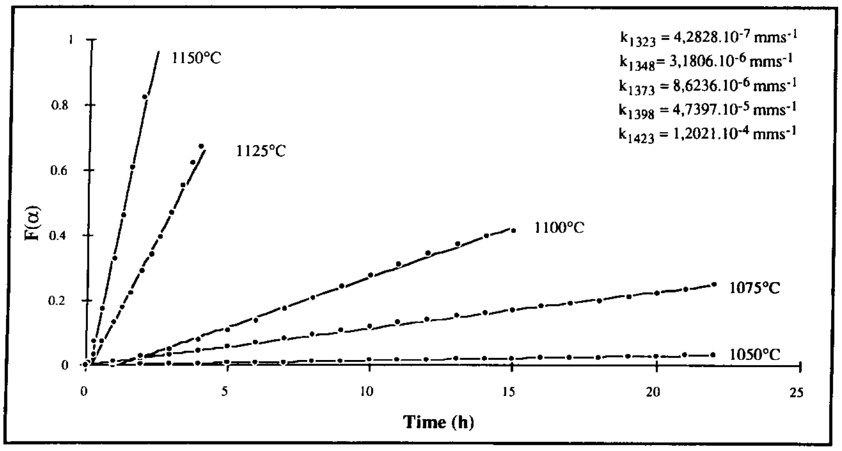

Fig. 7. Transformation as a function of time (YSi17G16).

apparent activation energy calculated from the slope of the transformation curves is E = 848 ± 50 kJ/mol.

3.3 Influence of the oxygen pressure

The influence of oxygen pressure on the oxidation resistance of oxynitride glasses was studied at 1075°C on YSi17G16 at oxygen pressures in the range 15–100 kPa with nitrogen added up to atmospheric pressure. Two experiments were carried out:

(1) Samples were oxidised for 8 h at different oxygen pressures since α_0= 0 (Fig. 8(a)).

(2) Samples were first oxidised in air for 4·5 h corresponding to α_0= 0·153, after which they were put in the cold zone while the furnace was evacuated and lowered again into the hot zone when the mixture of oxygen and nitrogen had been introduced (Fig. 8(b)).

The kinetics of oxidation of YSi17G16 are affected by the oxygen pressure. The transformation as a function of time calculated using expression (1) are linear in the studied interval which permits the determination of a pressure law as:

$$k = k_0 P^n$$

where k is the oxidation rate constant (mm.s^{-1}), k_0 a constant, P is oxygen pressure and n is a coefficient determined from the slope of the curve log$_{10}$k as a function of log$_{10}$P (Fig. 9). For the experiments in this study n = 0·5 ± 0·05 which is in agreement with the presence of a porous oxide layer which facilitates the access of oxygen to the internal interface.

4 Discussion

The influence of the glass composition, oxidation conditions and oxygen pressure on the oxidation resistance of oxynitride glasses have been studied. The wide range of glass compositions investigated permits us to explain the role played by each constituent on the oxidation behaviour of oxynitride glasses. As for the glass transition temperature (T_g) the incorporation of nitrogen increases the oxidation resistance of glasses. The aluminium concentration has a direct influence on the oxidation of these glasses which is due to the influence of aluminium on viscosity which decreases as aluminium content increases[36] and this results in a higher reactivity of the glass network. A high concentration of silicon is necessary to improve the oxidation resistance of oxynitride glasses, as seen

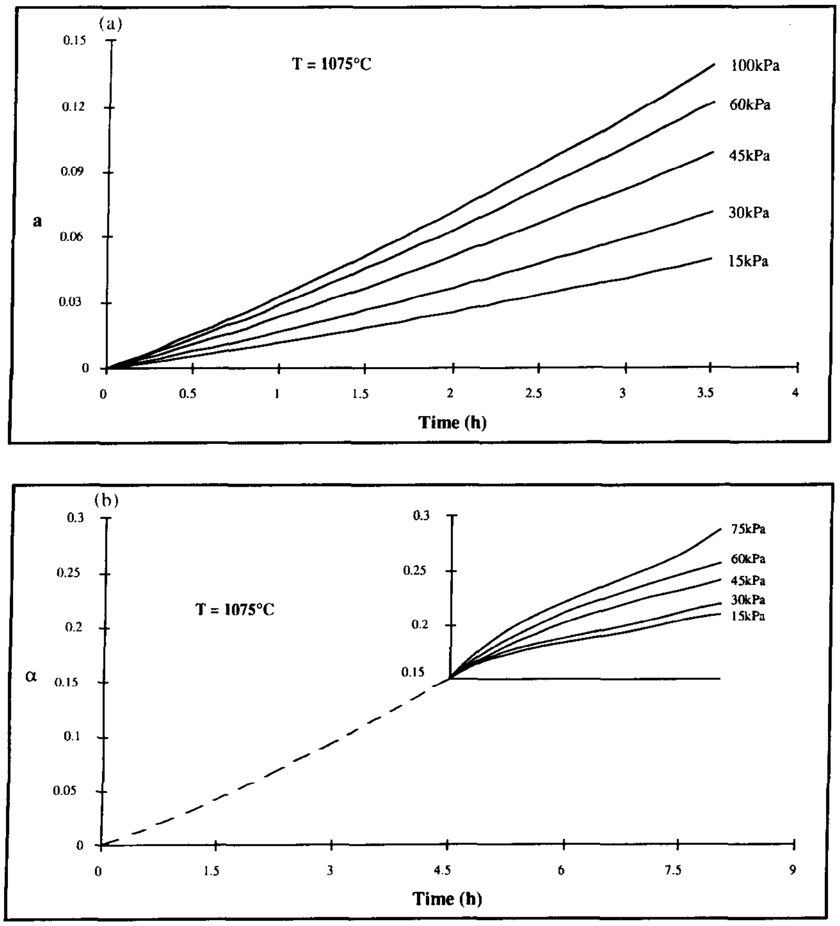

Fig. 8. Oxidation curves of YSi17G16 at different oxygen pressures: (a) T = 1075°C (α_0 = 0); (b) T = 1075°C (α_0 = 0·153)

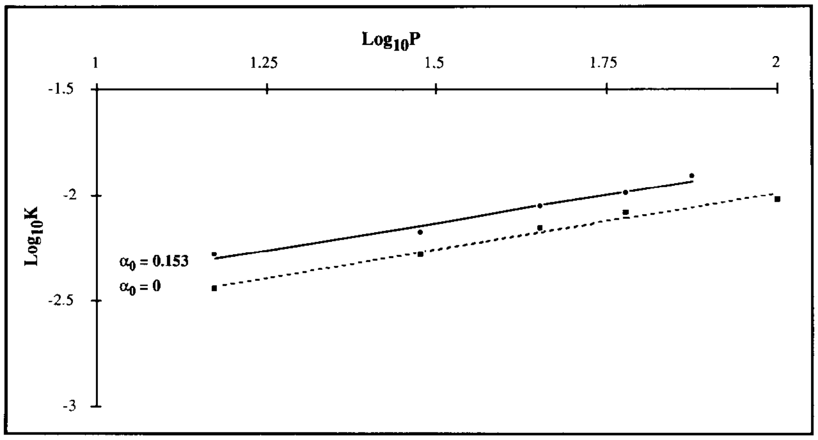

Fig. 9. $Log_{10}k$ as a function of $log_{10}P$.

also for the physical properties of yttrium alumino-silicate glasses.[37]

Temperature has a strong influence on the oxidation behaviour of the studied oxynitride glasses. At low temperatures (T < 1075°C), the oxidation is low and the samples preserve their cubic geometry. For higher temperatures, an extensive oxidation is produced, even during the initial stages of heat treatment, which favours the formation of a very porous and expanded product.

Study of thc influence of pressure has confirmed the direct access of oxygen to the internal interface of samples.

The sigmoïdal shape of the oxidation curves of the all studied glasses suggests that oxidation is governed by a similar mechanism which is a reaction-controlled process as found for YSi17G16. The increase of temperature or time of oxidation leads to the formation of disorder in the glass structure. This disorder is followed by an increase in the average number of non-bridging oxygens per polyhedron which decreases the glass viscosity. Considering that at a fixed temperature above the glass transition temperature, the glass viscosity decreases with time, a little enhancement of the mobility of the glass constituents can be observed. The mobility of the glass constituents results in glass crystallisation under inert atmospheres and favours oxidation in the presence of oxygen. This hypothesis correlated with the formation of a non-covered oxide layer and the continuous changes in the oxidation products can be used as a basis to explain the presence of a reaction controlled process for global oxidation.

These investigations provide a guide for understanding the effects of the nature and concentrations of sintering additives in silicon nitrides on their oxidation behaviour. Yttria is preferred to neodymia and the Al_2O_3 concentration must be lower than that of Y_2O_3. The sintering of silicon nitride with a low concentration of additives allows an increase in its oxidation resistance.

5 Conclusions

The oxidation behaviour in air of oxynitride glasses is strongly dependent on the composition. The oxidation resistance increases when nitrogen content increases, when aluminium is substituted by yttrium or silicon and when yttrium replaces neodymium.

The oxynitride glasses oxidised rapidly in air at temperatures above the glass transition temperature by forming a porous oxide scale, probably due to the evolution of gaseous nitrogen during the oxidation. X-ray investigations of the oxide scale reveal the presence of different forms of yttrium silicates and mullite.

The sigmoïdal shape of the oxidation curves, the porous oxide scale which grows with the maltese cross symmetry and the linearity of the transformations as a function of time indicate the presence of a reaction process where the progress of the internal interface is the limiting step. The oxidation of oxynitride glasses is very sensitive to the oxygen partial pressure.

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