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Oxidation Resistance of Nd-Si-Al-O-N Glasses and Glass-Ceramics

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Abstract

Glasses containing up to 20% (e.o.) nitrogen were prepared in Nd-Si-Al-O-N system. Compositions, which crystallise in single and multiphase materials, were heat-treated under various conditions, and oxynitride glasses were found to be self-nucleating. The crystalline phases formed depend on both the composition of the parent glass and the heat-treatment conditions. X-ray investigations show that U-phase ($Nd_3Si_3Al_3O_{12}N_2$) is stable at 1150°C for many crystallisation durations. The microstructural changes were studied by scanning electron microscopy (SEM) and image analysis. The reactivities in air of different glasses and glass-ceramics were compared in the temperature range of 975–1250°C. Sialon glasses oxidised rapidly in air at a temperature above the glass transition temperature by forming a porous oxide scale, due to the evolution of gaseous species at the internal interface. The nature and morphology of oxidised samples were characterised by optical microscopy, X-ray diffraction (XRD), and SEM. The nature and the concentration of the crystalline phases present in the glass-ceramics were found to control the oxidation behaviour of the resulting materials. © 1997 Elsevier Science Limited.

Résumé

Des verres oxyazotés contenant jusqu'à 20% (e.o.) d'azote ont été préparés dans le système Nd-Si-Al-O-N. Des compositions qui cristallisent en formant une seule phase ou plusieurs phases, ont été traitées sous différentes conditions. Les verres oxyazotés sont autonucléants. La séquence de formation des phases cristallines dépend simultanément de la composition et du traitement thermique. Les résultats de la diffraction des rayon X montrent que la phase U ($Nd_3Si_3Al_3O_{12}N_2$) est stable à 1150°C pour différentes durées de traitement. Les changements de la microstructure ont été suivis par microscopie electronique à balayage (MEB) et par analyse d'images. L'oxydation sous air de verres et de vitrocéramiques est étudiée pour des températures comprises entre 975 et 1250°C. Les verres oxyazotés s'oxydent rapidement au dessus de la température de transition vitreuse en formant une couche d'oxydes poreuse, due au départ de gaz à l'interface interne. L'étude des vitrocéramiques a montré que la nature et la teneur de phases cristallines dans le matériau conditionnent leur comportement à l'oxydation. La nature et la morphologie des échantillons oxydés ont été caractérisés par la diffraction des rayons X et par MEB.

1 Introduction

Studies on oxynitride glasses are of special interest due to their presence at grain boundaries in silicon nitride ceramics sintered with oxide additives such as Al_2O_3, Nd_2O_3, MgO and Y_2O_3. Glasses in Mg-Si-Al-O-N and Y-Si-Al-O-N systems were first reported by Jack,[1] then 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[2–18] (M = Ba, Ce, Ca, La, Li, Mg, Mn, Na, Nd or Y) including the effects of increasing nitrogen content. One of the first systematic studies of the physical properties of M-Si-Al-O-N glasses as a function of nitrogen content was published by Hampshire *et al.*[9,10] They found that glass transition temperature, viscosity, microhardness and refractive index increase with nitrogen content. These findings are in agreement with other studies.[2–13]

Oxynitride glasses could be converted into glass-ceramics with good mechanical properties but

Table 1. Glass compositions and characteristics

Glasses	Composition (e/o)					N (weight %)		Properties	
	Nd	Si	Al	O	N	cal	exp	Density	Tg (°C)
NdSi00G16	28	56	16	100	00	0	—	4·32	845
NdSi10G16	28	56	16	90	10	1·79	1·83 ± 0·08	4·44	885
NdSi17G16	28	56	16	83	17	3·03	3·08 ± 0·05	4·56	905
NdSi20G16	28	56	16	80	20	3·54	3·431 ± 0·15	4·58	920
NdSi20G30	30	40	30	80	20	3·34	3·226 ± 0·15	4·98	910

crystallisation exhibits a quite complex behaviour and the nucleation mechanisms are not clearly understood. Many crystalline phases are reported in the literature,[19–22] and their nature and concentration will determine the properties of glass-ceramics and in particular their oxidation resistance. For optimum performance, it is therefore important to identify glass compositions which can be crystallised into a single-phase product.[23] An appropriate heat treatment is then required, to prepare oxynitride glass-ceramics with particular characteristics. Ramesh *et al.* and Morrisey *et al.* [24,25] have shown that further improvements in properties are possible if glass-ceramic processes using two-stage heat treatments are introduced. In this case, more control can be exercised over the microstructure of the final product.

The glass-forming region in the Nd-Si-Al-O-N system is similar but larger than in the Y-Si-Al-O-N system, but few investigations have been carried out describing the preparation and properties[6–9] of oxynitride glasses in the Nd-Si-Al-O-N system. Glass crystallisation has not been extensively reported[24–26] in comparison with glasses in other systems. In addition to the aluminates $NdAlO_3$ and $NdAl_{11}O_{18}$ and the silicates, Nd_2SiO_5, $Nd_4Si_3O_{12}$ and $Nd_2Si_2O_7$, two 5-component phases exist, namely: U-phase, $Nd_3Si_3Al_3O_{12}N_2$ and W-phase, $NdSi_2Al O_{6.65}N_{0.23}$.

Above the glass transition temperature, oxynitride glasses are in a non-equilibrium state, and in an oxidising environment oxidation and crystallisation take place in the same temperature range.[27] The aim of this paper is to investigate the nature and the thermal stability of crystalline phases formed during the heat treatment of neodymium glasses in order to determine the effect of microstructural changes on the oxidation kinetics of glasses and glass-ceramics.

2 Materials and Experimental

2.1 Glass preparation and characterisation

Glasses have been prepared[28] from mixtures of 99·99% pure silicon nitride powder with high purity oxides (Al_2O_3, Nd_2O_3 and SiO_2). These were mixed together 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. The nominal compositions in equivalent percent (e/o) cations/anions and the values of nitrogen content were determined using a gas chromatographic analyser (Carlo Erba 1106) and are detailed in Table 1. The experimental nitrogen content values are consistent with the calculated ones, which indicates that the loss of nitrogen during melting was small.

Oxynitride glasses in the Nd-Si-Al-O-N system are dark and violet in colour. Thin slices 0·5 mm thick were cut from glass billets and polished for optical and scanning electron microscopy observations. Optical micrographs of polished specimens were taken using a Video Micro Scalar (VMS 300) with a high resolution and a high accuracy video reading system. These studies revealed that glasses contain some metallic-looking spherical inclusions.[29–31] EDAX analysis showed that these particles consist mainly of iron, nickel and silicon.

Oxynitride glass densities were determined by the Archimedes technique using water as the immersion liquid. Measurements were made at 22 ± 1°C using a density of 0·998 for water. The glass transition temperature was obtained from dilatometric curves using bars ($4 \times 4 \times 10\,mm^3$) heated in a SETARAM TMA 92 dilatometer under argon at atmospheric pressure (Table 1). As shown by previous authors, the density and glass transition temperature of oxynitride glasses increase with nitrogen content.[5,8,11,12] The substitution of oxygen by nitrogen in silicon co-ordinated tetrahedra increases the degree of reticulation and individual negative charges, leading to an increase in the coulombic forces between tetrahedra and cations, thus enabling a higher compactness of the network to be observed.

2.1.1 Crystallisation experiments

Specimens (bars of $4 \times 4 \times 6\,mm^3$) were placed in a silicon nitride bed in alumina boats and heat-treated in a vertical tube furnace under a flow of pure

Table 2. Influence of nitrogen content on the nature of crystalline phases

Glass	*O/N*	*1000°C—36 h*	*1150°C—5 h*	*1150°C—36 h*
NdSi00G16	100/0	A-$Nd_2Si_2O_7{}^s$ G-$Nd_2Si_2O_7{}^m$	A-$Nd_2Si_2O_7{}^s$ G-$Nd_2Si_2O_7{}^m$ $NdAlO_3{}^w$	A-$Nd_2Si_2O_7{}^s$ G-$Nd_2Si_2O_7{}^m$ $NdAlO_3{}^w$
		$Nd_4Si_3O_{12}{}^m$	$Nd_4Si_3O_{12}{}^s$	$Nd_4Si_3O_{12}{}^s$
NdSi10G16	90/10	A-$Nd_2Si_2O_7{}^w$	Phase W^w $Nd_2Si_2O_7{}^w$	Phase W^m A-$Nd_2Si_2O_7{}^w$
NdSi17G16	83/17	$Nd_4Si_3O_{12}{}^m$ A-$Nd_2Si_2O_7{}^{vw}$	$Nd_4Si_3O_{12}{}^s$ Phase W^w A-$Nd_2Si_2O_7{}^w$	Phase W^s $Nd_4Si_3O_{12}{}^s$ A-$Nd_2Si_2O_7{}^w$

vw: very weak, w: weak, m: medium, s: strong. Phase W: $NdSi_2AlO_{6.65}N_{0.23}$. A-$Nd_2Si_2O_7$: JCPDS 22-1177 neodymium disilicate. G-$Nd_2Si_2O_7$: JCPDS 38-1456 neodymium pyrosilicate.

nitrogen (N50) at atmospheric pressure. Glasses were weighed before and after heat treatment to check for weight changes and were analysed by X-ray diffraction, using a diffractometer (Philips PW1130) and a Guinier camera. Phase identification was facilitated by the use of a computer search/match program.

2.1.2 *Oxidation experiments*

Cubic samples ($4 \times 4 \times 4\,mm^3$) were cut from pellets using a low-speed diamond saw and then carefully polished with diamond pastes and cleaned in an ultrasonic bath. The oxidation resistance, in air, was measured 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 oxidised only during the isothermal treatment. Specimens were examined by optical microscopy (Olympus PMG3) and scanning electron microscopy (SEM) (Philips XL30) with integrated EDAX.

3 Results and Discussion

3.1 Crystallisation of glasses

Glasses were heat-treated to promote crystallisation under various conditions in order to study the influence of composition and crystallisation conditions on the formation of different crystalline phases.

3.1.1 *Single-phase glass-ceramics*

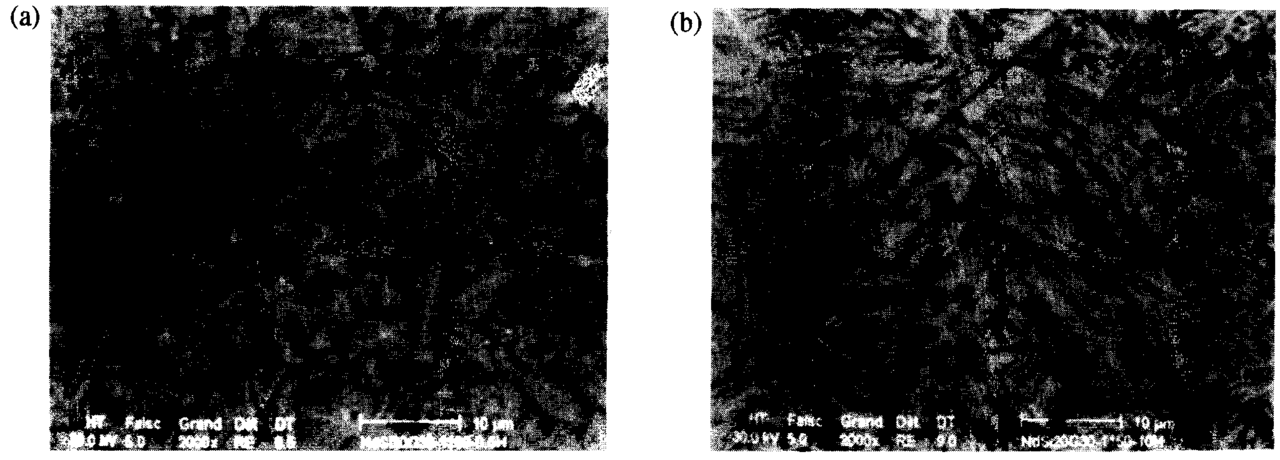
U-phase was originally observed as a minor phase in low temperature (1050°C) heat treatments of Y-Si-Al-O-N glasses.[32] It occurs in M-Si-Al-O-N systems (M = La, Nd, Ce) at compositions of the type of $M_3Si_{3-x}Al_{3+x}O_{12+x}N_{2-x}$ $(0 < x \leq 0{\cdot}5)$. Glasses of the above composition can be prepared if the glass melting temperature is not too high (1650–1700°C).

The appropriate composition NdSi20G30 for neodymium U-phase was heat-treated at 1150°C for various crystallisation durations (0·5–36 h) to check for the influence of heat-treatment time on stability. The X-ray diffraction patterns revealed that the obtained glass-ceramics exhibited spectra corresponding to U-phase ($Nd_3Si_3Al_3O_{12}N_2$) in the JCPDS files (42-1485) and traces of wollastonite.

Typical microstructures of U-phase glass-ceramics are presented in Fig. 1. These consist of thick crystals which grow in size with heat-treatment time. After 30 min of heat-treatment, the glass-ceramic appears in the form of dendritic crystals. At the beginning these crystals are delimited by a thin film of vitreous phase. Increasing heat-treatment duration results in a decrease in vitreous film concentration and further crystal growth is accompanied by a gradual appearance of some porosity. It has been shown by some authors that U-phase materials free of residual glass can be prepared at temperatures above 1250°C[23,26] using a one heat-treatment stage. The influence of a two-stage treatment on NdSi20G30 was studied by Ramesh *et al.*[24] at temperatures corresponding to optimum nucleation and crystal growth. They reported the formation of U-phase with trace amounts of wollastonite and an aluminium-rich residual glassy phase. The microstructural features of single-stage heat-treated samples are different to that obtained with two stages. This shows that apart from the stability of the crystalline phases, the morphology of the crystalline phases also depends largely on the heat-treatment schedules. In the present study, the glass was crystallised at 1150°C for various durations in order to avoid the formation of porosity.

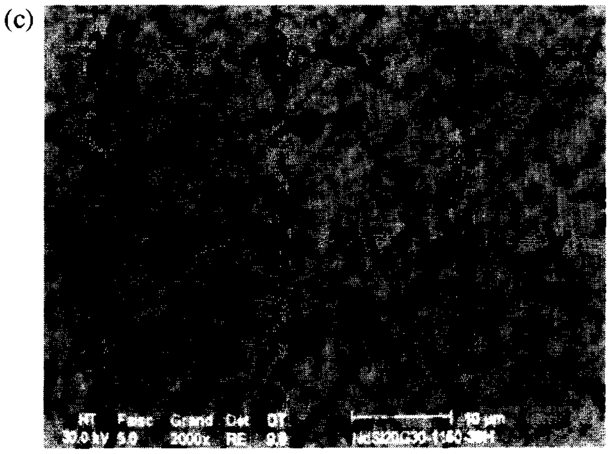
3.1.2 *Multiphase glass-ceramics*

3.1.2.1 Influence of nitrogen content. Glasses, with varying nitrogen contents and a constant ratio of cations, were crystallised at 1000°C for 36 h and at 1150°C for 5 and 36 h. The X-ray diffraction results in Table 2 show that the oxide glass crystallises



1150°C- 0.5 hour 20 µm

1150°C- 10 hours 20 µm



1150°C- 36 hours 20 µm

Fig. 1. Microstructure of U-Phase glass-ceramics crystallised at 1150°C for (a) 30 min, (b) 10 h, (c) 36 h.

rapidly, forming neodymium silicates $Nd_2Si_2O_7$ and $NdAlO_3$, the latter at higher temperatures. The incorporation of nitrogen leads to a change in the nature of the silicate phases; at 1000°C, a substitution of $Nd_2Si_2O_7$ by $Nd_4Si_3O_{12}$ is observed. This change of phases was previously observed in Li-Si-O-N glasses by Unuma *et al.*[15] and Y-Si-Al-O-N glasses by Sebaï.[27] Increasing temperature favours the formation of W-phase ($NdSi_2AlO_{6.65}N_{0.23}$). For high nitrogen glasses, the increase of the degree of crystallisation facilitates the formation of W-phase as the main crystalline compound in these glass-ceramics.

The effect of nitrogen content on crystal growth was determined in glass-ceramics prepared at 1150°C for 5 h using optical and scanning electron microscopy. The microstructure consisted of needle-like crystallites growing into the bulk of the samples as seen in Fig. 2. Oxide glass crystallises into thick crystals A- and G-types of neodymium silicates ($Nd_2Si_2O_7$) [Fig. 2(a) and (b)]. The addition of nitrogen results in a quite different crystal morphology than that observed for the oxide glass. This morphology is characterised by the substitution of $Nd_2Si_2O_7$ by apatite ($Nd_4Si_3O_{12}$) as the main crystalline phase, which is followed by a decrease in crystal thickness [Fig. 2(c) and (d)]. The decrease in the volume fraction of crystalline phases with increasing nitrogen content can be related to the viscosity of the glass. At a given temperature low mobility of atoms is observed in glasses with high Tg; reduction in the mobility of atoms inhibits the precipitation of crystalline phases and shows that increasing nitrogen content leads to a decrease in the crystallisation rate.

3.1.2.2 Influence of crystallisation conditions As shown in Table 2, several crystalline phases form in multiphase glass-ceramics. It is therefore important to follow the kinetics of formation of these phases under various conditions in order to optimise the final glass-ceramic compositions. A systematic study was carried out on NdSil7G16 glass, the content of each phase being calculated by the following equation:

$$R = I / \sum I_i \qquad (1)$$

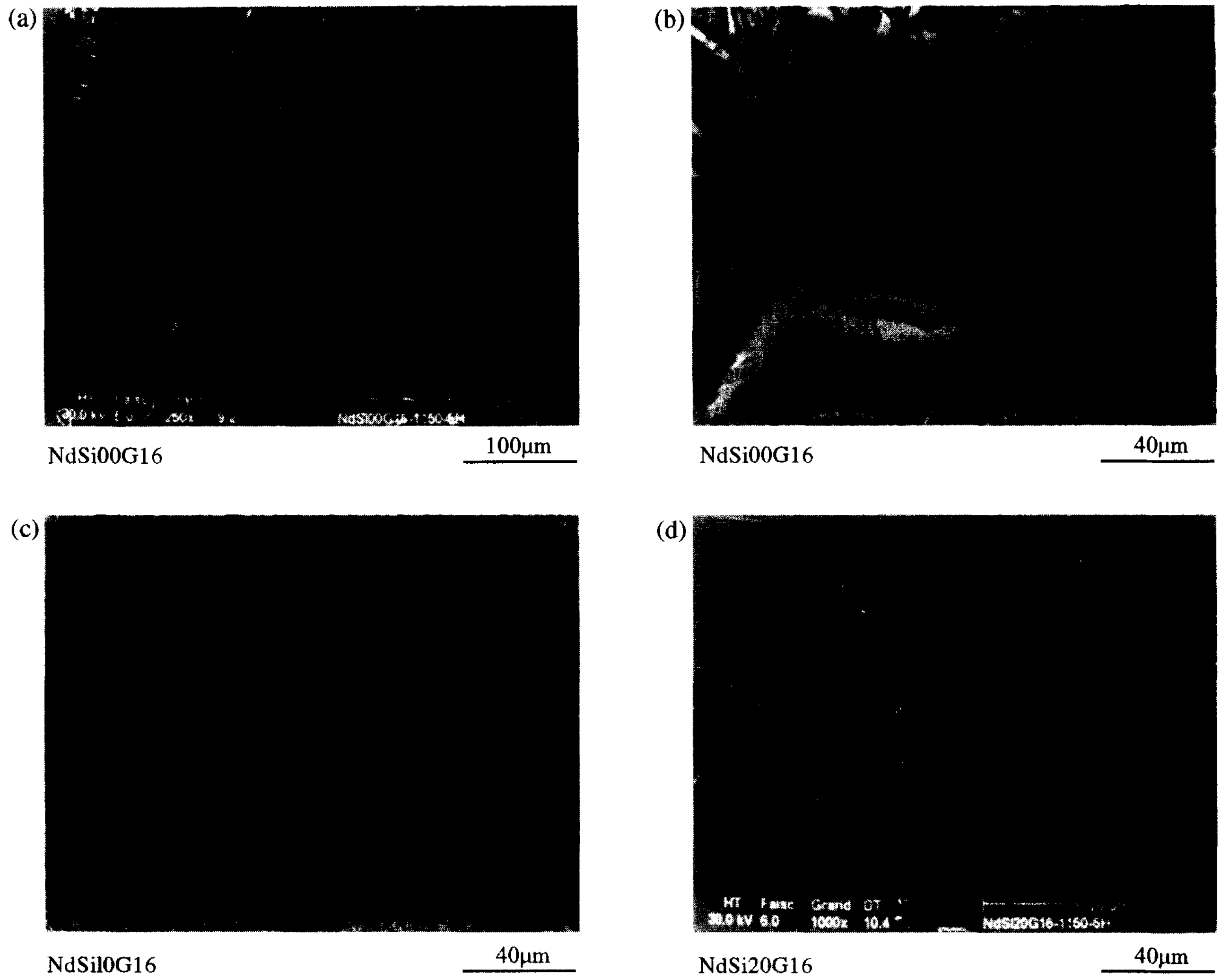


Fig. 2. Effect of nitrogen on the microstructure of multiphase glass-ceramics (a,b) 0%N, (c)10%N and (d) 20%N.

I: the intensity of the strongest X-ray diffraction peak of a given phase; $\sum I_i$ the sum of the strongest peaks of all crystalline phases present after crystallisation.

3.1.2.3 Effect of crystallisation temperature - NdSil7G16 glasses were heat-treated at 1000, 1050, 1100, 1150, 1200 and 1250°C, and the evolution of crystalline phases is shown in Fig. 3. Crystallisation of NdSil7G16 at low temperatures resulted in the formation of a small amount of $Nd_4Si_3O_{12}$. A significant increase in the crystallisation rate was then observed above 1100°C, with the formation of neodymium disilicate (A-$Nd_2Si_2O_7$)and W-phase ($NdSi_2AlO_{6.65}N_{0.23}$). Progressive changes occurred above 1150°C, where W-phase became the main crystalline phase. At higher temperatures a glass-ceramic rich in W-phase and poor in neodymium disilicates was obtained.

3.1.2.4 Effect of crystallisation duration For NdSil7G16 glasses heat-treated at 1150 and 1200°C for various durations (2–85 h), the evolution of precipitated crystalline phases, identified by X-ray diffraction, as a function of the logarithm of heat-treatment time is presented in Fig. 4. The order of appearance of the various crystalline phases was strongly linked to heat-treatment time, the process starting with the formation of $Nd_4Si_3O_{12}$. With increasing heat-treatment duration, small amounts of neodymium disilicate (A-$Nd_2Si_2O_7$) and W-phase ($NdSi_2AlO_{6.65}N_{0.23}$) were detected. After 55 h of crystallisation at 1150°C and 24 h at 1200°C a substitution of apatite by W-phase as the main crystalline phase occurred. For longer crystallisation times, the resulting glass-ceramic assemblage was rich in W-phase.

Microstructural changes for the various crystalline phases formed during crystallisation were studied by SEM and image analysis to follow crystal growth as a function of time from the beginning of the heat treatment.

NdSil7G16 glasses were heat-treated at 1150°C for different times and specimens were polished for SEM observation. For each sample, nine SEM micrographs were analysed to give a good statistical analysis of the different crystal parameters.

Two computer programs (OFOTO and OPTILAB) were used for this study and the results indicate the crystal growth in only two dimensions

Table 3. Image analysis results of apatite crystals with crystallisation time

Annealing time	0·5 h	2 h	5 h	10 h	36 h
Apatite crystal surface (%)	6·72	20·65	25·37	28·06	29·57

(Fig. 5) of $Nd_4Si_3O_{12}$ identified previously by X-ray diffraction and EDAX (Table 3).

NdSil7G16 crystallises rapidly at 1150°C with the formation of a small amount of $Nd_4Si_3O_{12}$ after 30 min of heat treatment. Its content increases significantly between 0·5 and 2 h, after which time the progress of its concentration is reduced because of the appearance of other crystalline phases. These results are complementary to the X-ray diffraction ones, which indicated that $Nd_4Si_3O_{12}$ content decreased—see Figs 3 and 4—followed by the increase of the degree of crystallisation due to the levelling off of $Nd_4Si_3O_{12}$ concentration and the devitrification of W-phase rather than actual disappearance of $Nd_4Si_3O_{12}$.

Nucleation mechanisms in sialon glasses are very complex and different studies reported in the literature offer many possibilities. According to various authors,[20,33] Y-sialon glasses appear to be self-nucleating, but this is usually related to the presence of fine-grained dispersions of $FeSi_2$ and silicon in the glass. These metallic precipitates may offer easy nucleation sites on which crystallisation can occur. Recently, Lemercier[34] has shown, using a transmission electron microscope, the formation of nuclei of B-phase (Y_2SiAlO_5N) thinner than 10 nm which indicates that the metallic inclusions are not acting as the nucleating sites in this case. Thomas and Ahn[35] only obtained an appreciable amount of crystallisation in Y-Si-Al-O-N glasses by incorporating 5 wt% ZrO_2, indicating the importance of using nucleating agents to promote the crystallisation of some oxynitride glasses. Jameel and Thompson[36] showed that the nature of the nucleating agent could change the composition and the microstructure of the resulting glass-ceramic. They found that devitrification of an Mg-Si-Al-O-N glass without additional nucleating agents gave a mixture of forsterite and Mg_2SiAlO_4N, whereas in the presence of β Si_3N_4 or β'-sialon nuclei crystallisation occurred to form β'' magnesium sialon below 1100°C. Above this temperature they obtained glass-ceramics consisting of forsterite and Mg_2SiAlO_4N. They have reported that the use of TiO_2 as a nucleating agent in nitrogen containing cordierite-based glasses favoured the formation of a more dendritic microstructure than in TiO_2 -free materials.

Ramesh *et al.*[37,38] have studied the influence of the nature and concentration of metallic cations on the crystallisation. Attempts have been made to correlate the varying cation compositions (Y and Al) at a fixed Si and O:N ratio with changes in nucleation mechanisms. Aluminium has been shown to exert a considerable influence on the crystallisation process of Y-Si-Al-O-N glasses. Bulk nucleation has been found to be the predominant nucleation mechanism for glasses containing > 8 eq% Al while surface nucleation is the dominant nucleation mechanism for glasses containing 8 $\leq$ eq% Al.

The present study has shown that the nature and the concentration of crystalline phases depends on both the composition of the parent glass and the heat-treatment conditions. The data collected for different crystallisation conditions do not confirm or otherwise indicate the occurrence of homogeneous or heterogeneous nucleation. Glasses which crystallise as multiphase products are characterised by a complex mechanism due to the simultaneous precipitation of the various crystalline phases. The devitrification always starts with the formation of a

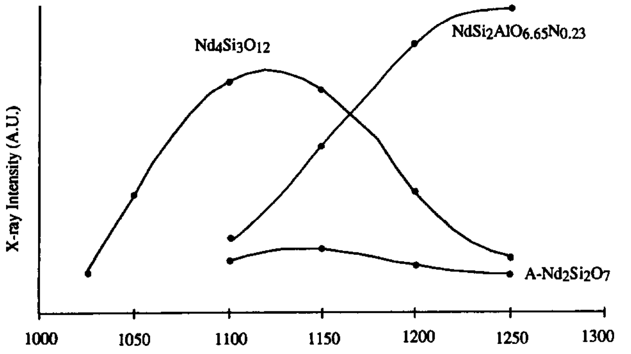


Fig. 3. Effect of crystallisation temperature on the formation of crystalline phases in NdSil7G16 glass annealed for 36 h.

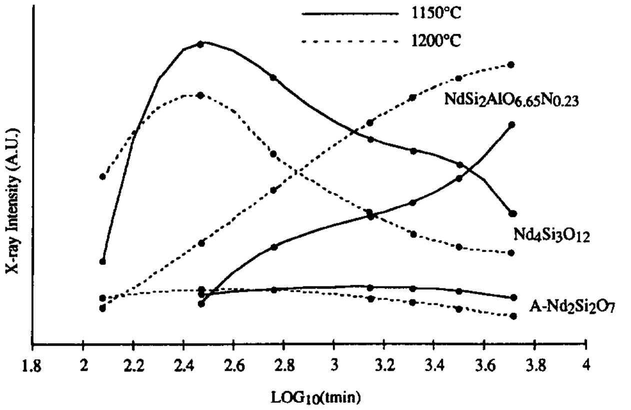


Fig. 4. Effect of crystallisation duration on the formation of crystalline phases in NdSil7G16 glass annealed at 1150 and 1200°C at various times.

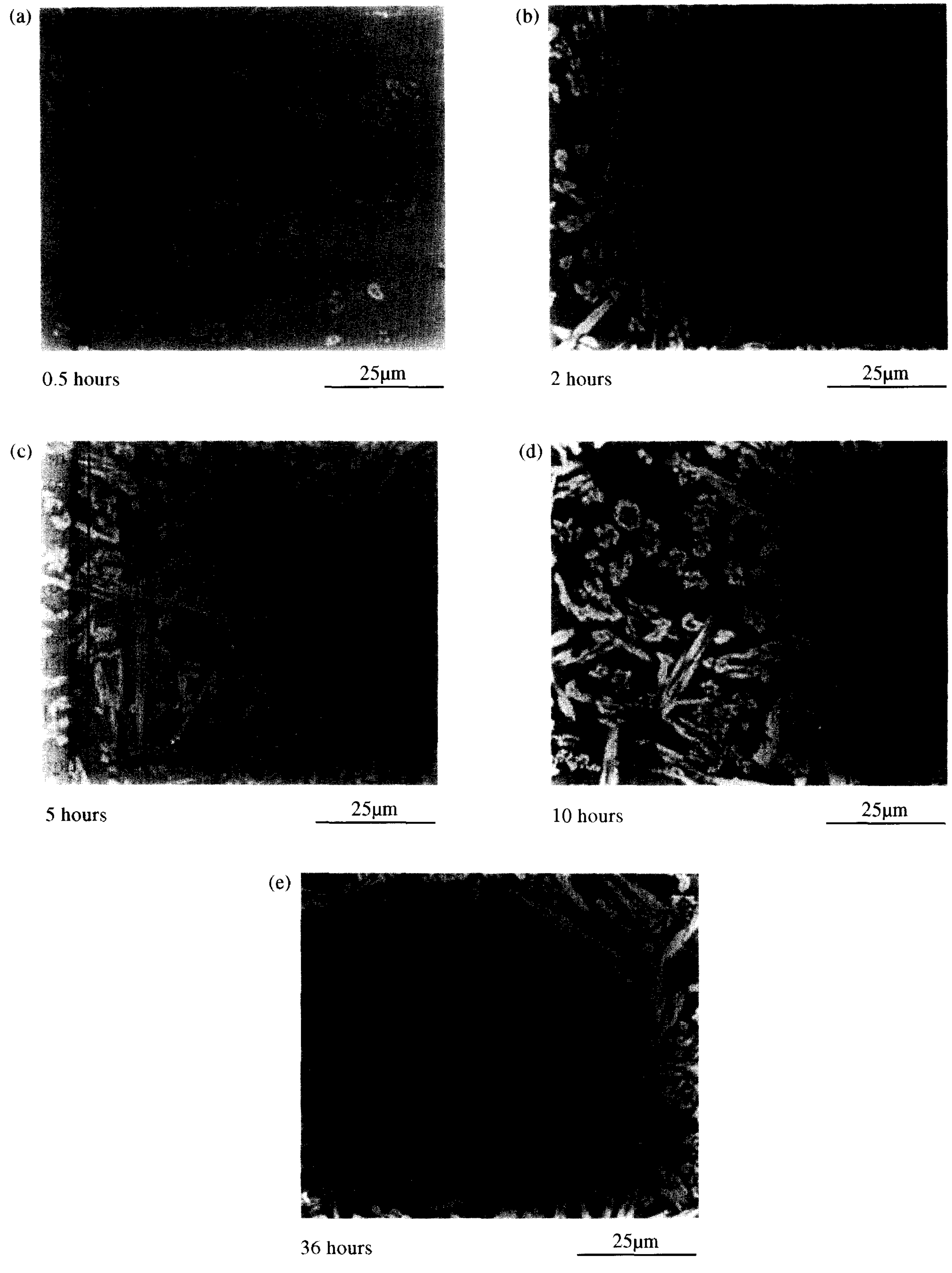


Fig. 5. SEM micrographs of NdSil7G16 glasses after annealing at 1150°C for (a) 0·5 h, (b) 2 h, (c) 5 h, (d) 10 h and (e) 36 h.

silicate phase. The nature of the formed silicate influences the composition of the residual vitreous phase and induces the presence of the other crystalline phases. For example, after the formation of apatite in NdSil7G16, the glass became rich in aluminium and nitrogen which favoured the precipitation of W-phase. In the case of single-phase glass-ceramics, the compositions of the first formed

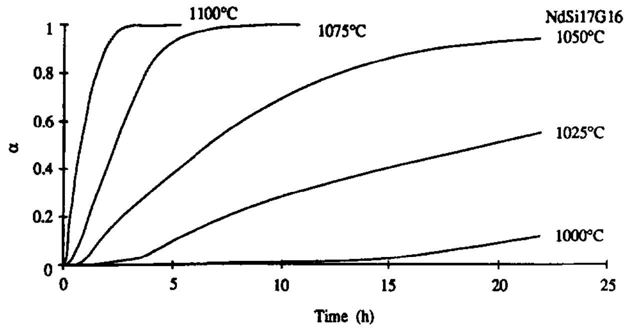


Fig. 6. Oxidation kinetics in air of the oxynitride glass NdSil7G16.

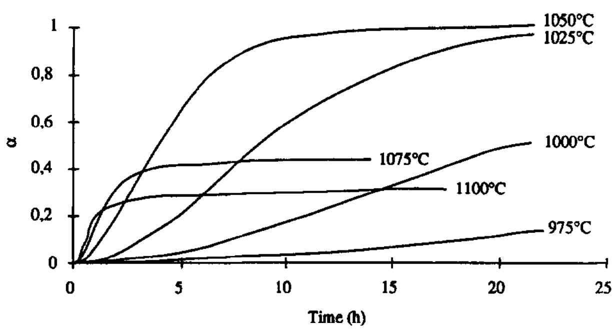


Fig. 7. Oxidation kinetics in air of the oxynitride glass NdSi20G30.

crystalline phase and the residual glass are very similar and this results in the formation of only one kind of phase. In some cases nucleation takes place homogeneously as seen by Lemercier[34] and the crystallisation mechanisms are less complex than in the case of multiphase glass-ceramics. Clearly the crystallisation data obtained for single-phase materials is not applied to multiphase glass-ceramics and this explains the variety of mechanisms reported by different authors.[20,34,38]

3.2 Oxidation of glasses

The heat treatment of oxynitride glasses in oxygen provokes a release of nitrogen and the formation of an oxide layer containing a large number of crystalline phases according to the following general reaction:

$$\text{NdSi-Al-O-N(glass)} + aO_2 \rightarrow bNd_2Si_2O_7 + cAl_2O_3 + dNdAlO_3 + \text{amorphous oxide} + N2 \nearrow$$

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

$$\alpha = {}^{\Delta W_t} / {}_{\Delta W_\infty} \qquad (2)$$

where ΔW_t is the weight gain for a given time t and ΔW_∞ is the weight gain corresponding to complete oxidation of the oxynitride glass. ΔW_∞ is calculated from experimental values of nitrogen content by considering that for complete oxidation, trivalent nitrogen is substituted by divalent oxygen in the glass network.

The oxidation of sialon glasses has been investigated in air between 975 and 1100°C for compositions NdSil7G16 and NdSi20G30 in order to determine the influence of microstructural changes in the substrate on the oxidation mechanism. Degradation starts above Tg and the weight gain curves of the studied glasses exhibit a sigmoidal shape. No initial weight loss was observed at lower temperatures. The results for glasses of varying nitrogen content on the oxidation resistance of Nd-Si-AI-O-N glasses are in agreement with those obtained for Y-Si-Al-O-N glasses,[33] where the incorporation of nitrogen into the glass composition was found to increase the oxidation resistance for a given temperature.

The oxidation of NdSil7G16 begins around 1000°C with a small weight gain (Fig. 6), then increasing temperature accelerates the oxidation rate. At 1075°C, complete oxidation is observed.

The reaction of NdSi20G30 (Fig. 7) with oxygen starts around 975°C. Above 1000°C the oxidation rate increases significantly and is complete at 1050°C. For higher temperatures the oxidation rate is very high initially and then the reaction stops after a few hours. This behaviour is determined by the rapid crystallisation of the substrate as shown in more detail later.

The crystalline phases present in the oxide scale, detected by X-ray diffraction. are given in Tables 4 and 5. The difference expected between the theoretical oxidation products of glasses and the experimental results suggests the presence of a small amount of amorphous silica-rich phase which cannot be detected by X-ray diffraction.

X-ray diffraction was also used to follow the crystallisation of the substrates. For NdSil7G16 a small amount of apatite ($Nd_4Si_3O_{12}$) was detected in the temperature range 1000–1050°C. Above 1050°C the crystallisation rate remained very slow. The same changes were observed for NdSi20G30 glasses, where a small amount of U-phase was formed at 1000 and 1025°C. At 1050°C the crystallisation rate was still low, but for higher temperatures more rapid crystallisation of the substrate was detected after the first stage of heat treatment. The difference in devitrification rates for the substrates of the two glasses is clearly illustrated in Fig. 8, where very limited crystallisation in NdSil7G16 and a complete crystallisation in NdSi20G30 were observed in samples oxidised at 1100°C for 2 h.

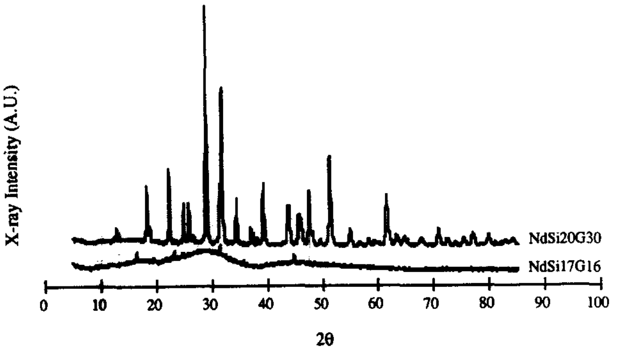


Fig. 8. X-ray diffraction patterns of the substrates of NdSil7G16 and NdSi20G30 oxidised at 1100°C for 2 h.


(a) (b)

Fig. 9. Optical micrographs of NdSil7G16 morphology as a function of oxidation temperature; (a) the formation of maltese cross symmetry at 1000°C (b) an expanded sample at 1050°C.

At low temperatures, samples were covered with a thin oxide layer which grew slowly with increasing oxidation time and temperature [Fig. 9(a)]. The increase of temperature favoured the formation of bubbles and of porosity at the internal interface which facilitated the access of oxygen. The presence of the bubbles led to the formation of an irregular interface. The porosity in the oxide scale induced an increase of the volume and the development of a maltese cross symmetry below 1050°C [Fig. 9(b)].

Temperature has a strong influence on the oxidation behaviour of the glasses studied. With increasing temperatures a disorder in the glass structure is induced. This disorder is followed by a greater average number of non-bridging anions (oxygen and nitrogen) per polyhedron which decreases the glass viscosity. The glass transition temperatures of the two glasses are very similar (Table 1) which explains the fact that their reactivity towards oxygen starts at relatively the same temperature. Normally the reaction rate of an amorphous solid with oxygen is always higher than that of a crystalline one, so the formation of crystals in the substrate, during glass oxidation, leads to reduced reactivity of the sample with oxygen. The crystallisation of NdSi20G30 (which crystallises into U-phase) apparently happens at a lower temperature than for NdSil7G16, probably because NdSi20G30 composition is near that of an oxynitride phase. This finding is in agreement with crystallisation results where we have seen a small amount of crystallisation of NdSil7G16 at 1150°C after 30 min as shown in the SEM micrograph of [Fig. 5(a)] and complete devitrification of NdSi20G30 glass heat treated under the same conditions as illustrated by [Fig. 1(a)] and the results of [Fig. 8]. For NdSil7G16 glass, only one oxidation domain is observed due to the weak crystallisation of the substrate, while NdSi20G30 is characterised by two oxidation domains. The first one occurs at low temperatures and is similar to the NdSil7G16 one. The second domain appears above 1050°C and oxidation occurs quickly during the initial stages of heat-treatment, due to the rapid

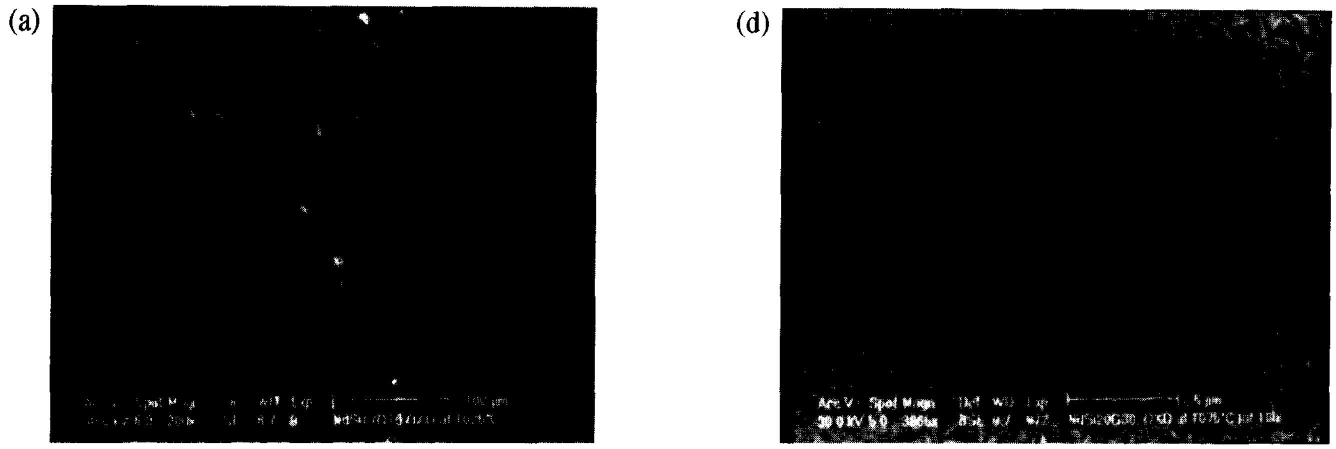
Table 4. Crystalline phases in the oxide layer after heat treatment in air at various temperatures (NdSil7G16)

Temperature	*Time (h)*	*Reaction products*
975°C	22	A-$Nd_2Si_2O_7$, G-$Nd_2Si_2O_7$, $NdAlO_3$, SiO_2
1000°C	22	A-$Nd_2Si_2O_7$, G-$Nd_2Si_2O_7$, $NdAlO_3$, Al_2O_3, SiO_2
1025°C	22	G-$Nd_2Si_2O_7$, A-$Nd_2Si_2O_7$, $NdAlO_3$, Al_2O_3, SiO_2
1050°C	22	G-$Nd_2Si_2O_7$, A-$Nd_2Si_2O_7$, $NdAlO_3$, SiO_2
1075°C	22	G-$Nd_2Si_2O_7$, A-$Nd_2Si_2O_7$, $NdAlO_3$, SiO_2
1100°C	22	G-$Nd_2Si_2O_7$, A-$Nd_2Si_2O_7$, $NdAlO_3$, SiO_2

A-$Nd_2Si_2O_7$: JCPDS 22-1177 neodymium disilicate. G-$Nd_2Si_2O_7$: JCPDS 38-1456 neodymium pyrosilicate.

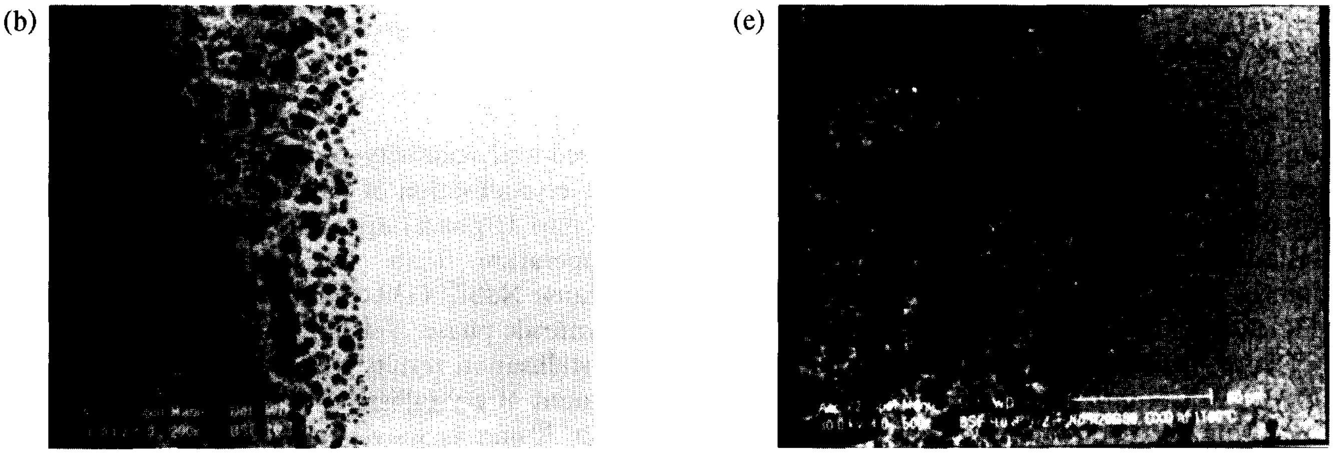
Table 5. Crystalline phases in the oxide layer after heat treatment in air at various temperatures (NdSi20G30)

Temperature	*Time (h)*	*Reaction products*
1000°C	22	A-$Nd_2Si_2O_7$, Al_2O_3, Al_2SiO_5, SiO_2
1050°C	22	Al_2O_3, A-$Nd_2Si_2O_7$, Al_2SiO_5, SiO_2
1100°C	18	A-$Nd_2Si_2O_7$, Al_2O_3, Al_2SiO_5, SiO_2



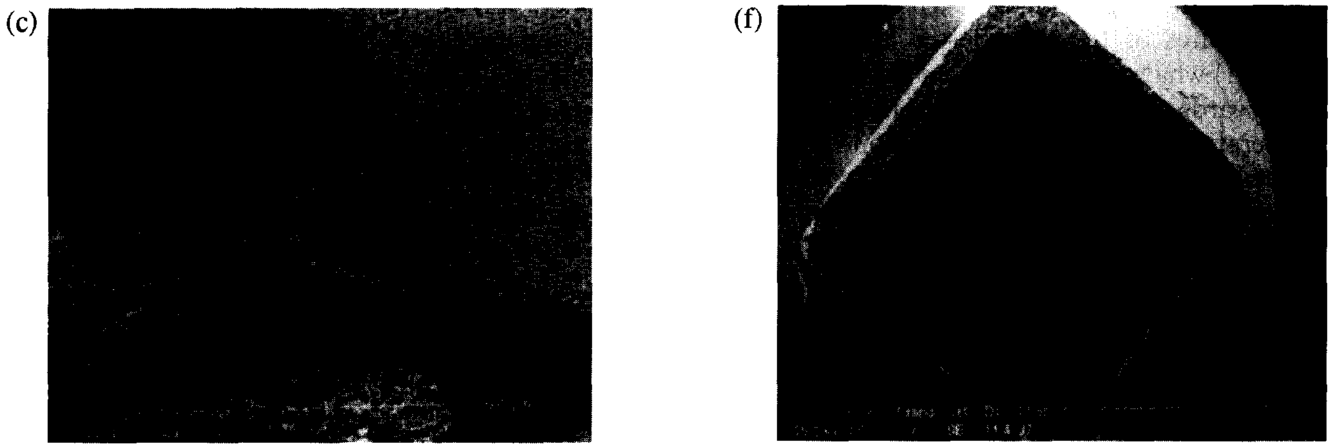
NdSi17G16, 1025°C-22 hours 100 μm

NdSi20G30 at 1075°C-18 hours 5 μm



NdSi20G30, 975°C-22 hours 100 μm

NdSi20G30 at 1100°C-18 hours 50 μm



NdSi20G30, 1000°C-22 hours 500 μm

NdSi20G30 at 1100°C-18 hours 2 mm

Fig. 10. SEM cross-section micrographs of oxidised samples showing (a, b) the formation of porous oxide scale and irregular interface, (c) the formation of a maltese cross symmetry (NdSi20G30), (d, e) the crystallisation of the substrate at 1075 and 1100°C, (f) the final geometry of NdSi20G30 sample at 1100°C.

degradation of the glass. It then stops because of the rapid crystallisation of the substrate which gives a better oxidation resistance to the sample (Fig. 10). It shows that, above 1050°C, NdSi20G30 remains as a glass only at the beginning of the oxidation treatment, and behaves as a glass-ceramic after the crystallisation of the substrate.

The sigmoidal shape of the oxidation curves (NdSi17G16 and NdSi20G30), the growth of the porous oxide scale and the formation of a maltese

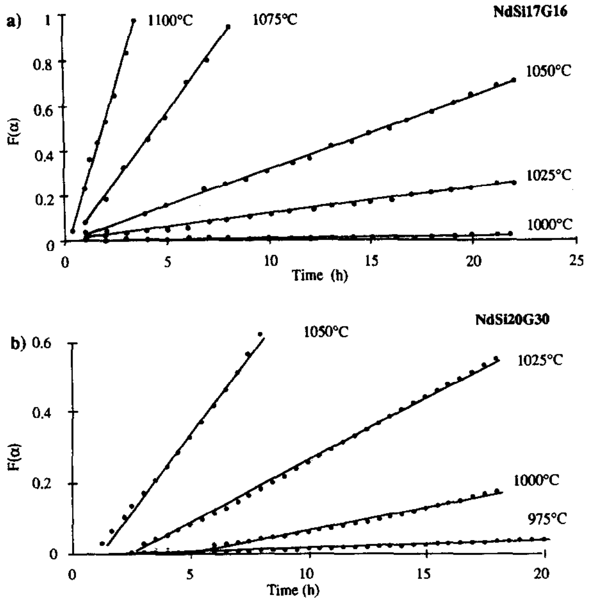


Fig. 11. Transformation versus time curves for NdSil7G16 and NdSi20G30 glasses.

cross symmetry suggest that oxidation is governed by a reaction-controlled process as found for glasses in the Y-Si-Al-O-N system.[33] For cubic samples the oxidation kinetics are represented by the following equation:

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

where α is the fractional weight gain, α_0 is the initial cube edge, k is the rate constant for the given temperature and t is the time.

The transformation curves versus time for the NdSil7G16 glass [Fig. 11(a)] exhibit a linear behaviour in the studied temperature range, but for NdSi20G30 the equation is verified only below 1075°C. The apparent activation energies calculated from the slopes of the transformation curves are $E = 940 \pm 50\,\mathrm{kJ\,mol^{-1}}$ for NdSil7G16 and $E = 780 \pm 50\,\mathrm{kJ\,mol^{-1}}$ for NdSi20G30.

Limited crystallisation of the substrate and the formation of various crystalline phases in the oxide scale make it difficult to determine accurately all the reactions taking place during the oxidation of the glasses and complicate the explanation of the activation energy. The high values of the activation energy are similar to that obtained for oxidation[33] of glasses in Y-Si-Al-O-N system.

3.3 Oxidation of glass-ceramics

The crystallisation of Nd-Si-Al-O-N glasses has been investigated recently, but no data is available on glass-ceramic properties. Most studies are concerned with optimising the crystallisation conditions for producing multiphase materials[24,25] or evaluating the stability and determining the structure of sialon materials.[39] The development of oxynitride glass-ceramics necessitates the preparation of materials with improved mechanical properties, but the presence of nitrogen- containing phases leads to a decrease of their oxidation resistance. So, the behaviour of glass-ceramics in an oxidising atmosphere has been studied to compare the oxidation resistance of single and multiphase glass-ceramics.

NdSil7G16 was heat-treated, in nitrogen, in a vertical tube furnace at one atmosphere pressure. The glass was nucleated at 950°C for 10 h and then crystallised at 1100°C for 36 h; the heating rate was $5°\mathrm{C\,min^{-1}}$. The resulting glass-ceramic, which contained $Nd_4Si_3O_{12}$, W-phase and $Nd_2Si_2O_7$ is designated NdSil7C16. Its reactivity with oxygen starts at 1050°C [Fig. 12(a)], and the weight gain is low until 1100°C. Above this temperature, the oxidation rate increases rapidly and induces total degradation of the sample at 1250°C.

NdSi20G30 oxynitride glass was heat-treated at 1150°C for 36 h to give NdSi20C30 glass-ceramics. X-ray diffraction patterns revealed the presence of U-phase ($Nd_3Si_3Al_3O_{12}N_2$) and a small amount of wallastonite. Oxidation began below 1100°C [Fig. 12(b)], an increase in temperature accelerated the oxidation rate, and at 1300°C a complete oxidation was observed after 10 h of heat treatment.

The oxidation resistance of glass-ceramics, in comparison with the parent glasses, is increased. As seen from Fig. 6, the weight gain α of NdSil7G16 oxidised at 1050°C is close to 1 after 20 h of oxidation, while α is below 0·2 in the case of

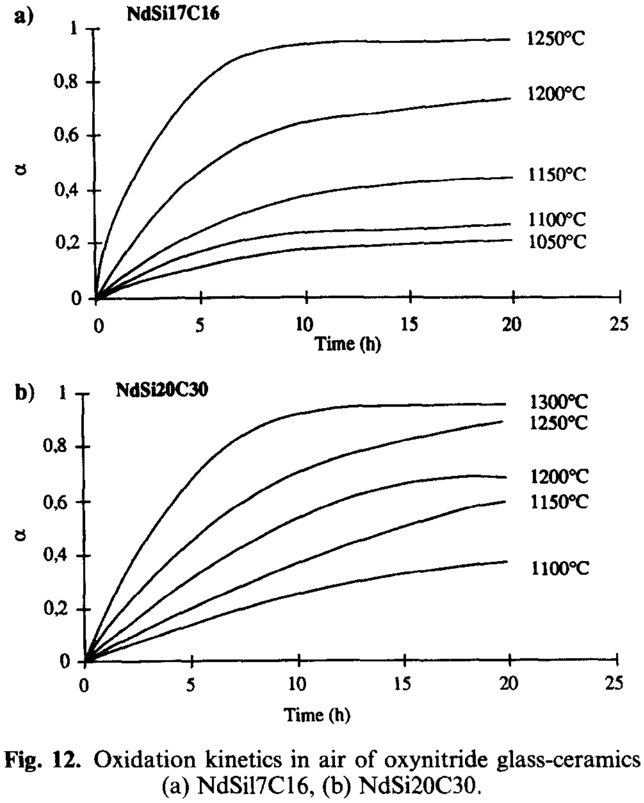


Fig. 12. Oxidation kinetics in air of oxynitride glass-ceramics (a) NdSil7C16, (b) NdSi20C30.

Table 6. Crystalline phases in the oxide layer of NdSil7C16

Temperature	*Time (h)*	*Reaction products*
1050°C	20	G-$Nd_2Si_2O_7$, A-$Nd_2Si_2O_7$, $NdAlO_3$
1100°C	20	G-$Nd_2Si_2O_7$, A-$Nd_2Si_2O_7$, $NdAlO_3$
1150°C	20	G-$Nd_2Si_2O_7$, A-$Nd_2Si_2O_7$, $NdAlO_3$ Al_2SiO_5
1200°C	20	G-$Nd_2Si_2O_7$, A-$Nd_2Si_2O_7$, $NdAlO_3$, Al_2SiO_5

Table 7. Crystalline phases in the oxide layer of NdSi20C30

Temperature	*Time (h)*	*Reaction products*
1100°C	20	G-$Nd_2Si_2O_7$, A-$Nd_2Si_2O_7$, $NdAlO_3$, Al_2O_3
1150°C	20	G-$Nd_2Si_2O_7$, $NdAlO_3$, Al_2O_3
1200°C	20	G-$Nd_2Si_2O_7$, $NdAlO_3$, Al_2O_3, $Al_6Si_2O_{13}$
1250°C	20	G-$Nd_2Si_2O_7$, $NdAlO_3$, $Al_6Si_2O_{13}$

NdSil7C16 (glass-ceramics) oxidised under the same conditions. The presence of well-structured crystals reduces the mobility of atoms in the material.

The reaction products were analysed by X-ray diffraction the results given in Tables 6 and 7 show the absence of oxynitride phases. The various aluminate phases in the oxide layer of U-phase samples can be related to the high aluminium content of the NdSi20C30 material. The formation of neodymium pyrosilicate (G-$Nd_2Si_2O_7$) as the main crystalline phase instead of neodymium silicate (A-$Nd_2Si_2O_7$) is due to the higher oxidation temperatures in comparison with equivalent glass samples.

The oxidation of glass-ceramics in the Nd-Si-Al-O-N system promoted the growth of a purple oxide layer. The observations with scanning electron microscopy showed the existence of a porous oxide scale at low temperatures (Fig. 13) which facilitated direct access of large quantities of oxygen into the substrate and explained the large increase in the volume observed. Accurate determination of the coefficient of expansion of oxidised samples is very difficult due to the formation of porosity and many crystalline phases. These observations also revealed important changes in the substrate with temperature, essentially for single-phase material. As seen in Fig. 14, the increase of temperature induces growth of U-phase crystals and leads to the formation of some porosity in the substrate. This porosity acts as a bridge to the diffusion of oxygen into the substrate and accelerates the oxidation of the material. In this case, the degradation is more regular due to the homogeneity of the composition and the microstructure. The oxidation of oxynitride crystals leads to tan increasing in volume, this expansion favouring the appearance of cracks. The poor mechanical properties of the porous scale and the appearance of stresses between the oxide layer and the substrate induce the formation of a maltese cross symmetry at 1100°C. The same degradation occurs in the multiphase glass-ceramics but due to the lower oxynitride phase content the stresses induced by the increase in volume during the oxidation of W-phase are reduced, which explains the absence of a maltese cross symmetry. Above 1250°C, a total degradation of the material is observed.

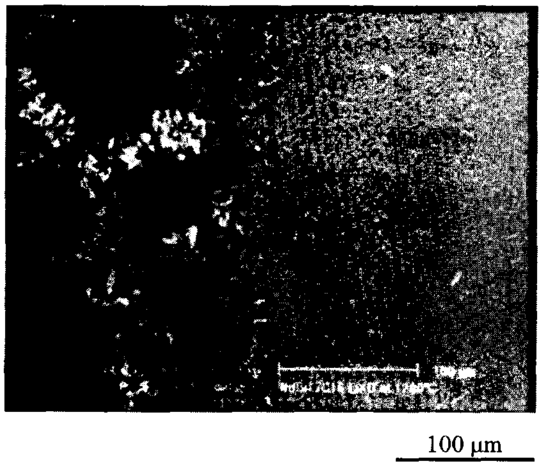


Fig. 13. Cross-section micrograph of NdSil7Cl6 oxidised at 1200°C.

The oxidation curves and the significant levels of porosity in the oxide layer indicate that the oxygen has direct access to the substrate and predict a reaction process. The calculation of the transformation curves as function of time using eqn (3) shows the linearity of the curves in the studied temperature range which confirms the fact that the oxidation of NdSi20C30 and NdSil7C16 glass-ceramics is controlled by a chemical reaction where the progress of the internal interface is the limiting step (Fig. 15). Single-phase glass-ceramic transformation curves are linear for a wide range of time compared with multiphase glass-ceramic samples. This can be attributed to structural changes of oxide phases in

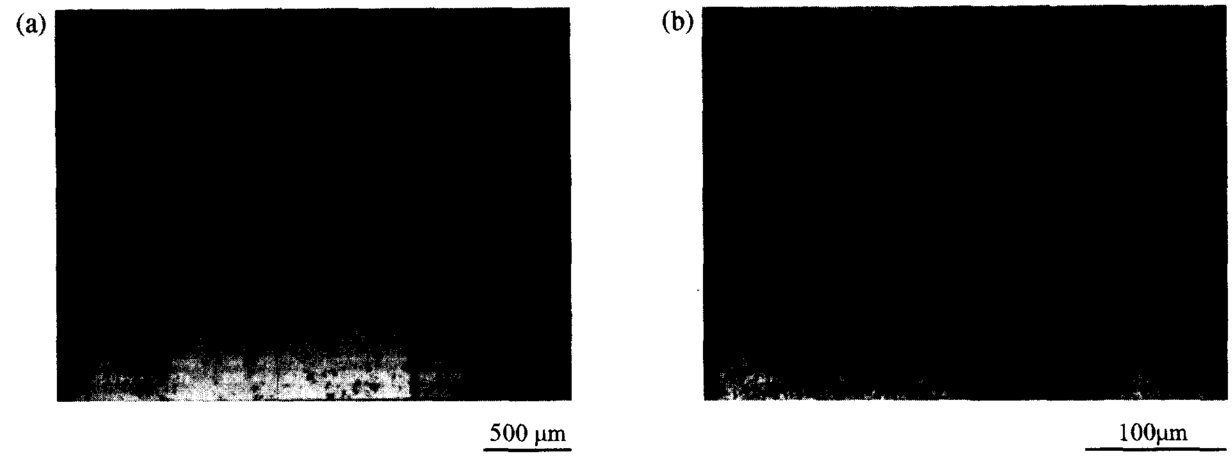


Fig. 14. Evolution of the substrate of NdSi20C30 oxidised at 1200°C.

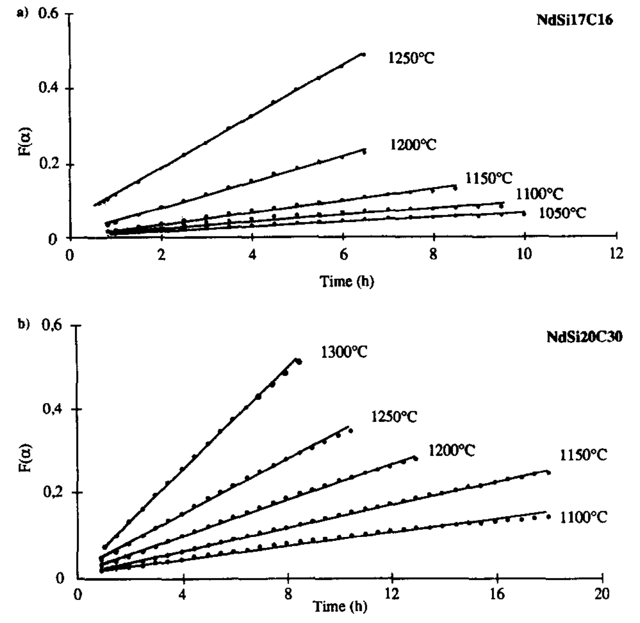


Fig. 15. Transformation curves versus time of oxynitride glass-ceramics (a) NdSi17C16 and (b) NdSi20C30.

the multiphase materials which modify the oxidation kinetics.

4 Conclusions

Crystallisation studies of sialon glasses provide an attractive route for the preparation of glass-ceramics for thermomechanical applications but the mechanisms governing their transformation are still unknown and the crystallographic structures of some of the crystalline phases are not yet determined. Moreover these glasses have quite complex crystallisation mechanisms and this explains the inconsistent results found in the literature.

Glasses with compositions which can be crystallised into single and multiphase products in the Nd-Si-Al-O-N system have been prepared. A study of the crystallisation behaviour of selected glasses shows a wide variation in the formed crystalline phases. U-phase has been found to be stable at 1150°C for various crystallisation times. However, for compositions which crystallised as multiphase products, various crystalline phases were formed on changing the heat-treatment conditions. These phases vary also with nitrogen content, and for example the formation of $Nd_4Si_3O_{12}$, which is not observed in oxide glasses, is promoted by the incorporation of nitrogen.

Oxynitride glasses oxidised rapidly in air at temperatures above the glass transition temperature by forming a porous oxide scale, due to the evolution of gaseous nitrogen during oxidation. Glass-ceramic degradation occurred at temperatures higher than for the parent glasses, and was controlled by the oxynitride phase content. For all materials the oxidation was governed by a reaction process where the progress of the internal interface was the limiting step.

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