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Formation, Crystallisation and Oxidation of Selected Glasses in the Y–Si–Al–O–N System

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Abstract

Oxynitride glasses were prepared which correspond to the compositions of the intergranular phase in Si_3N_4 ceramics fabricated with additions of Y_2O_3 and Al_2O_3 as sintering aids. Transparent glasses were obtained after melting for 10 h at a firing temperature of 1450°C. Two distinct melting temperatures of 1310°C and 1375°C were obtained for all compositions within the oxynitride glass-forming region. For all N-containing compositions the glass softening point (Mg) was 975°C which is an increase of ≈110°C over that of the corresponding oxide glass. Devitrification of the glasses in N_2 required 12 h at 1200°C and the phases present after crystallisation included $Y_2Si_2O_7$, Si_2N_2O and $3Y_2O_3.5Al_2O_3$ (YAG). The oxynitride glasses oxidised rapidly in air at temperatures in excess of the softening point. Porous oxide 'scales' developed from the evolution of nitrogen was during oxidation and the main crystalline phases that formed in the scale were $Y_2Si_2O_7$ and $3Al_2O_3.2SiO_2$ (mullite).

Es wurden Oxinitridgläser hergestellt, die in ihren Zusammensetzungen derjenigen intergranularen Phase entsprechen, die beim Sintern von Si_3N_4 unter Verwendung von Y_2O_3 und Al_2O_3 als Sinterhilfsmittel auftritt. Bei 1450°C und einer 10-stündigen Schmelzzeit konnten klare Gläser gewonnen werden. Im oxinitridglasbildenden Bereich des Phasendiagramms ergaben sich für alle Zusammensetzungen zwei spezifische Schmelztemperaturen von 1310°C und 1375°C. Für alle stickstoffhaltigen Zusammensetzungen lag der Transformationsbereich (T_g) bei 975°C und somit ca. 110°C über demjenigen des entsprechenden Oxidglases. Die Gläser kristallisierten in N_2 erst bei 12 h und 1200°C. Dabei bildeten sich $Y_2Si_2O_7$, Si_2N_2O und $3Y_2O_3.5Al_2O_3$ (YAG). Die Gläser oxidierten in Luft bei Temperaturen über dem Transformationsbereich rasch. Während der Oxidation bildeten sich durch den entweichenden Stickstoff poröse 'Oxidschuppen'. In den Schuppen fand sich vor allem $Y_2Si_2O_7$ und $3Al_2O_3.2SiO_2$ (Mullit).

On a préparé des verres oxynitrures correspondant aux compositions de la phase intergranulaire de céramiques Si_3N_4 élaborés avec les ajouts de frittage Y_2O_3 et Al_2O_3. Après 10 h de fusion à 1450°C, on obtient des verres transparents. On a obtenu, pour toutes les compositions situées à l'intérieur du domaine de formation du verre oxynitrure, deux temperatures de fusion distinctes égales à 1310 et 1375°C. Pour toutes les compositions contenant N le point de ramolissement du verre (M_g) était de 975°C, correspondant à un accroissement d'environ 110°C par rapport à celui du verre oxyde. La dévitrification des verres dans N_2 a nécessité 12 h à 1200°C et les phases présentes après cristallisation incluaient $Y_2Si_2O_7$, Si_2N_2O et $3Y_2O_3.5Al_2O_3$ (YAG). Les verres oxynitrures étaient rapidement oxydés dans l'air à des températures supérieures au point ramolissement. Des couches poreuses d'oxyde se développaient du fait de l'évolution du gaz azote pendant l'oxydation, les phases cristallines principales formées dans les couches étant $Y_2Si_2O_7$ et $3Al_2O_3.2SiO_2$ (mullite).

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1 Introduction

The high-temperature properties of β-Si_3N_4-based materials formed within the Y–Si–Al–O–N system are mainly controlled by the intergranular microstructure.[1] In as-sintered materials the microstructure is mainly determined by phase relationships at the sintering temperature and can be considered to consist of three major elements: the principle phase β-Si_3N_4 (or β'-sialon), secondary crystalline phase(s) and an intergranular amorphous phase.[2] It is generally agreed that the high-temperature properties of these materials can be improved through controlled crystallisation of the amorphous phase.[2-4] Knowledge of the relationships between composition and properties of nitrogen glasses that are formed within this system is therefore of value in understanding the behaviour of these materials.

The present work examines the formation and properties of oxynitride glasses for a selection of compositions which have been chosen to correspond with likely compositions of the glassy phase in β-Si_3N_4 materials which are sintered with additions of Y_2O_3 and Al_2O_3 as sintering aids in the mass ratio of 3:1.

The base mixture of oxides for the glass-forming experiments was estimated assuming that in β-Si_3N_4 material all of the oxygen in the starting Si_3N_4 powder is available for glass formation. Si_3N_4 was used as a nitrogen source to move the compositions, with a fixed ratio of the three component oxides, from the oxide face of the six component Jänecke prism towards more nitrogen-rich compositions (see Fig. 1). Characterisation of the glasses was carried out by X-ray diffraction and scanning electron microscopy (SEM). The microstructures of selected glasses were investigated using optical and analytical transmission electron microscopy (STEM/EDX).

The melting temperatures of the glass-forming compositions were determined by differential thermal analysis (DTA). This knowledge is important in indicating the lowest temperature at which a liquid can occur in corresponding β-Si_3N_4 materials. The dilatometric softening points (M_g) of the glasses were also determined. Isothermal annealing experiments were carried out to compare the crystallisation products that were obtained by devitrification in either nitrogen or air and also to examine the oxidation behaviour of the pure oxynitride glasses.

2 Experimental

2.1 Glass preparation and characterisation

The compositions which were examined are given in Table 1. For the melting experiments the furnace of a thermobalance (Mettler TAI) was used with an atmosphere of flowing nitrogen at 0·1 MPa. The compositions were fired at 1450°C for 1 h and 10 h. This temperature corresponds to the eutectic temperature for the base oxide mix.[5] Procedures for preparation and characterisation of glass-forming compositions, which are summarised in Fig. 2, were as follows:

(i) High-purity oxide powders in the proportion (wt%) 30 SiO_2, 53 Y_2O_3, 17 Al_2O_3 were thoroughly mixed by ball-milling in an agate jar with agate balls. The mass ratio of Y_2O_3: Al_2O_3 (3:1) that was used is similar to that used in the production of several β-Si_3N_4 materials.[6] Pick-up of SiO_2 during the milling process was negligible.

(ii) Compositions containing between 0–20 wt% Si_3N_4 were then prepared by adding Si_3N_4 to the base oxide powder mixture and mixing thoroughly with a mortar and pestle. These compositions are detailed in Table 1. Speci-

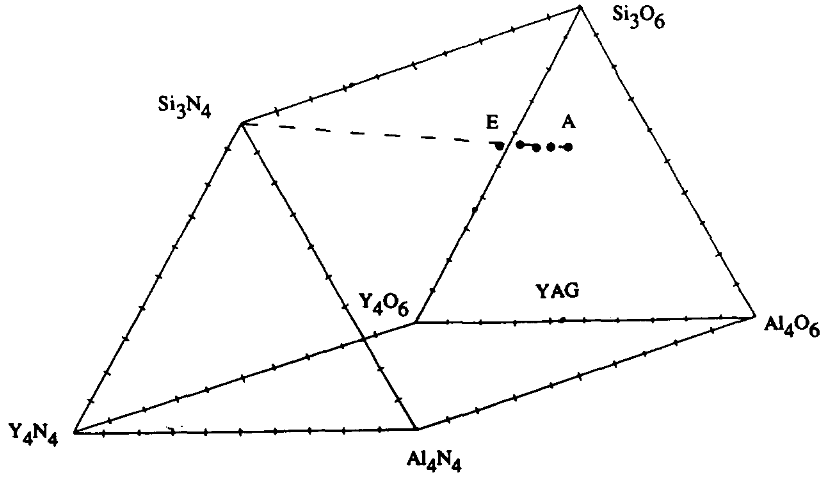

Fig. 1. Jänecke composition prism for the Y–Si–Al–O–N system. The compositions marked A–E cover the region investigated and represent additions of up to 20 wt% Si_3N_4.

Table 1. Composition and phase content of the experimental glasses (after 1 h firing at 1450°C)

Glass	*Composition (wt%)*				*Phase content (X-ray diffraction)*
	Si_3N_4	Y_2O_3	Al_2O_3	SiO_2	
1	0	53	17	20	Amorphous
2	2	51·5	17·1	29·4	Amorphous, β-$Y_2Si_2O_7$, $Y_3Al_5O_{13}$
3	5	50	16·5	28·5	Amorphous, β-$Y_2Si_2O_7$, $Y_3Al_5O_{13}$
4	7·5	48·6	16·2	27·4	Amorphous, β-$Y_2Si_2O_7$
5	8	48	16·2	27·8	Amorphous
6	10	47·3	15·8	27	Amorphous
7	12·5	45·9	15·3	26·3	Amorphous
8	14	45	15	26	Amorphous
9	15	44·7	14·8	22·5	Amorphous
10	17·5	43·3	14·4	24·8	Amorphous
11	18	43	14·2	24·3	Amorphous, α-$Y_2Si_2O_7$
12	20	42	14	24	Amorphous, α-$Y_2Si_2O_7$

men pellets (1 g) were formed by cold pressing.

(iii) All samples were fired individually in boron nitride crucibles for 1 h and 10 h at 1450°C (heating rate 10°C/min) in N_2 (flow rate 10 litres/h) at 0·1 MPa and then cooled to room temperature (10°C/min) before removal from the furnace.

(iv) The formation of glass in the resulting samples was investigated using X-ray diffractometry and scanning electron microscopy (backscattered electron mode).

2.2 Microstructural characterisation

Optical microscopy on polished specimens was carried out using a Leitz Orthomat microscope. Thin foils for transmission electron microscopy (TEM) were prepared from glass samples containing 8 and 10 wt% Si_3N_4 addition which had been fired for both 1 h and 10 h. The specimens were examined in a Jeol 2000 FX STEM/TEM instrument equipped with a Link Systems AN 10 000 EDX spectrometer.

2.3 DTA and dilatometry

Powdered samples of successful glass-forming compositions (see Tables 1 and 2) and also their fully devitrified products were subjected to differential thermal analysis (DTA). Each specimen (approximate weight 50 mg) was contained in a molybdenum crucible and Al_2O_3 powder was used as reference. A sensitivity of 50 μV was used on a Mettler TAI DTA apparatus. The DTA experiments were carried out with the specimens in a N_2 atmosphere (flow rate 10 litres/h). All samples were heated to 1450°C at 10°C/min followed by slow cooling to room temperature.

Polished glass pellets of the same compositions (Table 2) and an oxide glass prepared from the base oxide mixture (SiO_2:Y_2O_3:Al_2O_3 = 30:53:17) were investigated by dilatometry. A N_2 atmosphere with a heating rate of 5°C/min was used in a Harrop TDA 716 dilatometer.

2.4 Crystallisation heat treatments

Glass pellets of selected samples (8 and 10 wt% Si_3N_4 addition) within the glass-forming region

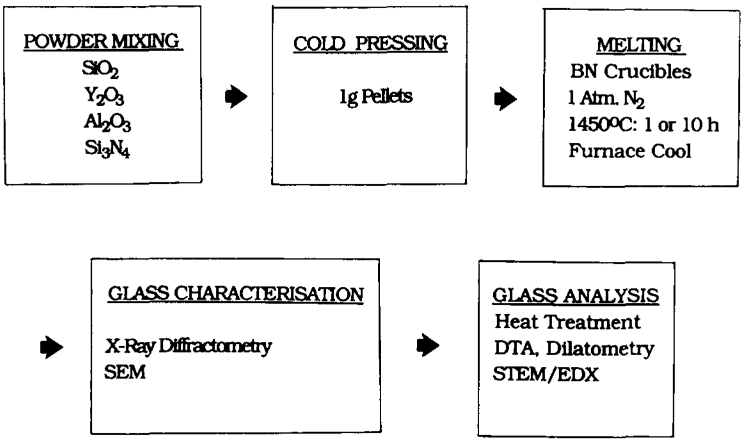

Fig. 2. Procedures for the preparation and characterisation of the Y–Si–Al–O–N glasses.

Table 2. Melting temperatures and glass softening points (M_g)

Glass	*Composition (wt% Si_3N_4)*	*Melting temperature (°C)*		*Softening point (M_g; °C)*
		As-prepared powder	*Devitrified glass*	
1	0			865
5	8	1310, 1375	1310, 1375	975
6	10	1310, 1375	1310, 1385	965
7	12·5	1310, 1375	1310, 1370	975
9	15	1310, 1375	1310	970

(Table 1) were heat treated in nitrogen and air. Nitrogen annealing was carried out in flowing N_2 in a tube furnace. Specimens were placed in a Si_3N_4 powder bed in alumina boats. Heat treatments in an oxygen environment were undertaken in air in a rapid high-temperature furnace. For these experiments the specimens were placed in platinum boats. All heat treatments were isothermal and were carried out in the temperature range 1000 to 1200°C. The duration of the heat treatments ranged from 10 to 50 h for heat treatment in N_2 annealing and from 5 min to 50 h for heat treatment in air.

In order to reduce the influence of heterogeneous nucleation at the specimen surfaces, all the specimens were in the form of uniform polished cylinders (3 mm × 2 mm). Phase analysis of the heat-treated material was carried out primarily by X-ray diffractometry and where possible complementary analytical transmission electron microscopy was undertaken. Thin foils for microscopy were prepared as described previously. Transverse sections of oxidised glass specimens were examined using optical microscopy and SEM in the secondary electron mode.

3 Results and Discussion

3.1 Glass preparation and characterisation

Twelve compositions on a line from a point on the oxide surface of the Jänecke prism (Fig. 1) towards the Si_3N_4 corner were investigated. In order to maintain a Y_2O_3:Al_2O_3 ratio of 3:1 in the glasses, only compositions where no crystallinity could be detected by X-ray diffraction after firing and slow cooling were accepted as glass forming. The primary criterion for acceptance was the absence of any crystalline peak above the background in the glass-broadening region of the X-ray diffractograms. As is shown in Table 1, a glass-forming region was found for the compositions containing 8–17·5 wt% Si_3N_4.

This demarcation of the glass-forming region was confirmed using SEM in the backscattered mode. As is shown in Fig. 3(a) a homogeneous backscattered image was observed for the 'all-glass' specimens. Local differences in elemental distributions were frequently observed for glasses melted for just 1 h at the firing temperature (Fig. 3(b)).

Normally, to ensure sufficient melting and homogenisation of the nitrogen-containing component in

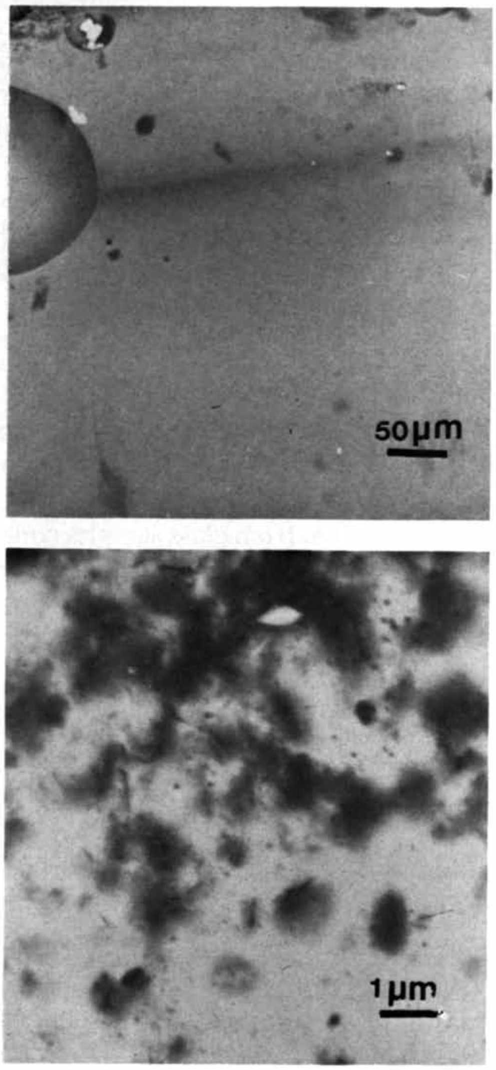

Fig. 3. SEM backscattered compositional mode (BS) images of a glass specimen (10 wt% addition of Si_3N_4) showing: (a) the generally uniform distribution of elements in the glasses which results in a homogeneous BS image and (b) a region of the specimen with local differences in elemental concentration.

the glass, temperatures in the range of 1600 to 1750°C are used when attempting to form oxynitride glasses in this system. The upper temperature limit is determined by the decomposition of Si_3N_4 and the lower by the melting temperature of the particular composition.[7] In this work the composition of the oxide base mix lay in a compatibility triangle with a relatively low eutectic temperature (1450°C).

The final nitrogen contents of the 8 and 10 wt% Si_3N_4 glasses formed in this work are relatively low (≤ 7 at %) due to the loss of $\approx 25\%$ of the ingoing N during firing. However, this is thought to be representative of the intergranular amorphous phase in β-Si_3N_4 materials as all existing information on the elemental composition of these phases indicates that they are highly siliceous.[8] Electron energy loss spectroscopy (EELS) carried out by Clarke *et al.*[8] indicated that the nitrogen content of the intergranular glassy phase was <5 at.%.

3.2 Microstructures of the glasses

On melting, the powder pellets formed discs of approximately 10 mm in diameter and 2·5 mm in thickness. Two firing times, 1 h and 10 h, were investigated, and it was found that the optical transparency of the resulting glasses improved with increasing firing time. The glasses that were formed after 1 h at the melting temperature were generally dense and translucent grey. As can be seen in Fig. 4 the glasses that were formed after 10 h at melting temperature were transparent, although they appeared slightly 'grey' when compared to a pure oxide glass. The difference in the optical transparencies of the 1 h and 10 h glasses could be explained by differences observed in the microstructures of the glasses. Glass compositions containing 8 and 10 wt% Si_3N_4 addition were used for microstructural examination. Analysis of these compositions by gas chromatography indicated that a 25% loss of nitrogen occurred during melting and that the final nitrogen content of the glasses was 4–7 at.%.

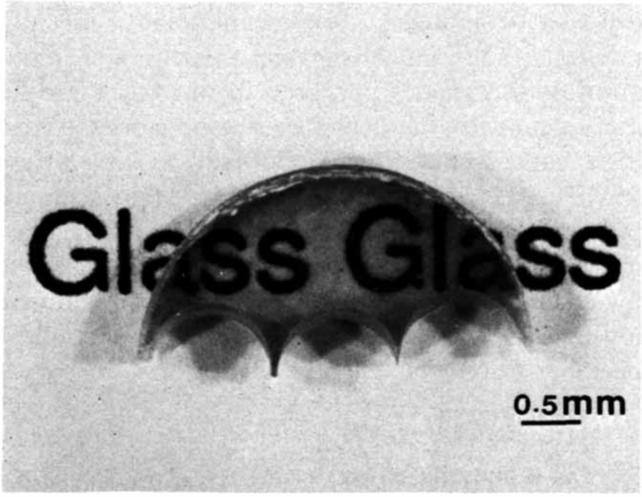

Fig. 4. Highly transparent glass sample that was melted for 10 h at 1450°C and which had a final nitrogen content of 7 at%. The sample is approximately 2·5 mm thick.

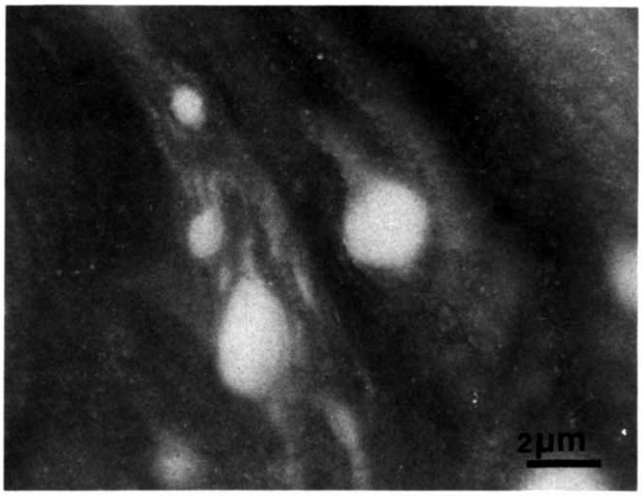

Fig. 5. Optical micrograph (reflected mode polarised light) of a glass sample which was melted for just 1 h showing the occurrence of inhomogeneities in the composition of the glass.

The glasses which had been fired for 1 h were opaque in transmitted light microscopy (samples were $\approx 2{\cdot}5$ mm thick) and inhomogeneities in the glass structure were frequently observed in reflected polarised light (Fig. 5). Although TEM showed that these glasses were mainly amorphous, isolated areas of small crystals were occasionally found and additional spheroidal crystalline particles were scattered throughout the microstructure. The volume fraction of these crystals was too small to enable their identification by X-ray diffraction and their occurrence is probably due to devitrification on slow cooling. The spheroidal crystalline structures (see Fig. 6) were 0·02–0·5 μm in size and EDX analysis showed them to contain mostly Fe and Si. They are thus impurity aggregates, possible silicides. In some parts of the specimens regions of amorphous phase with dark contrast were separated by regions of light contrast, as shown in Fig. 7. EDX analysis showed that the regions of darker contrast were richer in Y than the light contrast regions, indicating a lack of complete homogenisation upon melting for only 1 h.

In transmitted mode optical microscopy the glasses, which had been formed after 10 h melting, were seen to contain the small 'string-like' structures shown in Fig. 8. These structures were found throughout the depth of the glass and consisted of a spheroidal 'head' and a narrowing 'tail'. Similar structures have been previously observed in nitrogen glasses by Thompson,[9] who identified them to be Si–Fe impurity precipitates which had sunk, due to

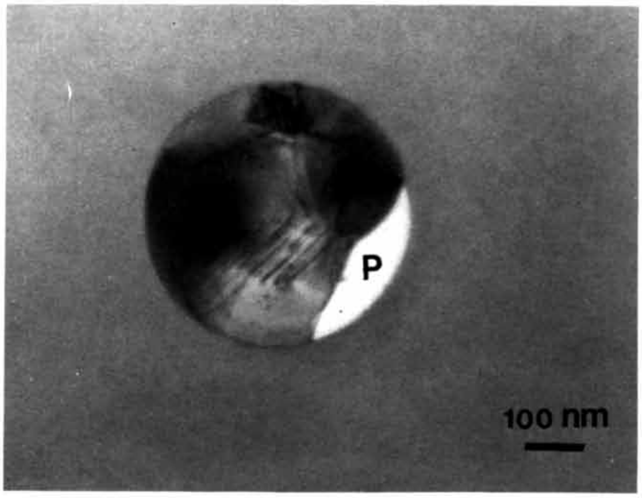

Fig. 6. TEM micrograph of a spheroidal crystalline particle which contained a large amount of Fe and Si. These particles were found in the microstructures of glasses which had been melted for both the 1 h and 10 h. The pore (P) probably results from a reduction in volume upon crystallisation.

gravity, towards the bottom of the glass specimens during cooling. The precipitates leave a trail of this movement in the glass because of the increasing viscosity that arises during cooling. In TEM these same glasses were observed to be entirely amorphous except for the occurrence of spheroidal impurity aggregates similar to those observed in the 1 h glasses (Fig. 6). The size of these aggregates was similar to that of the 'heads' of the strings seen in optical microscopy. Thus, the slight 'greyness' of the 10 h glasses probably results from the presence of these impurity precipitates. The difference, therefore, in optical transparency between the 1 h and 10 h glasses can be ascribed to the areas of crystallinity and local compositional inhomogeneity occurring in the microstructure of the 1 h glasses.

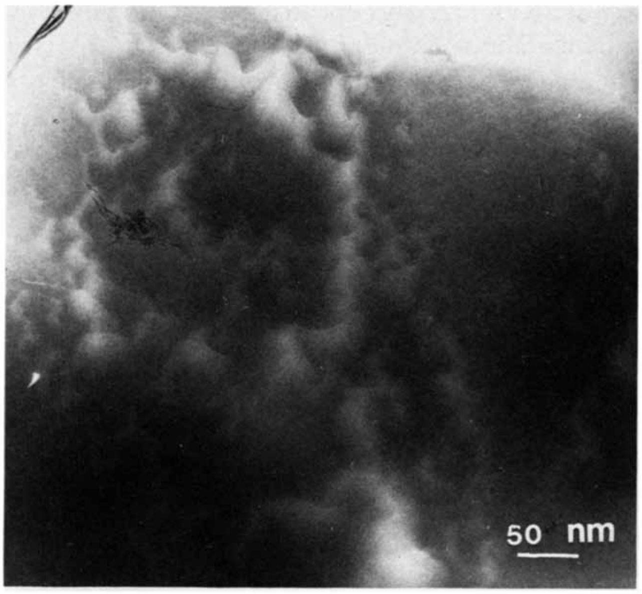

Fig. 7. Coexistence of dark contrast Y-rich (Y) and bright contrasting Si-rich (S) glassy phases in a specimen (10 wt% Si_3N_4 addition) which was melted for just 1 h at 1450°C.

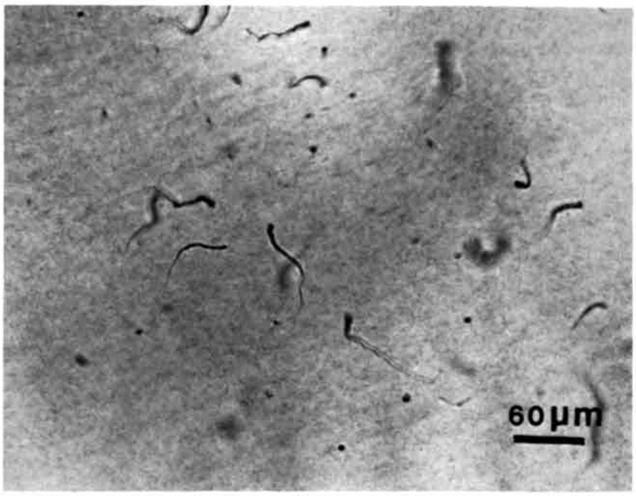

Fig. 8. Optical micrograph (transmitted light) of a 10 h glass showing the presence of small 'string-like' structures throughout the depth of the glass. The sample thickness is ~2·5 mm.

The transparency of the 10 h glasses is higher than that which has been reported by other authors[7,10–12] for oxynitride glasses that were prepared using Si_3N_4 as the source of nitrogen. Such glasses have previously been found to be of limited transparency and grey to black in colour.[12] Messier & Daguire have shown that the greyness of these glasses is probably due to precipitation of Si, which results from decomposition reactions at temperatures $\geq 1650°C$. The decomposition reaction is of the form:

$$Si_3N_4 + SiO_2 \rightarrow Si(l) + 2SiO(g) + 2N_2(g)$$

It follows from this that increasing the purity of the Si_3N_4 does not necessarily decrease the number of precipitates, i.e. there need not be improved transparency. Thompson[9] believes that the transparency can also be limited by Si–Fe contaminant precipitates and the results of the microstructural examination of the glasses prepared in this work are in agreement with this view. It seems therefore that the high transparency which was obtained after firing for 10 h was due to the small number of precipitates present in the glass. A major reason for the low number of precipitates is probably due to the use of a low melting temperature (1450°C) which is much lower than that temperature at which significant decomposition of Si_3N_4 is known to start ($\approx 1650°C$).

3.3 DTA and dilatometry

For all samples examined by DTA, endotherms were recorded at ~1310°C and ~1375°C (see Table 2). As no mass change occurred in association with the endotherms they were interpreted as representing melting reactions. The eutectic temperature of the base mixture of oxides has previously been determined by the present authors to be 1450°C.[5] The first reaction occurred at 1310°C. This implies that during the sintering of β-Si_3N_4 materials with additions of Y_2O_3 and Al_2O_3 as sintering aids a liquid phase already forms at this low temperature. Several experimental studies on the sintering behaviour of β-Si_3N_4 materials have reported indications that a liquid phase is present at this temperature.[6,13] The detection of a second endotherm at 1375°C is interpreted as indicating that the reaction at this higher temperature is due to monotectic melting. The liquids which formed at 1310°C and 1375°C are therefore immiscible. The melting process is thus assumed to occur as follows:

$$S_1 + S_2 + \cdots + S_n \xrightarrow[1310^\circ C]{} S \quad (\text{compounds}) + L_I \xrightarrow[1375^\circ C]{} L_{II}$$

where S represents solid phases and L represents liquid phases.

This result suggests that, because of the possible presence of two compositionally separated glass phases, the crystallisation products from the intergranular glassy phase in comparable β-Si_3N_4 materials will be different for heat treatments below and above 1375°C. In addition the volume of glass in the microstructure should be larger upon heat treatment at temperatures $\geq 1375^\circ C$. Experimental examination of the crystallisation behaviour of the glassy phase in a β-Si_3N_4 material with the same Y_2O_3:Al_2O_3 mass ratio as was used in this work lends support to these results.[14]

The dilatometric softening point (M_g) of the oxynitride glasses was determined to be $\sim 975^\circ C$, which is an increase of $\approx 110^\circ C$ over that of the comparable oxide glass. This increase in M_g is consistent with the structural model for oxynitride glass formation, in which trivalent nitrogen substitutes for bivalent oxygen to produce a more tightly linked glass network.[7,10,15] The softening point indicates the temperature at which reduction of the mechanical strength of β-Si_3N_4 materials can be expected to occur. In this context it is interesting to note that the hot-hardness values of some β'-sialon materials have been found to deteriorate rapidly at temperatures above $\approx 980^\circ C$.[16]

3.4 Crystallisation heat treatments

3.4.1 Nitrogen environment

Devitrification of the glasses occurred within 12 h when heated in N_2 at 1200°C. Table 3 shows the devitrification products which were identified by X-ray diffraction. Yttrium disilicate ($Y_2Si_2O_7$) was the predominant crystalline phase present and YAG was also found in significant quantities. Si_2N_2O was only identified for the higher N compositions. At temperatures $< 1200^\circ C$ no significant crystallisation was observed to occur within 50 h. The X-ray diffractograms from these specimens showed only a few poorly formed crystalline peaks above the glass broadening peak. However, investigation by TEM revealed that the specimens were amorphous except for the presence of impurity crystallites.

Table 3. Devitrification products after heat treatment of oxynitride glasses in nitrogen for 12 h at 1200°C

Glass	*Composition (wt% Si_3N_4)*	*Devitrification product*
5	8	β-$Y_2Si_2O_7$, α-$Y_2Si_2O_7$, $Y_3Al_5O_{12}$
6	10	β-$Y_2Si_2O_7$, α-$Y_2Si_2O_7$, $Y_3Al_5O_{12}$
7	12·5	β-$Y_2Si_2O_7$, $Y_3Al_5O_{12}$, Si_2N_2O
9	15	β-$Y_2Si_2O_7$, $Y_3Al_5O_{12}$, Si_2N_2O

3.4.2 Oxygen environment

The behaviour of the glasses during heat treatment in air was strongly temperature dependent. At temperatures $\leq 1000^\circ C$ the oxidation reaction was relatively slow and only thin outer oxide films formed on specimens heat treated for 50 h. The rate of oxidation increased significantly at 1050°C, the specimens being totally consumed after ≈ 10 h (Fig. 9). Oxidation occurred very rapidly at temperatures $\geq 1100^\circ C$ with only hollow skeletons of the samples remaining after 5 h exposure (Fig. 10). Table 4 details the crystallisation products in the bulk of the specimens as determined by X-ray diffraction. It can be seen from this table that at all temperatures

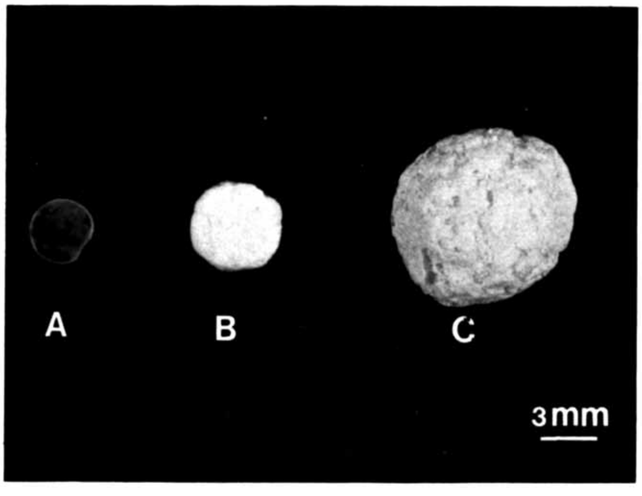

Fig. 9. Increase in volume of glass specimens due to oxidation at 1050°C for (a) 0·5 h, (b) 3 h and (c) 10 h.

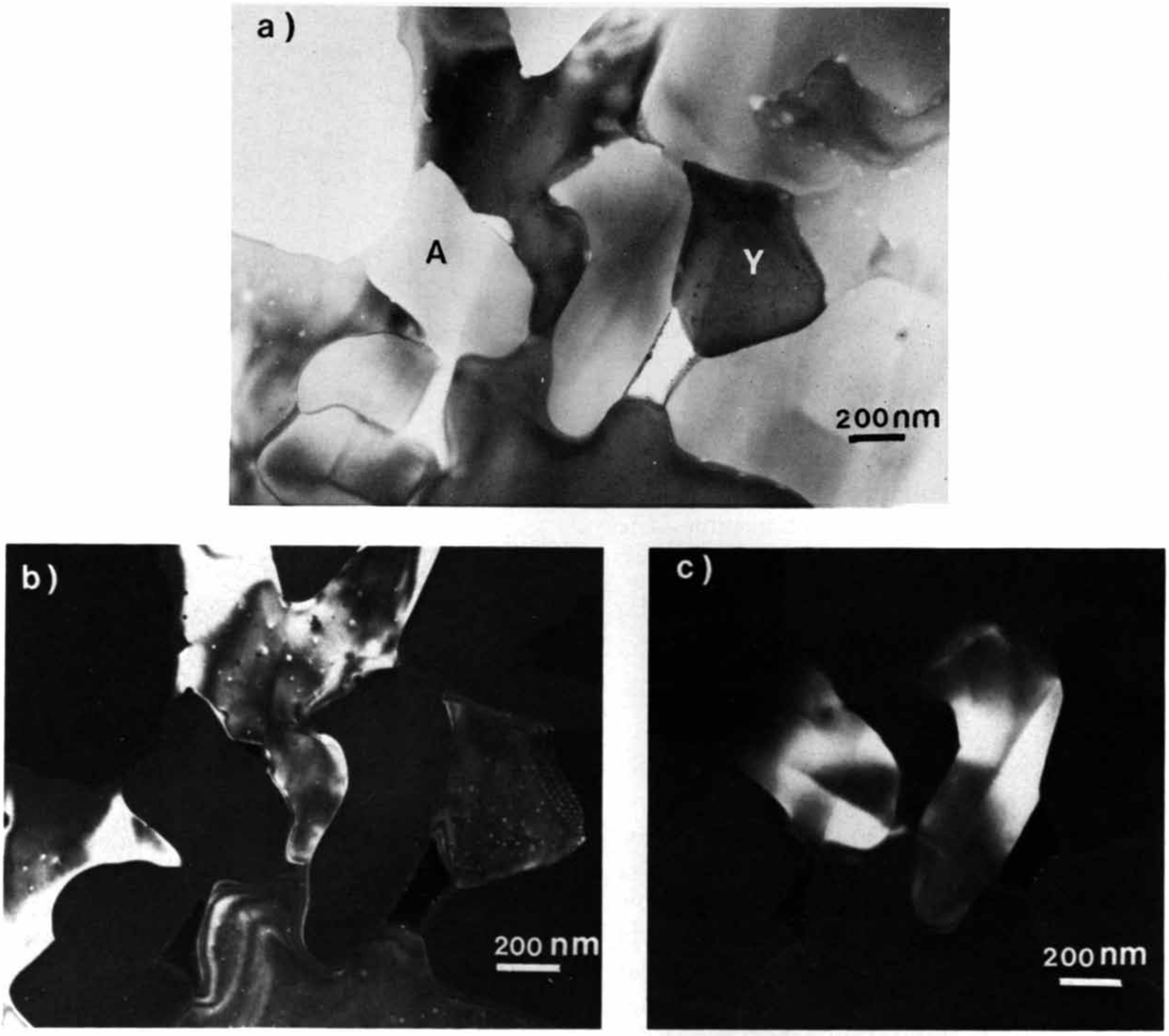

Fig. 10. TEM micrographs of a glass sample which were oxidised for 10 h at 1050°C: (a) bright-field image showing the distribution of the $Y_2Si_2O_7$ (Y) and $Al_5Si_2O_{13}$ (A) crystalline phases; (b) dark-field image of the $Y_2Si_2O_7$ phase showing the presence of small inclusions; (c) dark-field image of the $Al_5Si_2O_{13}$ phase.

examined the main crystalline phases to form were α-$Y_2Si_2O_7$ and mullite ($Al_6Si_2O_{13}$). A TEM micrograph of the microstructure of a sample oxidised for 10 h at 1050°C is shown in Fig. 11. For the longer heat treatment times a nitrogen-containing phase could sometimes be detected.

The heat-treatment experiments in N_2 and air environments imply that homogeneous nucleation of crystalline phases in the glasses during times less than 50 h is most unlikely at temperatures < 1200°C. Of course in β-Si_3N_4 materials, existing grain surfaces may act as heterogeneous nucleation sites. The N_2 experiments were carried out with a view to identifying nitrogen heat-treatment schedules for β-Si_3N_4 materials. The glasses were found to crystallise, forming predominantly $Y_2Si_2O_7$, Si_2N_2O and YAG, following short heat-treatment times at 1200°C. The results indicate the possibility of reducing the volume of the intergranular glassy phase in β-Si_3N_4 materials, by holding the materials for short times at ≈ 1200°C during cooling from the sintering temperature.

Oxidation of the glasses occurred rapidly at temperatures above the glass softening point (i.e. $T > 975$°C) with the formation porosity in the material due to the release of N_2 gas. Although the exact mechanism by which oxygen diffuses through multicomponent silicate glasses is as yet unknown,[17] the high-temperature oxidation of these glasses should occur via the diffusion of oxygen through the glass network. As the softening point of these glasses is ~ 975°C the resistance to oxidation should deteriorate, as observed, at temperatures higher than this because of a decrease in glass viscosity and consequent increase in the rate of diffusion of oxygen. Thus oxidation becomes significant at ~ 1000°C and the microstructural evidence from the early stages of oxidation at 1050°C indicates that as

Table 4. Temperatures, times and phase contents (X-ray diffraction) of glasses containing 8 or 10 wt% Si_3N_4 (addition) that were subjected to heat treatment in air

Temperature (°*C*)	*Time* (*h*)	*Phase content*
900	50	Amorphous
1 000	1–12	Amorphous
1 050	0·5	Amorphous, $Y_2Si_2O_7$,
1 050	3	Amorphous $Y_2Si_2O_7$, $Al_6Si_2O_{13}$
1 050	8–10	$Y_2Si_2O_7$, $Al_6Si_2O_{13}$, occasional N-YAM traces, traces of other unidentified phases, traces of amorphous phase
1 100	1–12	$Y_2Si_2O_7$, $Al_6Si_2O_{13}$ traces
1 200	1–12	$Y_2Si_2O_7$, $Al_6Si_2O_{13}$ traces

oxygen diffuses into the glass, bubbles of N_2 gas evolve below the specimen/air interface (Fig. 12). Since nitrogen can only be incorporated into the glasses under reducing conditions and the equilibrium in the chemical reaction of N solution depends upon the partial pressures this nitrogen will be released under oxidising conditions.[18]

4 Conclusions

(1) Oxynitride glasses were prepared by melting a base mixture of oxides in the weight ratio of $SiO_2:Al_2O_3:Y_2O_3 = 30:17:53$ together with 8–17·5 wt% Si_3N_4 at 1450°C.

(2) Glasses which had been fired for 10 h at 1450°C were transparent. The transparency of these glasses was attributed to the substantial reduction of decomposition reactions which was obtained by using a low firing temperature.

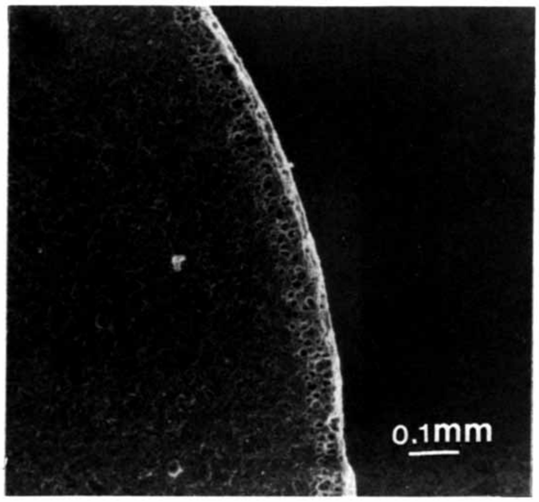

Fig. 11. SEM (secondary electron mode) image of a transverse section of a glass specimen following oxidation at 1050°C for 0·5 h. A thin (up to ~0·2 mm) porous scale surrounds the specimen.

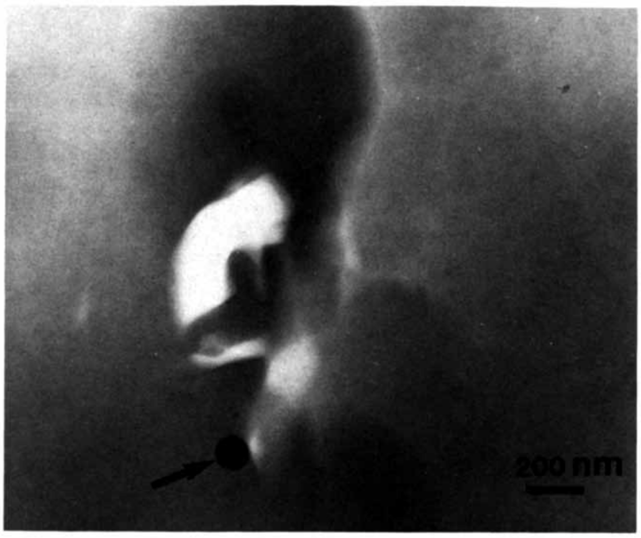

Fig. 12. TEM micrograph of bulk glass after oxidation for 3 h at 1050°C showing a region of heterogeneity associated with an impurity aggregate (arrowed).

(3) Two melting temperatures, 1310°C and 1375°C, were obtained for all composition within the oxynitride glass-forming region. The higher melting temperature is probably due to a monotectic reaction.

(4) For all N-containing compositions the glass softening point (M_g) was 975°C. This is an increase of ≈110°C over that of the corresponding oxide glass.

(5) Virtually full devitrification of the glasses required heat treatment for 12 h in N_2 at 1200°C. The main phases present after crystallisation were $Y_2Si_2O_7$, Si_2N_2O and $3Y_2O_3 . 5Al_2O_3$ (YAG).

(6) The oxynitride glasses oxidised rapidly at temperatures in excess of the softening point (i.e. $T > 975°C$).

(7) Porous oxide 'scales' developed because of the evolution of nitrogen gas during oxidation. The main phases that formed in the scale were α-$Y_2Si_2O_7$ and mullite.

(8) No evidence was found for crystallisation in the glasses heat treated at temperatures $< 1200°C$ in either N_2 or O_2 environments for times up to 50 h.

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