Oxynitride Glasses

DEVELOPMENTS IN OXYNITRIDE GLASSES: FORMATION, PROPERTIES AND CRYSTALLIZATION

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ABSTRACT

Oxynitride glasses are effectively alumino-silicates in which nitrogen substitutes for oxygen in the glass network. They are found at triple point junctions and as intergranular films in silicon nitride based ceramics. The properties of silicon nitride, especially fracture behaviour and creep resistance at high temperatures are influenced by the glass chemistry, particularly the concentrations of modifyer, usually Y or a rare earth (RE) ion, and Al, and their volume fractions within the ceramic. This paper provides an overview of the preparation of M-Si-Al-O-N glasses and outlines the effects of composition on properties. As nitrogen substitutes for oxygen, increases are observed in glass transition (T_g) and dilatometric softening (T_{ds}) temperatures, viscosities, elastic moduli and microhardness. If changes are made to the cation ratios or different rare earth elements are substituted, properties can be modified. The effects of these changes on mechanical properties of silicon nitride based ceramics are discussed.

This paper also outlines new research on M-Si-Al-O-N-F glasses. It was found that fluorine expands the glass forming region in the Ca-Sialon system and facilitates the solution of nitrogen into glass melts. T_g and T_{ds} decreased with increasing fluorine substitution levels, whilst increasing nitrogen substitution resulted in increases in values for these thermal properties. Nitrogen substitution for oxygen caused increases in Young's modulus and microhardness whereas these two properties were virtually unaffected by fluorine substitution for oxygen.

Oxynitride glasses may be crystallized to form glass-ceramics containing oxynitride phases and a brief outline is presented.

INTRODUCTION

Oxynitride glasses were first discovered as intergranular phases in silicon nitride based ceramics[1,2] in which the composition, particularly Al content as well as N content, and volume fraction of such glass phases determine the properties of the silicon nitride. Oxynitride glasses can be formed when a nitrogen containing compound, such as Si_3N_4 (or AlN), dissolves in either a silicate or alumino-silicate liquid at ~1600-1700°C which then cools to form a M-Si-O-N or M-Si-Al-O-N glass (M is usually a di-valent [Mg, Ca] or tri-valent [Y, Ln] cation). In particular, the chemistry of these oxynitride glasses has been shown to control high temperature mechanical properties and ambient fracture behaviour of silicon nitride based ceramics[1-4]. The desire to understand the nature of these grain boundary phases has resulted in a number of investigations on oxynitride glass formation and properties[5-12]

EXPERIMENTAL PROCEDURE

The extent of the glass forming regions in various M-Si-Al-O-N systems (M = Mg, Y, Ca, etc.) has been studied previously[5,7,8] and represented using the Jänecke prism with compositions expressed in equivalent percent (e/o) of cations and anions[5,7] instead of atoms or gram-atoms. One equivalent of any element always reacts with one equivalent of any other element or species. For a system containing three types of cations, A, B and C with valencies of v_A, v_B, and v_C, respectively, then:

Equivalent concentration of A = $(v_A [A])/(v_A [A] + v_B[B] + v_C[C])$,
where [A], [B] and [C] are, respectively, the atomic concentrations of A, B and C, in this case, Si^{IV}, Al^{III} and the metal cation, M, with its normal valency.

If the system also contains two types of anions, C and D with valencies v_C and v_D, respectively, then:

Equivalent concentration of C = $(v_C [C])/(v_C [C] + v_D[D])$,
where [C] and [D] are, respectively, the atomic concentrations of C and D, i.e. O^{II} and N^{III}.

Fig. 1 shows the glass forming region in the Y-Si-Al-O-N system which was studied by exploring glass formation as a function of Y:Si:Al ratio on vertical planes in the Jänecke prism representing different O:N ratios. The region is seen to expand initially as nitrogen is introduced and then diminishes when more than 10 e/o N is incorporated until the solubility limit for nitrogen is exceeded at ~28 e/o N.

Preparation of glasses involves mixing appropriate quantities of silica, alumina, the modifying oxide and silicon nitride powders by wet ball milling in isopropanol for 24 hours, using sialon milling media, followed by evaporation of the alcohol before pressing into pellets. Batches of 50-60g are melted in boron nitride lined graphite crucibles at 1700-1725°C for 1h under 0.1MPa nitrogen pressure in a vertical tube furnace, after which the melt is poured into a preheated graphite mould. The glass is annealed at a temperature close to the glass transition temperature (T_g) for one hour to remove stresses and slowly cooled.

Bulk densities were measured by the Archimedes principle using distilled water as the working fluid. X-ray analysis was used to confirm that the glasses were totally amorphous. Scanning electron microscopy allowed confirmation of this and assessment of homogeneity.

Differential thermal analysis (DTA) was carried out in order to measure the glass transition temperature, T_g, which is observed as the onset point of the endothermic drift on the DTA curve, corresponding to the beginning of the transition range.

The viscosity results presented were obtained from a high temperature "deformation-under-load" (compressive creep) test on cylinders of 10 mm diameter in air between 750 and 1000°C. These have also been compared with results from three point bending tests (bars of dimensions: 25mm x 4mm (width) x 3mm (height) with a span of 21 mm. Viscosity, η, is derived from the relationships between (i) the stress/strain relations in an elastic solid and

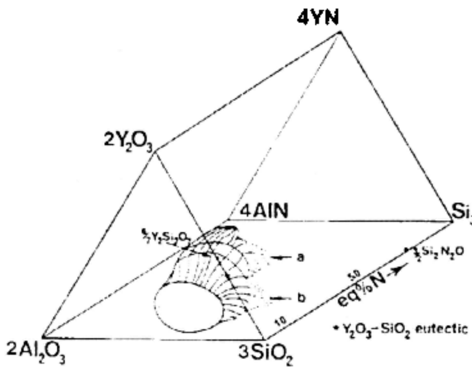

Fig. 1 Glass forming region of the Y-Si-Al-O-N system on cooling from 1700°C[5,7]

(ii) those that relate to a viscous fluid:

$$\eta = \sigma / [2(1+\upsilon)\dot{\varepsilon}] \quad (1)$$

where σ and $\dot{\varepsilon}$ are the applied stress and the creep rate on the outer tensile fibre and υ is Poisson's ratio (taken as 0.5). The results from both types of test show good agreement[5,7,12].

RESULTS AND DISCUSSION

EFFECTS OF NITROGEN ON PROPERTIES

The first systematic studies on the effect of replacing oxygen by nitrogen on properties of oxynitride glasses with fixed cation compositions were reported by Drew, Hampshire and Jack[5,7]. Fig. 2 shows that for all Ca-, Mg-, Nd- and Y- Si-Al-O-N glasses with a fixed cation composition (in e/o) of 28Y: 56Si: 16Al (standard cation composition), incorporation of nitrogen resulted in increases in glass transition temperature (T_g). They also reported that nitrogen increases microhardness, viscosity, resistance to devitrification, refractive index, dielectric constant and a.c. conductivity. In a more extensive study of the Y-Si-Al-O-N system[8], it was confirmed that glass transition temperature (T_g), viscosity, microhardness and elastic moduli all increase systematically while coefficient of thermal expansion (CTE) decreases with increasing nitrogen:oxygen ratio for different series of glasses.

As shown in Fig. 3, values of Young's modulus increase by 15 to 25% as ~17-20 e/o N is substituted for oxygen at fixed cation ratios[8,9]. The coefficient of thermal expansion (α) was found to decrease as N content increased[8] at fixed Y:Si:Al ratios.

Fig. 4 shows the effects of nitrogen content on viscosity for a series of glasses[13] with composition (in e/o) of 28Y:56Si:16Al:(100-x)O:xN (x=0, 5, 10, 18). It can be seen that viscosity increases by much more than 2 orders of magnitude as 18 e/o oxygen is replaced by nitrogen. Similar trends have been reported for other Y-Si-Al-O-N glasses with different cation ratios[12].

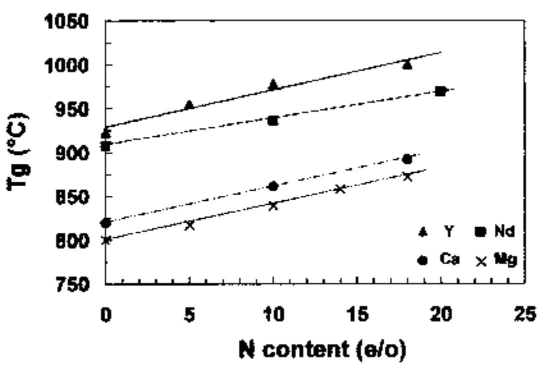

Fig. 2. Effect of N content (e/o) on the glass transition temperature, T_g, of Mg-, Ca-, Nd- and Y-Si-Al-O-N glasses with fixed M:Si:Al: ratio = 28:56:16 (after ref. 5).

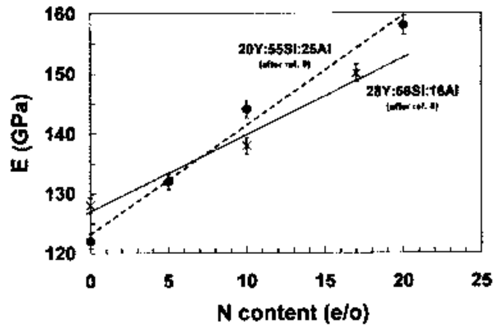

Fig. 3. Effect of N (e/o) on Young's modulus (E) for glasses with fixed Y:Si:Al ratios (data from refs. 8 and 9).

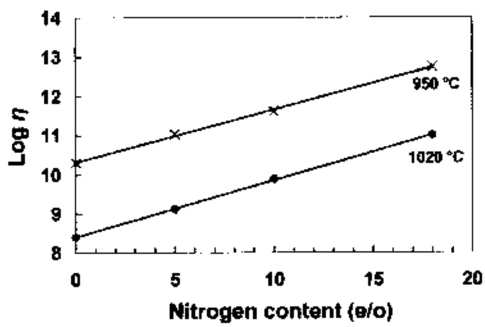

Fig. 4 Effect of N (e/o) on viscosity for glass with fixed Y:Si:Al ratio = 28:56:16 at 950 and 1020 °C (data from ref. 13).

All of these increases in properties are known to be due to the increased cross-linking within the glass structure as 2-coordinated bridging oxygen atoms are replaced by 3-coordinated nitrogen atoms[5-9]. In certain cases, some nitrogen atoms may be bonded to less than three Si atoms, as in:

(i) $\equiv Si - N^{-} - Si \equiv$

or

(ii) $\equiv Si - N^{2-}$

The local charge on the so-called "non-bridging" nitrogen ions is balanced by the presence of interstitial modifying cations (Y, etc.) in their local environment. In the case of silicate glasses, non-bridging oxygen atoms replace bridging oxygen atoms at high modifier contents. In (i) above, while the N atom links two silicon atoms rather than three, it still effectively "bridges" the network ions.

EFFECTS OF LANTHANIDE CATIONS ON PROPERTIES

Fig. 5 demonstrates the effects of different rare earth lanthanide cations on viscosity of Ln-Si-Al-O-N glasses[10] with fixed cation ratio of 28Ln:56Si:16Al. Viscosity changes by ~3 orders of magnitude in the series: Eu<Ce<Sm<Y<Dy <Ho<Er. As found also for other properties, viscosity increases almost linearly with increase in cation field strength, CFS (where CFS = v/r^2, v is valency and r is ionic radius) of the Ln ion. Viscosities of Ln-Si-Al-O-N liquids, containing Sm, Ce, Eu, where the ionic radii are larger than that of Y, are less than those of the equivalent Y-Si-Al-O-N liquids and this will have implications for easier densification of silicon nitride ceramics. However, there will also be consequences for high temperature properties, particularly creep resistance. Liquids and glasses containing Ln cations with ionic radii smaller than Y (Lu, Er, Ho, Dy) have been shown to have higher viscosities than the Y-containing glasses and, in silicon nitride these particular cations will form grain boundary glasses with higher softening temperatures and, hence, better creep resistance.

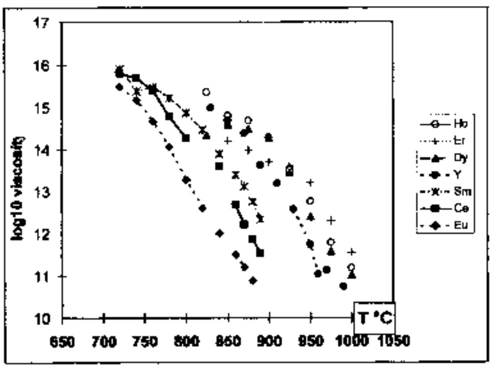

Fig. 5 Effects of Ln cation on viscosity of glasses with cation ratio (in e/o) of 28Ln:56Si:16Al (Ln = Y, Eu, Ce, Sm, Dy, Er, Ho; fixed N = 17 e/o).

The effects on properties of changes in grain boundary glass chemistry, as a result of changes in sintering additives to silicon nitride, can be summarised as follows[12-14]:

(i) As up to 20 e/o N is substituted for oxygen at a fixed cation ratio, viscosity increases by >2 orders of magnitude.

(ii) At a fixed N content, increasing the Y:Al ratio of the glass results in further increases in viscosity.

(iii) Changing the rare earth cation from a larger ion, such as La or Ce, to a smaller cation, such as Er or Lu, increases viscosity by a further 3 orders of magnitude.

Overall, a change of almost 6 orders of magnitude in viscosity can be achieved by increasing N and modifying the cation ratio and the type of rare earth ion. The implications for silicon nitride ceramics are that intergranular glasses containing more N and less Al and smaller RE cations will provide enhanced creep resistance.

CRYSTALLIZATION OF OXYNITRIDE GLASSES

The glass-ceramic transformations in a glass of composition (in e/o) 28Y:56Si:16Al:83O:17N have been studied[15] using both classical and differential thermal analysis techniques and these two methods were found to be in close agreement. Optimum nucleation and crystallisation temperatures were determined in relation to the glass transition temperature. The major crystalline phases present are mixtures of different forms of yttrium di-silicate and silicon oxynitride. Bulk nucleation was observed to be the dominant nucleation mechanism. The activation energy for the crystallisation process was found to be 834kJ/mol.

For a glass of composition (in e/o) 35Y:45Si:20Al:77O:23N, crystallization[8] results in formation of B-phase[16] (Y_2SiAlO_2N), Iw-phase ($Y_2Si_3Al_2(O,N)^{10e/o}$) and wollastonite ($YSiO_2N$) at temperatures below 1200°C while α-yttrium di-silicate ($Y_2Si_2O_7$), apatite ($Y_2Si_3O_{12}N$) and YAG ($Y_3Al_2O_{12}$) are formed at higher temperatures. At relatively low heat treatment temperatures of ~950-1100°C, the nucleation and growth of N-wollastonite ($YSiO_2N$) and the intermediate phases B and Iw are kinetically favoured over that of the more stable equilibrium phases YAG and Si_2N_2O. Further studies on the crystallisation of B and Iw phases in these Y-Si-Al-O-N glasses have been reported[17,18]. The properties of the glass-ceramics exceed those of the parent glasses with values of elastic modulus greater than 200GPa.

PREPARATION AND PROPERTIES OF OXYFLUORONITRIDE GLASSES

Current work has explored a new generation of oxynitride glasses containing fluorine and aims to develop an initial understanding of the effects of composition on glass formation, structure and properties. Fig. 6 shows the glass forming region found for the Ca-Si-Al-O-N-F system[19] with 20 e/o N and 5 e/o F at 1650°C. In the surrounding regions the different crystalline phases observed are also shown. All glasses were dense except for a region of Si-rich compositions where porous glasses were observed.

In the porous glass area of Fig. 6, there are bubbles on the surface in addition to the bubbles (pores) within the bulk of the glasses which is due to SiF_4 loss. Formation of SiF_4 is favored perhaps due to high Si:F ratios (>3) and low Al (6-15 e/o) and Ca (13-25 e/o) contents. In some areas of this glass forming region inhomogeneous and phase separated glasses were found. Effectively, fluorine extends glass formation in the previously known Ca-Si-Al-O-N system. The effect of fluorine addition on the structure of silicate or aluminosilicate glasses has been previously invetsigated[20] and it has been shown that fluorine can bond to silicon as Si-F, to Al as Al-F, and to Ca as Ca-F. Fluorine loss occurs under conditions where Si-F bonds are favoured. The bonding of fluorine to Al prevents fluorine loss as SiF_4 from the glass melt and explains the reduction in the glass transition temperature[20].

The liquidus temperatures for these oxyfluoronitride compositions were compared with data for Ca-Si-Al-O glasses and it was found that the addition of both nitrogen and fluorine reduces the liquidus temperatures of the high silica and alumina compositions by 100-250°C. At higher Ca contents, much greater reductions in liquidus temperatures of about 800°C were found. Fluorine also facilitates the solution of higher amounts of nitrogen (up to 40 e/o N) into glasses compared with the Ca-Si-Al-O-N system[19]. Fluorine has the effect of lowering glass transition temperature in these glasses but has no effect on the elastic modulus or microhardness[21].

CONCLUSIONS

Oxynitride glasses which occur as intergranular amorphous phases in silicon nitride ceramics have been studied to assess the effects of composition on properties such as viscosity which increases by more nearly three orders of magnitude as 18 e/o N is substituted for oxygen. Viscosity generally increases as more Si or Y is substituted for Al but this is a smaller effect than that of nitrogen. A further increase in viscosity of two to three orders of magnitude is achieved by substituting smaller rare earth cations in place of larger ones. The implications for silicon nitride

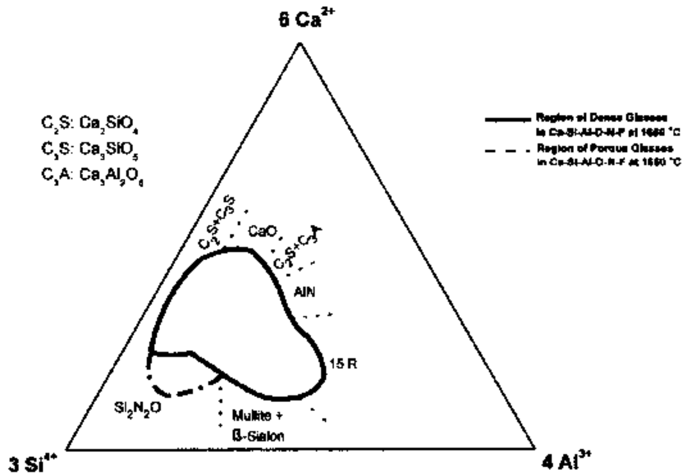

Fig. 6. The glass forming region at 1650°C found in the Ca-Si-Al-O-N-F system at 20 e/o N and 5 e/o F and the adjacent crystalline regions (after ref. 19).

ceramics are that intergranular glasses containing more N and less Al and smaller RE cations will provide enhanced creep resistance.

A new generation of oxynitride glasses containing fluorine have also been investigated. The glass forming region in the Ca-Si-Al-O-N-F system at 20 eq.% N and 5 eq.% F is larger than the glass forming region at 20 eq.% N in the Ca-Si-Al-O-N system. Fluorine expands the range of glass formation in this oxynitride system. Considerable reduction of liquidus temperatures by about 800°C at higher calcium contents occurs. Fluorine facilitates the solution of much higher amounts of nitrogen into the melt than are possible in the Ca-Si-Al-O-N system.

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