JOURNAL OF MATERIALS SCIENCE **28** (1993) 506–512

The transparency of oxynitride glasses

P. KORGUL*, D. P. THOMPSON
Wolfson Laboratory, Materials Division, Department of Mechanical, Materials and Manufacturing Engineering, University of Newcastle upon Tyne, NE1 7RU, UK

Nitrogen-containing glasses in the Mg–Si–Al–O–N and Y–Si–Al–O–N systems were prepared at 1700–1750 °C under 1–5 atm pressure of nitrogen and their microstructures subsequently examined by optical and electron microscopy. The main reason for the diminished transparency of oxynitride glasses was found to be the formation of Fe–Si alloy-based precipitates which, on cooling, decompose into grains of $FeSi_2$ and a smaller number of grains of silicon. These "precipitates" also contain other metals (chromium, nickel, etc.) and act as heterogeneous nucleation centres for decomposition of the melt. It is therefore suggested that the best way of producing transparent nitrogen glasses is to use starting materials of extremely high purity.

1. Introduction

Interest in oxynitride glasses has stemmed mainly from the fact that they occur in the grain boundaries of silicon nitride-based engineering ceramics and play a significant role in determining the high-temperature properties [1–5]. However, attempts to saturate oxide glasses with nitrogen were made several years before the present interest in nitrogen ceramics [6]. The introduction of nitrogen into oxide glasses increases the viscosity and the devitrification temperature [7] and also improves mechanical properties such as hardness and elastic modulus [4]. Unfortunately, compared to oxide glasses, nitrogen-containing glasses are of limited transparency, having colours varying between greyish-blue and almost black [7]. The blackness of oxynitride glasses has been the subject of many investigations [8–11] but this has not led to significant progress being made towards the production of fully transparent glasses with high nitrogen contents. The most commonly discussed reason for the blackening of oxynitride glasses is precipitation of silicon [8, 9], which is assumed to result from the decomposition of Si_3N_4 [12] or from the reaction of Si_3N_4 with SiO_2 [8]. To prevent this, two methods have been suggested, namely preparation at high nitrogen pressures (1.6 MPa) [8], or substitution of Si_3N_4 by AlN as the starting source of nitrogen [8, 11]. Despite evidence provided by thermodynamic calculations and sintering experiments on Si_3N_4-based materials [13] indicating that higher nitrogen pressures should suppress the decomposition of Si_3N_4, Messier and Deguire [8] concluded that it is not effective in preventing silicon precipitation in yttrium sialon glasses. However, they claimed to produce fully transparent glasses by AlN substitution for Si_3N_4.

Another problem also claimed to be related to the decomposition of silicon nitride [9] is frothing during glass melting. It has been suggested that frothing can be suppressed by the addition of 5 wt% Si powder to the starting mix. However, it must be pointed out that although additions of silicon might limit frothing, this also creates a number of silicon inclusions in the final product, reducing its transparency.

The aim of the present work was to explore reasons for the darkening of oxynitride glasses and, if possible, devise methods of producing transparent glasses containing substantial levels of nitrogen.

2. Experimental procedure

Preparation of oxynitride glasses was carried out using mixtures of the following powders:

SiO_2 (quartz, TSL, Wallsend), SiO_2 (precipitated, acid washed, BDH Chemicals Ltd, Poole), MgO (analar grade BDH Chemicals Ltd, Poole), Al_2O_3 (A15, ALCOA), Si_3N_4 (Grade LC10, Starck-Berlin, Goslar, Germany), AlN (Grade A, Starck Berlin, Goslar, Germany), Y_2O_3 (99.9% pure), Y_2O_3 (Berkshire Ores and Chemicals Ltd, 99.9% pure), Si_3N_4 (Toyo Soda Manufacturing Ltd, Japan).

Most of the samples were prepared using SiO_2 in the form of crystalline quartz but a few runs were also carried out using precipitated silica to see if the additional impurities had a detrimental effect on the final product. The hypothesis [8] that AlN substitution for Si_3N_4 had a beneficial effect was also examined. Powder mixes with the same nominal composition but with all the silicon nitride replaced by aluminium nitride were prepared and fired under the same conditions as those containing only Si_3N_4 as the nitrogen source. Starting compositions are listed in Table I. To

---

*Present address: School of Materials, University of Sheffield, Mappin Street, Sheffield, S1 3JD, UK.

0022–2461

TABLE I Examples of compositions and melting conditions for sialon glasses

Sample	Composition (wt %)	Melting conditions
MG 2-2	31.3 MgO 41.6 SiO_2 11.3 Si_3N_4 (Starck) 15.8 Al_2O_3	1700 °C, 1 h, 0.1 MPa N_2, tungsten furnace
Y6-1P	55.8 Y_2O_3 24.4 SiO_2 8.4 Si_3N_4 (Starck) 11.4 Al_2O_3	1700 °C, 1 h, 0.34 MPa N_2, tungsten furnace
Y6-12	55.8 Y_2O_3 24.4 SiO_2 8.4 Si_3N_4 (Toya Soda) 11.4 Al_2O_3	1720 °C, 2 h, 0.5 MPa N_2, tungsten furnace
Y8-1P5	45.2 Y_2O_3 28.6 SiO_2 5.8 Si_3N_4 (Starck) 20.4 Al_2O_3	1700 °C, 1 h, 0.5 MPa N_2, tungsten furnace

avoid additional contamination by metallic elements, powders were wet mixed in an agate mortar and after drying, the mixtures were pelletized by isotatic pressing. Usually the pellets were placed in an alumina crucible lined with boron nitride and fitted with a boron nitride lid, and then fired in a tungsten element furnace at 1700–1750 °C in a nitrogen atmosphere. The holding time at temperature varied from 5 min to 2 h. The effect of higher nitrogen pressures in the range 1–5 atm was also examined. A cooling rate of about 250 °C min^{-1} in the temperature range 1750–1000 °C was sufficient to prevent crystallization.

For optical estimation of glass transparency, transmission optical microscopy was used and sections about 2.5 mm thick were cut from each specimen and polished using SiC papers and diamond paste. Thin sections for transmission electron microscopy (TEM) were prepared by mechanical polishing followed by ion beam milling.

3. Results

3.1. Effects of time and temperature

After only 5 min at 1700 °C all samples of melted glass were very dull in appearance. Their transparency improved substantially when the holding time at the melting temperature was extended to 15 min. Glass transparency increased still further when samples were kept at the melting temperature for 1 h, but longer times did not result in marked improvements. Holding times of 30 min or more resulted in the production of glass samples with two distinct zones, especially in the case of samples in which silicon nitride was used as the source of nitrogen. The upper part of the samples was always more transparent than the lower part, suggesting gravitational segregation of the light-scattering centres. This observation implies that longer melting times may lead to the production of glasses with improved transparency.

The effects of time and temperature are to a certain extent strongly interrelated. By increasing the temperature it is possible to speed up the melting process but, as discussed later, there are substantial problems of melt decomposition with consequent weight loss or frothing as shown by experiments carried out at temperatures above 1750 °C.

Generally weight losses from both magnesium and yttrium sialon glasses melted at 1700–1750 °C were relatively low. For example, for melting times up to 1 h, weight losses were usually below 1 wt% and only slightly above 1 wt% for samples held for 2 h at the melting temperature. Weight losses for magnesium-containing samples were always somewhat higher than yttrium-containing equivalents.

To understand more fully the factors controlling melt decomposition, attempts were made to produce glasses under conditions which would certainly lead to substantial decomposition of the melt. For this purpose samples were melted at 1800–1830 °C in an essentially reducing environment. Weight losses were very high (up to 15 wt%) and, as a result, parts of the samples were crystalline. The remaining glassy regions were dark as before.

3.2. Effects of nitrogen pressure

The tungsten element sintering furnace used for the preparation of glass samples was redesigned in such a way as to allow melting under nitrogen at pressures up to 0.5 MPa. According to thermodynamic calculations discussed later, increased nitrogen pressure should inhibit decomposition of the melt and hence limit weight losses. Indeed it was observed that samples melted at 0.5 MPa nitrogen sustained, as anticipated, smaller weight losses compared to samples prepared under ~0.1 MPa nitrogen. However, no distinct improvement in glass transparency was detected as the nitrogen pressure was increased. This conclusion may not be entirely correct and may only reflect the limitations of using visual methods for assessing glass transparency.

3.3. Effect of raw materials

For the majority of glass samples prepared and examined in the present work, Starck LC10 silicon nitride powder was used as the source of nitrogen. The ~2.5 mm thick slices prepared from these glasses were never fully transparent. Samples of the same compositions and produced under identical conditions but with aluminium nitride replacing silicon nitride showed no noticeable difference in transparency. However, an experiment in which Starck silicon nitride was substituted by Toyo Soda high-purity silicon nitride produced a much more transparent glass. Most magnesium and yttrium sialon glasses prepared and examined had the same nitrogen content in the starting mix (~6.5 at %). It was observed that, in general, yttrium-containing oxynitride glasses melted under the same conditions as magnesium-based samples were more transparent. As discussed later, these differences are probably related to the different liquid formation temperatures, differences in the properties of the liquid phase and also the slightly different morphologies of the precipitates. Experiments with quartz and precipitated silica showed that under the same melting conditions, samples containing quartz sustained smaller weight losses. The transparency of the glass was certainly improved using high-purity quartz powder.

3.4. Light microscopy observations

Transmission optical microscopy was used both for the examination of polished bulk samples as well as polished thin slices. The latter was found to be a particularly useful technique for assessing blackness. Fig. 1 shows some typical examples; a high density of precipitates in the micrograph always correlates with the sample appearing dark under visual examination. Thus the glass shown in Fig. 1a is much darker than that shown in Fig. 1b. This clearly demonstrates that the transparency of oxynitride glasses is determined by the number of precipitates and the volume they occupy.

3.5. Transmission electron microscopy

Transmission electron microscopy including energy dispersive spectroscopic (EDS) microanalysis was used to characterize the precipitates observed by light microscopy. It was found that the precipitates in the most transparent sample of yttrium oxynitride glass were almost spherical with diameters somewhat below 1 µm (Fig. 2). In the centre they consisted of a number of grains most of which were identified by electron diffraction methods as tetragonal FeSi$_2$. The other crystalline phase present in the precipitates is silicon. This correlates with EDS analysis which showed the presence of silicon, iron and small quantities of chromium in each precipitate. Occasionally some precipitates also contained small amounts of nickel, titanium and other metals.

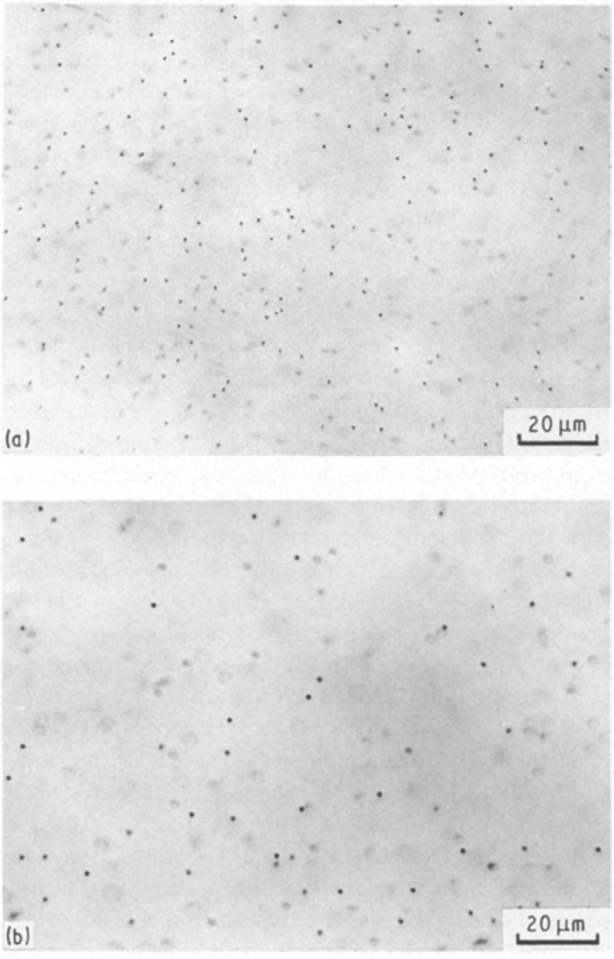

Figure 1 Typical microstructure of a yttrium sialon glass as observed by transmission optical microscopy. (a) Y8-1P5, (b) Y6-12.

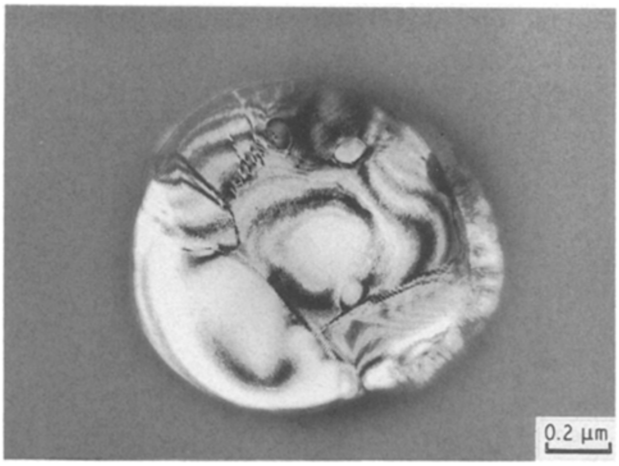

Figure 2 Transmission electron micrograph of a typical precipitate in Y6-12 sialon glass.

As shown by electron diffraction studies, the grains of FeSi$_2$ within the precipitates commonly exhibited the following orientation-relationship with each other: $(0\,0\,1)_1 \| (1\,0\,0)_2$, $(1\,0\,0)_1 \| (0\,0\,1)_2$. It was also observed that silicon grains were sometimes twinned on $\{111\}$ planes with $\langle 110 \rangle$ as the twinning direction and exhibited the following orientation relationship with grains of FeSi$_2$: $(001)\mathrm{FeSi}_2 \| (1\,0\,0)_{\mathrm{Si}}$, $[1\,1\,0]\,\mathrm{FeSi}_2 \| [0\,1\,1]_{\mathrm{Si}}$.

On the periphery of the precipitates a relatively thin layer existed consisting of very fine crystalline regions, showing a strong texture (Fig. 2). Combined electron diffraction and EDS microanalysis studies suggested that these are very fine crystallites of SiO$_2$. In the samples melted at 1800–1830 °C the precipitates were larger than those in samples prepared at 1700–1750 °C. Each precipitate has a relatively small core (Fig. 3) and a thick outside layer of low-density material. Moreover, the cores of most precipitates are very

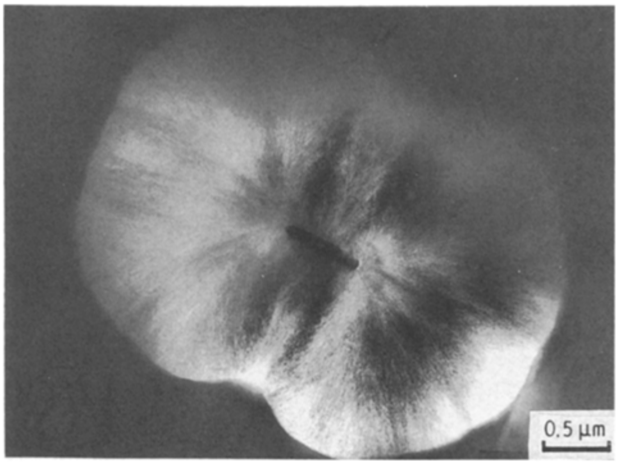

Figure 3 Transmission electron micrograph of the most common precipitate in Y6-1001 sialon glass (composition Y6 in Table I). Melting was carried out at 1830 °C for 35 min at 0.1 MPa N$_2$.

regular in shape resembling parallelepipeds while cores of precipitates formed at lower temperatures were approximately spherical. More importantly, the composition of most of the cores examined by EDS methods were markedly different from those observed in samples prepared at 1700–1750 °C. All regularly-shaped cores contained a very high proportion of titanium, and electron diffraction patterns indicated the presence of TiO_2 (rutile). In some cores these regular particles were accompanied by small grains of iron silicide. Also, the density of material immediately surrounding the core was different in the two cases. In glasses prepared at 1700–1750 °C this layer contained silicon (elements lighter than sodium could not be analysed using the system available), whereas in glasses produced at 1800–1830 °C, EDS microanalysis also indicated a considerable proportion of yttrium and aluminium. The non-spherical shape of the cores influenced the shape of the surrounding layer of low-density material (Fig. 3) which showed faster growth in places where the core radius of curvature was smallest.

Precipitates in magnesium oxynitride glasses are more numerous (Fig. 4) and their shapes are more complex (Fig. 5) than in equivalent yttrium-based glasses. The majority of precipitates consisted of two crystalline end regions surrounded and linked together by low-density material with cavities on the central axis. EDS analysis showed that this low-density material contained only silicon. On both TEM images (Fig. 5) and electron diffraction patterns, the preferred orientation of small crystallites is clearly visible and because of this and the very small crystallite size, the identification of the phase or phases present in those areas is difficult. The information obtained so far suggests that it is some form of SiO_2. Other noticeable features observed in TEM are the above mentioned cavities, the shape of which together with the texture of the material in the region linking the two ends (Fig. 5) seems to indicate that the cavities and the low-density material are strongly associated with the movement of the precipitates through the liquid phase during melting.

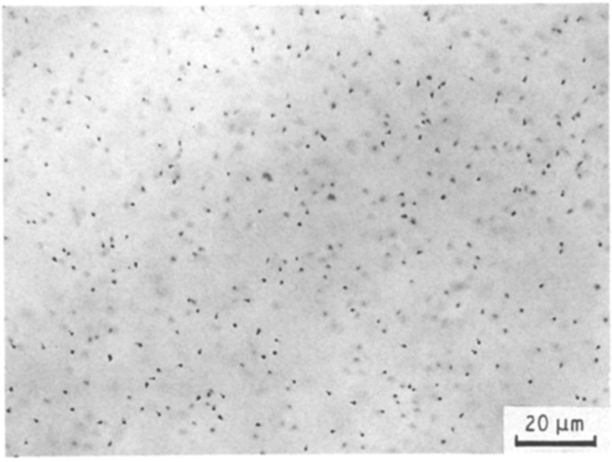

Figure 4 The microstructure of magnesium sialon glass MG2-2 (Table I) as observed by transmission optical microscopy.

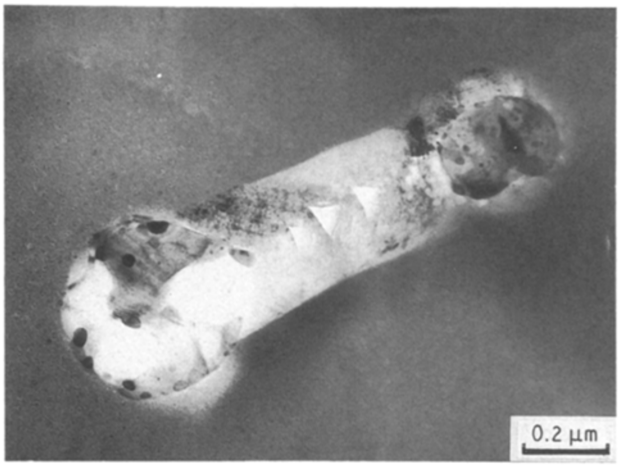

Figure 5 Transmission electron micrograph of a typical precipitate in MG2-2 sialon glass.

4. Discussion

Preparation of oxynitride glasses, although in principle very simple, becomes rather difficult if the objective is to produce a dense and fully transparent product. Common methods of oxynitride glass production consist of mixing suitable powders, pelletizing and firing usually in a furnace with tungsten or graphite heating elements. The temperature of glass melting in sialon-based systems may vary from 1550 °C to, in extreme cases, 1850 °C. The lower limit is imposed by the temperature at which the first liquid is formed [2] and of course somewhat higher temperatures are needed to obtain a homogeneous product, particularly if the chosen composition does not have the lowest melting point in the system under examination. The upper limit corresponds roughly to the decomposition temperature of silicon nitride under 0.1 MPa nitrogen.

Even in the most commonly used temperature range (1700–1750 °C), there is a common misconception that the decomposition of silicon nitride is responsible for the formation of silicon precipitates in the glass [8, 9]. From available thermochemical data [14] it can be estimated that silicon nitride will decompose at ~1880 °C, that is, silicon nitride at that temperature will be in equilibrium with pure silicon (of unit activity) and nitrogen at 1 atm pressure (Fig. 6). If, for some reason, the activity coefficient of silicon is less than one, the decomposition of silicon nitride at 1850 °C, or indeed any other temperature, could still be prevented by increasing the pressure of nitrogen in the furnace. For example, to prevent the decomposition of silicon nitride at 1850 °C when the activity of silicon is about 0.1, the pressure of nitrogen should be increased to ~3.2 MPa. Using similar arguments and assuming that the raw materials do not contain free silicon it is possible to show that silicon nitride can be unstable at temperatures even below 1200 °C (at very low partial pressures of nitrogen), but at such a low temperature the kinetics of decomposition are very slow. Because the activity of silicon nitride is affected by interaction with other elements, their presence in the powder mixture critically influences the decomposition of silicon nitride. The role of impurities in the decomposition of oxynitride glasses is discussed in

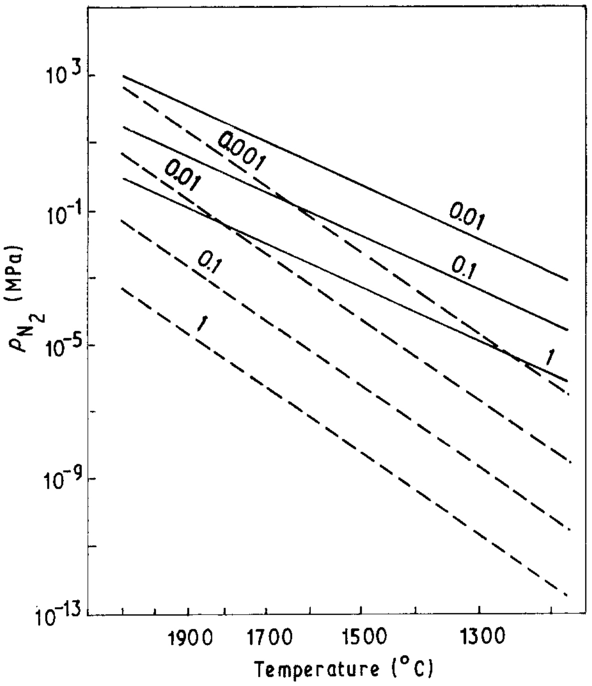

Figure 6 Comparison of partial pressures of nitrogen necessary to prevent decomposition of AlN and Si_3N_4 at different activities of (- - -) aluminium and (—) silicon (based on JANAF data [14]).

some detail below because, as the present results show, the darkening of those glasses is caused by the formation of rather complex precipitates. The origin of these precipitates must be associated with the impurities present in the raw materials and/or impurity pick-up during powder processing and melting of the glass. Among the elements usually present as impurities in the raw materials used for oxynitride glass preparation, iron is probably the most common and belongs to the group of metal oxides which readily oxidize silicon nitride [15] at quite low temperatures. Iron in the starting materials or introduced during powder processing might be in the form of oxides which can react with silicon nitride according to any of the following reactions

$$Si_3N_{4(s)} + 6FeO_{(s)} \rightarrow 3SiO_2 + 6Fe + 2N_{2(g)} \quad (1)$$

$$Si_3N_4 + 2FeO \rightarrow SiO_2 + 2FeSi + 2N_{2(g)} \quad (2)$$

$$Si_3N_4 + FeO \rightarrow SiO + FeSi_2 + 2N_{2(g)} \quad (3)$$

These are only a few examples of possible reactions of Si_3N_4 and FeO; if the iron is present as Fe_3O_4 or Fe_2O_3, the possible reactions with silicon nitride are very similar.

The temperature at which iron oxides start to oxidize silicon nitride effectively is not known, but thermodynamic data (Fig. 7) indicate that there is a driving force for oxidation even at room temperature. In addition, it is important to note that iron oxides melt well below the temperature range used for oxynitride glass preparation and the reaction of the liquid phase with solid silicon nitride would be substantially accelerated compared to all solid–solid reactions. In this context it is important to remember that small iron additions to silicon powder have been used for many years to enhance the kinetics of nitridation [16]. This would imply that the negative effects associated with the presence of iron must start to dominate Si_3N_4 decomposition at higher temperatures than those used for nitriding silicon powder. It is believed that the FeSi and $FeSi_2$ (formed by Reactions 2 and 3 above) can be enriched in silicon by further decomposition of silicon nitride. The extent to which the precipitates can be saturated with silicon is probably time and temperature dependent. It is expected that for longer melting times more silicon would go into the precipitates until an equilibrium is established. On the one hand, as the concentration of silicon in the Fe–Si alloy increases, the effect of iron on the activity coefficient of silicon decreases, particularly for compositions with less than 70 at % Fe [17]; on the other hand, the growth of Fe–Si alloy precipitates is probably inhibited by a layer of low-density material outside the silicide core. This hypothesis is supported by the results of TEM examination where coexistence of the $FeSi_2$ and silicon grains within one precipitate in the glass was very often observed. The results of the present work on oxynitride glasses are supported by observations made on sintered silicon nitride-based materials where precipitates of iron silicides are also detected [18].

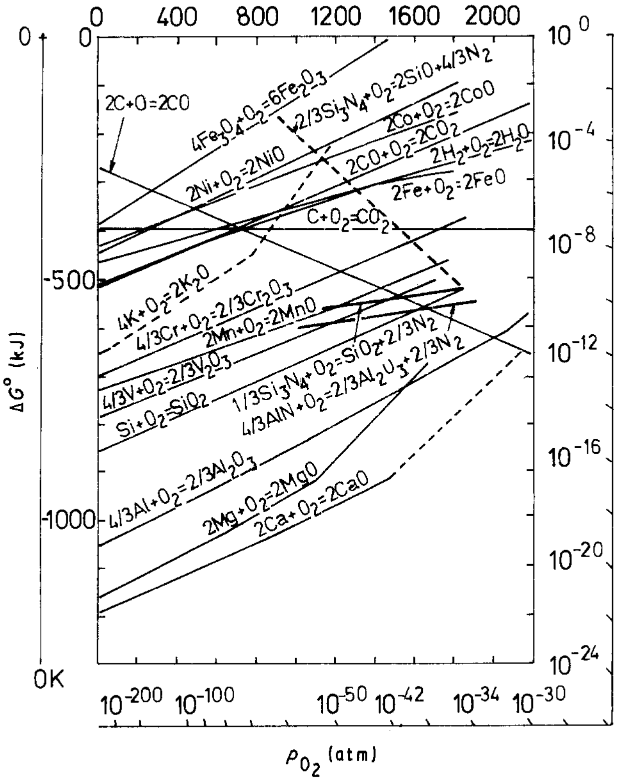

Figure 7 The Gibbs energy of formation of some metal oxides as a function of temperature (mostly taken from [19]). Data for the Gibbs free energy for oxidation of Si_3N_4 to SiO and SiO_2 and AlN to Al_2O_3 are included.

In the light of the above discussion the role of aluminium nitride substitution for silicon nitride does not seem to be as clear as suggested previously [8]. The samples prepared using AlN were slightly more homogeneous but their transparency was similar to that of equivalent silicon nitride-containing glasses. Thermochemical data [14] show that under 0.1 MPa nitrogen, aluminium nitride is considerably more stable than silicon nitride (Fig. 6). Assuming however that the activity coefficient of aluminium is lowered to

0.01 then, under 0.1 MPa nitrogen, aluminium nitride will start to decompose at around 1850 °C. This indicates that under the same temperature and pressure of nitrogen the activity of aluminium required to prevent the decomposition of aluminium nitride is about two orders of magnitude lower than the activity of silicon necessary to stabilize silicon nitride. Considering the composition of glasses under examination it is clear that the activity coefficient of aluminium is usually maintained at a higher level than 0.01.

However, if the emphasis is altered from that of pure decomposition to decomposition induced by reaction between nitrogen-rich compounds and oxides of impurities it can be shown that substitution of silicon nitride by aluminium nitride does not bring any obvious benefit. By plotting the free energy of the oxidation reactions

$$Si_3N_4 + 3O_2 \rightarrow 3SiO_2 + 2N_2 \qquad (4)$$

$$4\,AlN + 3O_2 \rightarrow 2Al_2O_3 + 2N_2 \qquad (5)$$

on the Ellingham diagram shown in Fig. 7 [19] it can be clearly seen that the same oxides which oxidize silicon nitride will have an even stronger tendency to oxidize aluminium nitride.

It is expected that under the conditions used for glass preparation, reactions which are possible in the systems under examination would not produce precipitates containing a substantial proportion of aluminium, because aluminium can be oxidized even by SiO_2

$$4Al + 3SiO_2 \rightarrow 2Al_2O_3 + 3Si \qquad (6)$$

Once a homogeneous liquid phase is formed there would be no difference between melts prepared from silicon nitride and those obtained using aluminium nitride except that the type of impurities and their concentration might be different.

The impurity precipitates which are believed to form mainly during melting would now act as the heterogeneous centres for further decomposition. There are at least two reasons for this. Firstly at certain stages in the melting process there will be some difference in the activity of silicon in the precipitate compared to the bulk of the material. Secondly, decomposition of the melt requires the removal of a certain amount of nitrogen and silicon monoxide at the free surfaces of the sample or by the formation of nitrogen-containing bubbles inside the melt. Formation of such bubbles via a homogeneous nucleation process is very difficult while heterogeneous nucleation is considerably easier [20]. Moreover, it is possible that in the present case at least some of the nuclei had formed even before melting was completed.

The effectiveness of the precipitates as the centres for melt decomposition is well illustrated by experiments carried out at different temperatures. At 1700 °C the silicate cores are relatively large and are encompassed by a thin layer of low-density material, which is believed to accommodate nitrogen and/or SiO released during the reaction. This layer, in the case of yttrium-containing oxynitride glasses very often covers only part of the interface between the silicide precipitates and the melt.

As the temperature of glass preparation is raised, the thickness of the low-density material layer increases considerably and the core is completely surrounded by it. This is particularly clearly visible in yttrium sialon glasses prepared at temperatures above 1800 °C, where the cores are very small compared to the overall size of the precipitate.

The differences in appearance of the precipitates in magnesium sialon glasses compared to those in yttrium-containing glasses are probably related to three factors. Firstly yttrium and magnesium differ in chemical and physical properties and in relation to that a liquid phase is formed in the Mg–Si–Al–O–N system at temperatures about 100 °C lower than the yttrium sialon system [2], secondly the density of the glasses, although variable in composition, is generally lower for magnesium oxynitride glasses. Typical values measured at room temperature for two compositions with the same initial nitrogen content were 2.81 $g\,cm^{-3}$ for Mg–Si–Al–O–N glass and 3.89 $g\,cm^{-3}$ for Y–Si–Al–O–N glasses. Thirdly, the viscosity of magnesium oxynitride glasses is considerably lower than that of yttrium-containing glasses [21].

Assuming that the density of a molten Fe–Si alloy is intermediate between that of $FeSi_2$ and silicon and considering the lower density and viscosity of Mg–Si–Al–O–N liquids, it is expected that Fe–Si droplets would "move" through a magnesium sialon liquid with greater ease than similar droplets ("precipitates") in an yttrium sialon melt. It might, therefore, be concluded that given a long enough holding time at the temperature of melting it should be possible to remove precipitates at least from magnesium sialon melts by gravitational means. Unfortunately, within the times used in the present work, such "purification" was not achieved, although effects of gravitational segregation were always observed in 15 mm thick samples of yttrium and magnesium sialon glasses in which the top of the sample was always more transparent than the bottom.

As discussed above, differences in densities between the melts and the cores of the "precipitates" might suggest that gravitational segregation of impurities would be easier in the case of magnesium sialon melts. However, examination of glass samples has shown that, in fact, magnesium sialon glasses are somewhat less transparent than their yttrium equivalents. As shown by TEM, the ratio of the volume of "low-density material" to the volume of the core was always larger for magnesium sialon glasses melted at the same temperature. This suggests that at the temperature of melting the overall density of the precipitates for magnesium sialons might be closer to the density of the bulk of the material than calculated from a consideration of the core alone.

The large volume of low-density material around the silicide cores in magnesium sialon glasses together with the higher weight losses indicate magnesium sialon glasses melt/decompose more easily than yttrium sialon melts, probably because of their lower viscosity and also as the result of their lower stability in a silicide environment as suggested by the high susceptibility of silicon nitride-based materials sintered with magnesia to surface pitting by localized sources of iron [22]. Similar material produced with Y_2O_3 addition showed better resistance to surface attack by iron [22].

5. Conclusions

The transparency of oxynitride glasses is determined by the concentration of small, black precipitates dispersed uniformly throughout the bulk of the glass. These consist mainly of $FeSi_2$ and silicon, and act as sinks for the other trace metal impurities present in the starting ingredients. The precipitates form by reaction between iron/iron oxide impurities (present in the starting nitride powders) at ~ 1200 °C, and at increasing temperatures these molten metallic globules catalyse further decomposition of Si_3N_4 and also promote some crystallization of SiO_2 in their immediate environment. Substitution of AlN for Si_3N_4 did not result in the production of more transparent glasses, because iron impurity in the AlN performs equivalent chemical reactions at high temperatures which still produces $FeSi_2$/Si-based precipitates.

Nitrogen glasses of high transparency can be prepared using either starting materials of essentially zero impurity metal content or by melting large batches for longer times to allow gravity segregation of the precipitates and subsequently discarding the lower part of the resulting glass. The technology associated with the production of these glasses requires exceptional experimental care to avoid pick up of metallic impurities. Indeed, it is noteworthy that all the glasses prepared in this study contained less than 0.05% total metal impurities and yet the samples were very obviously black to the naked eye and totally unsuitable for bulk optical applications.

Acknowledgement

Financial support from SERC (for P. K.) is gratefully acknowledged.

References

1. K. H. JACK, "Phase Diagrams": Materials Science and Technology, Vol. V, edited by A. M. Alper (Academic Press, New York, 1978) p. 241.
2. *Idem*, Proceedings "Science of Ceramics", Vol. II, (1981) p. 125.
3. *Idem*, Proceedings, NATO Advanced Study Institute, "Nitrogen Ceramics", Canterbury (1976).
4. R. E. LOEHMAN, "Treatise on Materials Science and Technology", Vol. 26 (1985) p. 119.
5. D. R. MESSIER, *Rev. Chim. Mineral.* **22** (1985) 518.
6. H. O. MULFINGER. *J. Amer. Ceram. Soc.* **49** (1966) 462.
7. S. HAMPSHIRE, R. A. L. DREW and K. H. JACK, *Phys. Chem. Glasses* **26** (5) (1985) 182.
8. D. R. MESSIER and E. J. DEGUIRE, *J. Amer. Ceram. Soc.* **67** (1984) 602.
9. S. BAIK and R. RAJ, *ibid.* **68** (1985) C168.
10. R. WUSIRIKA, *ibid.* **67** (1984), C232.
11. R. E. LOEHMAN, *ibid.* **62** (1979) 491.
12. C. GRESKOVICH and S. PROCHAZKA, *ibid.* **64** (1981) C96.
13. G. K. WATSON, T. J. MOORE and M. L. MILLARD, *ibid.* **67** (1984) C208.
14. D. R. STULL and H. PROPHET (eds). JANAF Thermochemical Tables, 2nd Edn, (US Government Printing Office, Washington DC, 1971).
15. A. V. PASTO, *J. Amer. Ceram. Soc.* **67** (1984) C178.
16. S. M. BOYER and A. J. MOULSON, *J. Mater. Sci.* **13** (1978) 1637.
17. J. F. ELLIOTT, M. GLEISER and V. RAMAKRISHNA, "Thermochemistry for steelmaking", Vol. II (Addison Wesley, Reading, 1963).
18. C. CHATFIELD, T. EKSTRÖM and M. MIKUS, *J. Mater. Sci.* **21** (1986) 2297.
19. F. D. RICHARDSON and J. H. E. JEFFES, *J. Iron Steel Inst.* **160** (1948) 261.
20. J. J. HAMMEL, in "Advances in Nucleation and Crystallization in Glass", edited by L. L. Hench and S. W. Freiman, Special Publication no. 5 (The American Ceramic Society, Westerville, 1971).
21. R. A. L. DREW, S. HAMPSHIRE and K. H. JACK, in "Special Ceramics 7", edited by D. Taylor and P. Popper, Proceedings of the British Ceramic Society No 31 (1981) p. 119.
22. F. F. LANGE, *J. Amer. Ceram. Soc.* **61** (1978) 270.

Received 16 January
and accepted 4 February 1992