SYNTHESIS REPORT

CONTRACT No. BRE2-CT92-0272

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PROJECT No. 5687

TITLE: OPTIMISATION OF NUCLEATION AND CRYSTALLISATION IN OXYNITRIDE GLASSES TO DEVELOP NOVEL GLASS-CERAMICS FOR ADVANCED THERMOMECHANICAL AND OPTICAL APPLICATIONS.
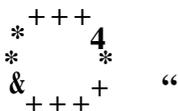
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STARTING DATE   :01.10.92   I)URATION:39 MONTHS

20 MPLETION DATE: 31-12-95

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OPTIMISATION OF NUCLEATION AND CRYSTALLISATION IN OXYNITWDE GLASSES TO DEVELOP NOVEL GLASS-CERAMICS FOR ADVANCED THERMOMECHANICAL AND OPTICAL APPLICATIONS

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Abstract
Silicon nitride based ceramics contain oxynitride glass phases at grain boundaries which can impair subsequent high temperature properties. Study of the fcxrnation and characteristics of oxynitride based glasses containing various rare earth cations have been carried out and the effects of nitrogen and the cations on properties such as glass transition temperature, Young's modulus, viscosity, thermal expansion coefficient etc., are reported. Structural analyses were made using NMR, Raman Scatternng Spectroscopy, EXAFS and Neutron Diffraction. Classical and thermal analysis methods of optimizing the nucleation and crystal growth temperatures have been achieved using two stage heat treatment sequences and the process parameters controlling the preparation of oxynitride glass-ceramics identified.

Introduction
Glass-ceramics are an important class of materiak that are formed by melting, shaping and subsequent controlled crystallisation of glasses. The possibility of producing gfass-ceramics containing refractory oxynitride crystalline phases with particular beneficial properties has led to further studies of oxynitride glass formation and properties.

Originally, small concentrations of nitrogen in oxide glasses were reported to increase their softening temperature, viscosity and resistance to devitrification &oehman, 1980; Drew et al., 1981]. Most previously reported work has concentrated on glasses in the Y-Si-Al-O-N system [Hampshire et al., 198A Messire and Deguire, 1984; Jack, 1986; Rouxel et al. 1989] and certain properties have been reported.   A number of crywalline phases, including the quaternary phases in the Y-Si-O-N system, exist which may have potential in the formation of glass-ceramics [Korgul and Thompson, 1989; Jack, 1986].

The main aim of the current work is a systematic study of nucleation and crystallisation in oxynitride glasses in order to form suitable novel gkcss-ceramics for advanced thermornechanical and optical applications. In pursuit of the aim, the principal objectives were defined as follows:

(f)   Study of the formation and characteristics of oxynitride based gIasses containing rare earth cations such as Y and Nd;

(2)   Study of the effects of nitrogen and the cations on properties such as glass transition temperature, Young's modulus, viscosity, etc.;

(3)   Study of the structure of these glasses and the formation of nuclei;

(4)   Study of the optimisation of the controlled crystallisation of these glasses in order to develop novel glass-ceramics with tailored properties.

(5)   Application of these techniques to silicon nitride-based ceramics to optimise the crystallisation of grain-boundary glasses to effect property improvements.

Glass Compositions

The following glass compositions have been investigated:

(a) A series of standard compositions with cation ratios of 28 e/o Y, 56 e/o Si and 16 e/o Al with varying nitrogen contents (e/o+equivalent percent).

(b) Varying cation compositions and fixed O:N ratios including:
   (1) Compositions with constant 28 e/o Y conten~ and the Si:Al ratio varying from 72:0 to 50:22 for 10 e/oN and horn 64:8 to 48:24 for 17 e/o N.
   (2) Compositions with constant 56 e/o Si content and the Y:AI ratio varying from 44:0 to 0:44.

(c) A series of standard compositions with cation ratios of 28 e/o Nd, 56 e/o Si and 16 e/o Al with varying nitrogen contents.

(d} Standard rare earth cation compositions with 10 and 17 e/oN contents (28 e/o RE, 56 e/oSi, 16 e/oAl where RE= rare earth metal, i.e. Ce, Nd, Sm, Dy, Ho, Er).

(e) Two standard cation compositions (28 e/oM, 56 e/oSi, 16 e/oAl where M= La, Er) with a fixed 20 e/o N content and a mixed composition with cation ratios of 14 e/o La, 14 e/o Er, 56 e/o Si, 16 e/o Al, 8CI e/o O and 20 e/o N.

(f)) Additional Y-Si-Al-O-N gIass compositions to complete the study on the 17 e/o N pIane.

In view of the large numbers of compositions which have been investigated, a coding system has been introduced for easy identitlcation of any glasses or glass-ceramics. For standard cation compositions, the coding system is as follows:

1st symbol identifies the modifying cation system	2nd symbol identifies the major cation kept constant	3rd column gives the e/o N	4th Symbol shows G-glass or C-ghs.s-ceramic	5th column gives the e/o Al
e.g. Y	e.g. Si	e.g. 17	e.g. G	e.g. 16

Therefore, YSi 17G 16 is a glass from a series in the YSiAION system where the Si is kept constant, the N content is 17 e/o and Al content is 16e/o. Following heat-treatment to a glass-ceramic, the code becomes YSi17C 16.

For non standard compositions, Si is dispensed with as it is present in all the compositions and the code starts with a number rather than a symbol to indicate immediately a non standard composition. Thus, for example, for the U-phase starting composition the code w-ill be 30Nd20G30 as shown below. The silicon content can then be calculated by subtracting the Al and Nd e/o from 100, to give the answer of 40.

1st number identifies the e/o M (M=Y or R.E cations)	2nd symbol identifies the system ie. M cation	3rd column gives the e/o N	4th symbol shows G-glass or C-glass-ceramic	5th column gives the e/o Al
e.g. 30	e.g. Nd	e.g. 20	e.g. G	e.g. 30

Preparation and Characterisation of Glasses

Parent glasses were prepmed from mixtures of silicon nitride powder together with high purity (99.9%) Al_2O_3, SiO_2 and rare earth oxides to give the required chemical compositions, in equivalent percent (e/o) cations/anions. The powders were wet ball milled in isopropanol for 24h followed by evaporation of the alcohol before pressing into pellets. Large batches (50-60g) were melted in a boron nitride lined graphite crucible under 0.1 MPa nitrogen at 1700°C

for lh in a vertical tube furnace after which the melt was poured into a preheated graphite motid at 850°C and annealed for lh prior to slow furnace cooling.

The pMcipaJ characterisation techniques used include visual observations, X-ray diffraction (XRD), wanni.ng electron microscopy (SEM), density, microlwdness, fracture toughness, elastic moduli, thermal expansion, viscosity, thermal analysis, oxidation resistance, etc.

Glass-Ceramics formation and characterisation
Detailed nucleation and crystallisation studies have been carried out on some of these glasses using a two stage nucleation and growth treatment. Classical, differential thermal analysis and ultrasonic techniques have been employed in order to ensure that the optimum heat-treatment schedule is applied. The schedule for determining the optimum nucleation studies, in general, involved individud heat treatments of glass specimens, to individual nucleation temperatures for 10h at temperatures ranging between Tg-40 to Tg+ 100K followed by a treatment at the crystal growth temperature (Tc_2) for 30 minutes. Crystal phases were analysed by XRD and observed using SEM and TEM. The volume fraction of the crystal phases and the crystal size were evaluated using a point counting technique [Dehoff et al. 1968]. Additional experiments were then carried out at optimum nucleation temperature for various durations to determine the optimum time required for maximum nucleation.   Likewise, the procedure adopted for determining the optimum crystal growth temperature involved a nucleation treatment at the earlier determined optimum temperature and time followed by individual crystallisation treatments for 30 minutes at temperatures ranging between 1170 and 1310*C.

Results and Discussion

Preparation and Annealing of Glass Compositions
The glass-forming regions for O, 10, 16 and **22 e/oN in the** Y-Si-Al-O-N system have been defined and the regions are similar to those found by Drew et al (1981) except for the region at 22 e/oN which does not extend into the more Y-rich compositional range reported in that previous study found by Drew et al. This discrepancy may be due to differences in weight Iosses as a result of nitrogen evolution.   Comparison of the La- Nd- and Y- sialon systems showed similar (=38 e/o) maximum Ln/Y content at high (=30 e/o) nitrogen levels, but with the yttrium region narrowing down markedly compared with the other two.   Glass compositions containing =50 e/o nitrogen were prepared in the La- and Nd- sialon systems. The standard Y compositions formed homogeneous glasses which were grey to black in colour up to 20e/oN.

Property Assesment of Oxynitride Glasses

Ultrasonic Investigation
The development and refinement of techniques for evaluation of Young's modulus have been made using ultrasonic low frequency pulse echoes in the "long beam" mode of propagation. These techniques are based on the measurement of the acoustic wave propagation velocity in the .@ass sample. An experiment consists in monitoring the change in ultrasonic wave velocity during heating and cooling at a constant rate. An isothermal stay can be included in the temperature cycle. A typical curve is shown in figure 1. Young's modulus decreases slowly as temperature rises up to the glass transition temperature. Above Tg, the decrease becomes more rapid. When crystallisation occurs, an increase in Young's modulus is observed.
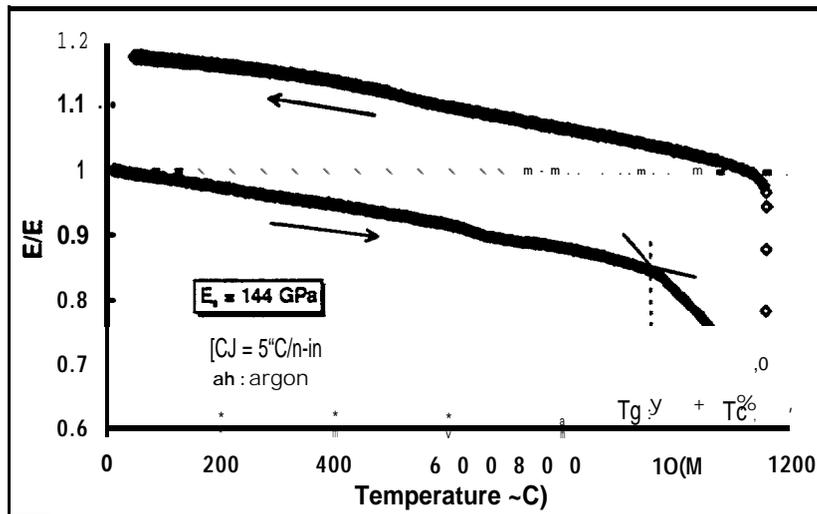
Figure 1: Young's modulus versus temperature for YSi 17G04 grade.

For the standard Y-sialon giass, the relative Young's modulus decreases linearly with the temperature up to 920"C at a rate of 1O-ZK-1. Above this temperature, it decreases more quickiy up to 1120"C, then more rapidly and, finally, shows a plateau from 1160 to 1300°C. From the results of viscosity determination, 920"C corresponds to the viscosity associated with the strain point (101s"5Pa.s). The relatively slow decrease of Young's modulus between 920 and 1120°C may be tentatively associated with the decrease in viscosity of the glass above the transition domain, partially hindered by the formation of ct-YJiz07 crystals. Then, the softening of the remaining glass becomes predominant until the formation of &Y#i$_2$0$_7$ counteracts it, resulting in a plateau observed above 1160"C.

The same features for the change in Young's modulus of silicon nitride sintered with yttria and alumina additions are strikingly evident, occurring over the same temperature ranges. The crystallisation leads to an irreversible change in the modulus. It has been shown that post-sintering heat treatments around 1200°C improve the creep resistance of this material by crystallizing the intergranular vitreous phase.

For the NdSiG 16 series of glasses, the elastic properties and Tg increase linearly with nitrogen content. For the YSi 17G series, Young's modulus decreases with increase in Al content while Tg measurements exhibit lower values corresponding to 12 and 16 eq% Al. In the case of both YY 10G and YY 17G series, the elastic moduli increase as AX% ratio increases whereas Tg decreases markedly. The absolute values of Tg and Young's modulus are, however, lower for YY 10G series due to the lower nitrogen content.

For LnSiAION compositions, both elastic and shear moduli were found to decrease with increase in rare earth atomic number.

Density
Density increases with N content suggesting that when N is substituted for oxygen in Si0$_4$ tetrahedral in the glass network, there are local increases in negative charges giving rise to increases in coulombic forces between the tetrahedral and the cations resulting in a more compact network. For varying cation compositions, density decreases with increase in Al content for YSi17G compositions, exhibits a minimum between 8 and 16 eq% Al for YY 10G

compositions while no significant trend was observed with YY17G compositions. For Re-SiAION compositions, density was found to increase with increase in rare earth atomic numlxr.

Thermal Analysis

Differential thermal analysis was carried out in order to detect the glass transition (Tg) and crystallisation temperatures (Tc). For alI the glasses investigated, an approximately linear increase in Tg was observed as nitrogen content increased from O to 25e/o nitrogen after which Tg levels off. Tc increases initially with nitrogen content and then levels off at higher nitrogen contents.

For YSi 17G and YY 10G compositions, Tg exhibits a minimum at 16 eq% Al while there appears to be no significant trend for Tg as a function of AI content for YY 17G compositions. With regard to Tc, the trend is different for different compositions; YSi17G compositions exhibit no si~lcant trend with Al YY 10G compositions show a minimum at 16 eq% Al whilst YY 17G compositions exhibit a maximum at 16 eq% AI.

For Re-SiAION compositions, Tg and Tc in general, appeared to increase with increasing rare earth atomic number

Hardness and Fracture toughness

Hardness generally increases with N content, exhibiting a minimum at 16 eq% Al for the YSi17G compositions which compares well with the similar trend seen for Tg measurements. Hardness measurements further substantiate that nitrogen has a much greater influence on properties compared with the varying cation concentrations. For LnSiAION compositions, the microhardness increases with Ln atomic number sirnikr to the trend observed for Tg, Fracture toughness of oxynitride glasses are slightly higher than for silicate glasses.

Viscosity

Viscosity was deduced from creep tests performed in air between 750 and 1000"C in three-point bending, The creep rate dependence on stress during stationary creep was measured ffom incremental stress steps at constant temperature (900"C). The stress exponent, q = (d.klE /dhs)T, was found to be equal to 1.01, which suggests a linear viscoelastic behaviour. Assuming an Arrhenius-type relationship between viscosity and temperature, the activation energy for viscous flow is estimated to be in the range 800 - 1000 KJ mol^{-1} at temperatures between the strain point and the dilatometric softening point (MJ. This is close to the range of activation energies for creep in silicon nitride-based ceramics sintered with Y_zO_3 and $A\$O_3$. The higher the nitrogen content of the glass, the higher is the glass transition range. For a given viscosity, the temperature shift is about 80"C between the oxide glass and the 25 e/oN oxynitride glass, and, at a given temperature, the viscosity increases by three orders of magnitude.   For Re-SiAION compositions, viscosity is seen to decrease in the order YX3m>Ce>Eu.

The glass transition range corresponds to a viscosity in the range 1012 to 10124 Pas. For the YSi 17G compositions, glass transition temperatures (from the viscosity curves) decrease with increase in Al content up to 16 e/o Al, but then increases thereafter. In contrast, for the YY 17G compositions, the glass transition temperature decreases as the A1/Si ratio increases.

Compactness

Compactness, which is defined as the ratio between the volume of the ions and the corresponding volume of the glass, has been computed for the YSi and YY series glass compositions.   **For the** YSi series, the compactness decreases by 4.94 % whereas it slightly increases for the YY series (AC/C= +1.14 %). Replacing Y by Al enhances the Ike volume of the giass whereas replacing Si by Al has little effect,

Thermal expansion

The coefficient of thermal expansion curves for all the glasses display similar characteristics. During the first period of heating and up to 200"C a very siight curvature is observed. Above this temperature the expansion curves are quite linear with temperature, although there is a continuous increase in the expansion coefficient up to the softening temperature point.

The coefficient of thermal expansion (CTE) in the YSiAION system decreases when Al replaces Y. Further, CTE for glasses in the YSiAION system, contrary to the situation for glasses in the NdSiAION system, is very sensitive to changes in chemical composition. CTE increases with decreasing silicon concentration, as is the case in most aluminosiIicate systEms. On the other hand, replacement of yttrium by aluminium decreases the CT'E significantly.

Correlation of structure and properties

NMR studies of nitrogen glasses

Previous [2g]Si spectra of oxynitride glasses showed broad overlapping peaks which could be deconvoluted into varying proportions of SiO_4, SiO_3N, SiO_2N_2, $SiON_3$ and (possibly) SiN4 tetrahedral units in the glass. The intensities of these peaks form an approximately Gaussian distribution, centred about the mean nitrogen content in the starting giass. Previous and current [27]Al spectra show broad spectra in the range 0-60 ppm, for which the interpretation is still not totally ciear.   An additional feature introduced into the present programme was to prepare glasses using [15]?4 and this has enabled nitrogen NMR spectra to be run. These have been very informative as r'egards glass structure.

Silicon-29s ctra run on the glasses produced in this work swved to confirm previous work. However, [2]AI spectra have indicated in most cases that there are three peaks in the range O - 60 ppm. Whereas peaks in the range 50-60 correspond to Al in [4]-fold coordination, and peaks in the range O -10 ppm correspond to Al in [6]-fold coordination, the third peak in the range 20-40 ppm, couId possibIy be interpreted in terms of [5]-fold coordination. Whereas this coordination is uncommon in crystalline Al-containing compounds, it is more likely in a glass due to the irregular atomic arrangement. Further work is needed to confirm this conclusion.

Nitrogen- 15 spectra for most of the glasses studies have shown two peaks at -250 and -300 ppm (Figure 2). The sharper peak at -300 pprn occurs in the same place as the strongest peak for &Si_3N_4 and is chwactenstic of nitrogen Sp^z coordinated by 3 silicon atoms. The peak at - 250 ppm is broader, and agrees with data obtained for other crystalline oxynitrides as corresponding to nitrogen joining two silicon-centred tetrahedral. To the authors IcnowIedge, this is the first time that [3]-fold coordination of nitrogen by silicon in oxynitride gIasses has been clearly demonstrated.   Spectra of different glasses over a range of different nitrogen contents showed that these two peaks were always present in approximately the same intensi~ ratio. Clearly, both environments increase in amount together as the nitrogen content is
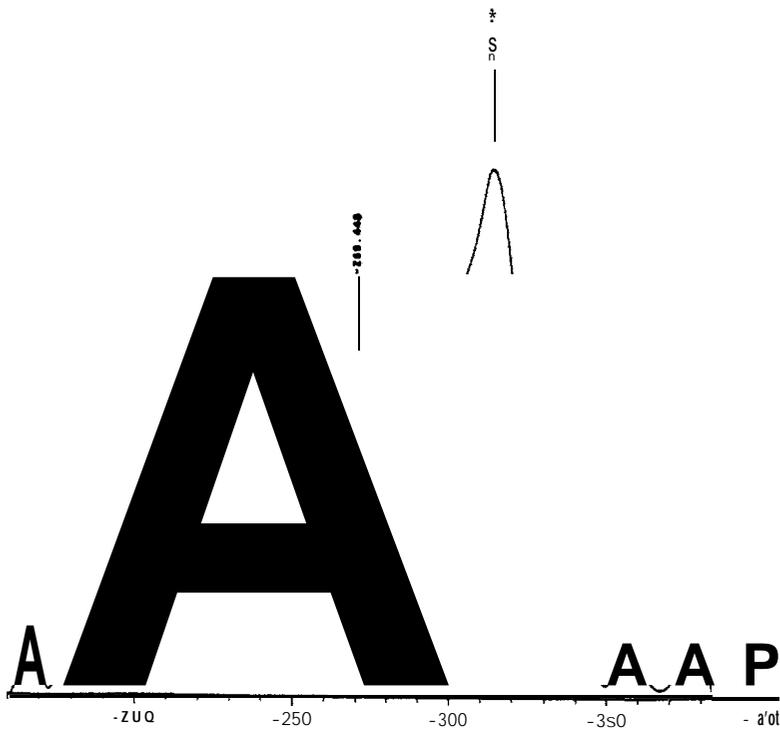
Figure 2: "N NMR spectrum of standard YSi17G16 glass.

increased. This conclusion agrees with well-established property data for oxynitride glasses which shows that elastic moduli, viscosi~, T_g, refractive index and hardness all increase as the nitrogen content increases and thermal expansion coefficient decreases.

By contrast, the influence of aluminiurn and yttrium has not been as clearly understood. The two series comprising variable Al/Y and A1/Si contents in the Y-Si-Al-O-N system were fimher subjected to Raman spectroscopy to get insight into the changes occurring in the glass network and to correlate with the changes in the properties. The results are surnma.rkd in table I.

Series	A1/Y	E (GPa)	G (GPa)	a (K')	Tg ("C)	NBO'	(2
YSil 7G	g	'%	\	\	% A	\	\

Series	A1/Si	E (GPa)l	G (G Pa)	a (K')	Tg ("C)	NBO*	c
YY17G	#	f l	g	g	\	g ""	g

Table 1. Changes in Young's modulus (E), shear moduIus (G), thermal expansion coefilcient (a), gk.ss transition temperature (Tg), number of non-bridging anions per silicon atom (NBO*) and compactness (C) obsemed with increasing Al/Y ratio (YSi17G series) and increasing AVSi ratio (YY 17G series).

The yttrium ahmi.nosilicate oxynitride glasses have a complex structure. Due to the high cationic field of the trivalent yttrium atoms, the Y-O **bonds,** though the weakest in the structure, are quite **strong. This** results in high values for Young's modulus, hardness and glass transition temperatum. Changing the ratios of the different cations hduces only Iirnited variations in the mechanical properties.

At constant ytlrium content, the increase of the A1/Si ratio does not modify significantly the degree of polymerisation but results in the replacement of Si-O-Si bndgings by A1-O-Si ones, The number of non-bridging anions increases slightly, though the compactness increases due to a higher number of cations in high coordinated sites, Room temperature Young's modulus, hardness and thermal expansion coefficient increase whereas the Tg decreases.

At constant silicon content, as the Al#Y ratio increases, the polymerisation of the glass network is enhanced by the continuous replacement of two NBOS by two AI-O-Si linkages. The compactness decreases as do Young's modulus, ixudness and CT%.

The comparison of the results obtained for the two series shows that room temperature Young's modulus is controlled primarily by the packing state of the glass structure, that is, the quantity of cations [Y, Al(5) or A1(6)] highly coordinated by anions, whereas the thermal expansion coefficient is controlled by the number of non-bridging anions.

Oxidation resistance of oxynitride glasses
The high temperature use of oxynitride glasses in air is limited by their oxidation resistance but relatively little data are available in the literature. This study has been undertaken to investigate the oxidation behaviour of some glasses in order to explain the degradation mechanisms. Cubic samples ($4x4x4$ mm^3) were cut and carefully polished. The oxidation resistance in air was carried out using a therrnobaIance (Ugine Eyraud B6(I)). While the furnace was heated at a constant rate of 20 °Cmin-1 to the oxidation temperature, the sample was kept in a cold zone.

The crystalline phases are formed according to the following general reaction :
$$YSiAlON + \mathbf{a0_2 + bY2Si_20_7 + cY2Si0_5 + dA1203 + A1_6Si_20_{13} + amorphous\ oxide + N_2}$$

The fractional weight gain is determined according to the equation :
$$u = Awt\ /\ Awm$$
where Aw_t is the weight gain for a given time t and Aw. is the weight gain which conesponds to a complete oxidation of the oxynitride gIass.

The experiments were carried out using the following series of samples :
(a) constant ratio Y/Si/Al and varying nitrogen content in order to evaIuate its influence;
(b) constant ratio M/Si/Al/'O/N and varying the type of metallic cation;
(c) constant ratio Y/O/N and varying Si/Al to explain the role of silicon and aluminiurn in the network;
(d) constant ratio Si/O/N and varying Y/Al to explain the role of yttrium and ahuniniurn as network modifiers.

After oxidation at 1075°C the glasses preserve their geometry and no change is seen in the morphology of samples or in the plasticity of the substrates.   The oxidation behaviour is strongly dependent on the glass structure.   The incorporation of nitrogen increases the oxidation resistance (Figure 3a) due to a higher refractoriness and compactness of the network.
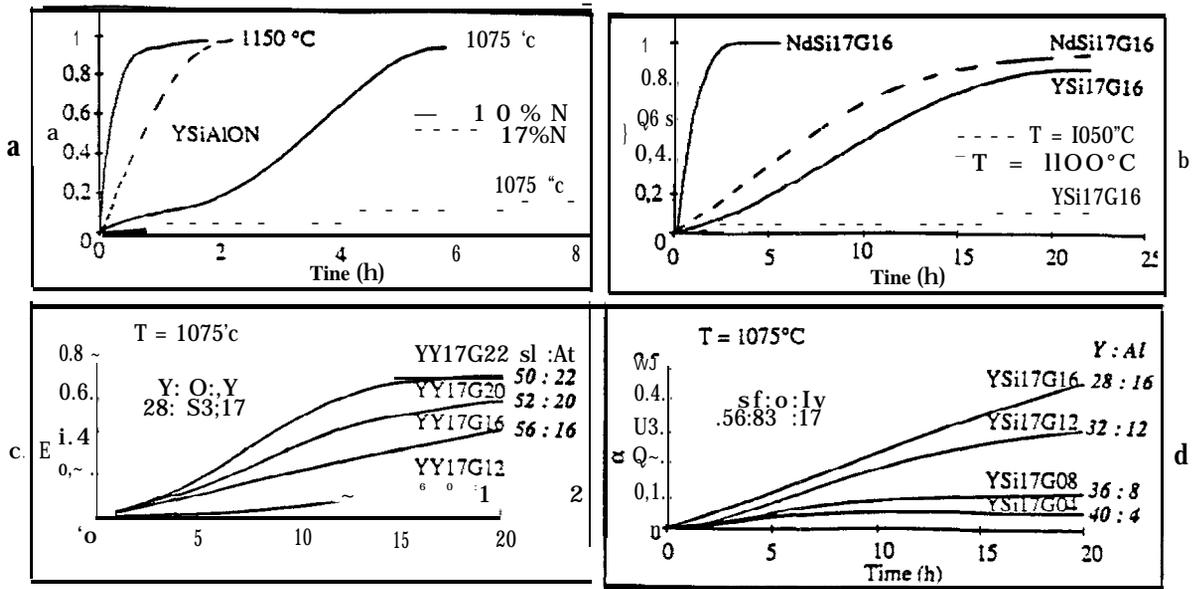
Figure 3: Oxidation kinetics in air of oxynitride glasses

A similar effect is observed when neodymium is substituted by yttrium (Figure 3b). This coul imply that the size of the cation alone is responsible for the changes at high temperatures; thi can be explained by the fact that the s~ength of the bonds between the metallic ions and th surrounding oxygen ions in the glass structure (M-O) where (M = Nd, Y) increases as the fiel strength of the metdic ion increases.

The field strength varies with the reciprocal of the ionic radius which means that the Y-(bonds are stronger than Nd-O ones. As the M-O bonds are weaker than the Al-O and Si-(bonds a more compact glass network is obtained with the stronger M-O bonds. The sam results were observed by Shelby et al. [1990] on the properties of oxide alumino-silicate glasses and by Persson et al. [1993] while oxidising silicon nitride with Y_2O_3 and $Nd_2($ additives.

Results for glasses that are oxidised at 1075"C for 20h are shown in figures 3c and 3d. Th role played by aluminium in the glass structure depends strongly on its concentration. For th low concentrations, aluminium is expected to exist in fourfold coordination with oxygen wher the presence of (A104) tetcahedra confers to a.lumin.ium the role of network former. As th aluminium content increases, it seems that the glass structure becomes more disordered ~ohl et ai. 1992] which could explain the decrease of the oxidation resistance. A negative effect (altium on the oxidation resistance of silicon nitride is also reported by Gogotsi et al [1993].

Comparing the oxidation cu.wes of YSi17G12 and YY17G 12 which are characterised by constant ratio of A1/O/N and a varying Y/Si ratio, the oxidation resistance of glasses decrease when yttrium replaces silicon. This is due to the fact that the substitution of silicon (networ forming) by @urn (network modifying) tends to make the glass structure more random. Th other explanation is that, for glasses with a constant ratio Al/O/N, the increase of Y/Si ratio i followed by a slight increase in the concentration of ahninium in fivefold coordination [KoM et al. 1992].

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The reactivity of YSiAION glasses with oxygen starts around 1000"C with a slight weight gain. For high temperatures the oxidation rate incmses significantly and the oxidation is almost complete m **a** few hours at 1150°C. The oxidation curves of the glasses exhibit **a** sigmoidal shape. The oxide scale changes continuously with oxidation conditions (temperature and time). The reaction of the glasses with oxygen leads to the release of nitrogen and the formation of voids at the internal interface which is followed by the growth of a white oxide layer. The presence of this porosity facilitates the rapid access of oxygen to the centre of samples.

At 1000"C and for 22 hours of heat treatment, the oxide layer contains cx-YQSiz07 and a small amount of yttria.llite (y- YzSiz@) and corundum. With an increase in oxidation time yttriallite occurs in place of ct-Y_2Si_2O7. After 100 hours the oxide layer is formed with yttriallite as the main oxide and the presence of a small quantity of mullite, corundum, cristobalite and ct-YzSiz@.

The sigmo~dal shape of the oxidation curves, the texture and the momholo~y of the Dorous oxide scale which show a direct access of oxygen to the internal intefi-ace ~d the gro'wth of the maltese cross symmetry imply that the oxidation of YSi 17G 16 is governed by a reaction process where the progress of the internal interface is the limiting step. The apparent activation energy calculated from the slope of the transformation curves is E = 848i50kJ/mol.

Preparation and Characterisation of CrystaI Phases

Further work was carried out on the known crystal phases: B (Y_2SiAIo_5N), U ($Ln3Si3A1_3O1_2N_2$), W (approx. $Ln_5Si@_5O_{27}N4$), the nitrogen pyroxenes ($LnMgSi_2O_5N$, where Ln also includes Y). No further attempts at phase identification were made on the previously identified phases I_w and Q. Other new phases, given the symbols M and K were identiled as a result of low temperature (1000- 1200*C) heat-treatments on previously unexplored giass compositions in the Y-Si-A1-O-N system.

B-phase is of interest because it contains a substantial amount (=23e/o) of nitrogen, and, prior to the present investigation, was the only 5-component oxynitride in the Y-Si-Al-O-N system. The disadvantages are that it is only stable to = 1100"C, and its composition lies just outside the glass-forming region in the Y-Si-Al-O-N system. Whereas samples can be prepared by melting and heat-treatment which show only B-phase on X-ray diffraction patterns, these samples contain quite Iarge (up to 30 vol. %) residual glass. Further attempts to obtain higher purities of B were unsuccessful, and the production of fully crystalline, multiphase samples of the B-phase composition are complicated by its low-temperature decomposition. It is therefore not a promising phase for further development as a glass-ceramic.

U-phase is barely stable in the Y-Si-Al-O-N system, but exhibits good stability in the La-, Ce- and Nd-sialon systems. Preparation of U-phase via a glass-ceramic route using the composition quoted above is complicated by eariy crystallisation of wollastonite ($LnSi0_2N$), but with care, the concentration of the latter can be minimised to bdow 5%. At more Al-rich compositions, U-phase can be prepared with glass as the second phase, but this is in greater quantity than the wollastonite ob,served at the exact U-phase composition. U-phase melts in the range 1350- 1400°C, and apart from the problem of wollastonite contamination is relatively easy to produce as a glass ceramic.

W-phase crystallises with large needle-shaped grains when prepared at compositions with high oxygen levels, but with increasing nitrogen content the microstructure refines and become more equiaxed. Optimum compositions for preparing pure W are slightly Ln and Si rich compared to the 5:9:5 atomic ratio quoted above, with the nitrogen content in the range 7-8 do. **This phase** melts in the range 1300- 1350"C.

In contrast, the nitrogen pyroxene group of phases show improved thermal stability (melting points = 1400*C), and can be eady prepared pure by melting followed by crystallisation. These phases offer the best promise of all the materials explored in this study, for use both a glass ceramics in their own right, and as secondary crystalline phases in silicon nitride ceramics.

The most interesting feature of the work in this section was that because most previous studies had focused either on glass compositions towwds the middle of the g.lass-fom.ing region (i.e "typic~" nitrogen glass compositions), or on lines of composition varying one compositional variable, or along the edges of the glass forming region in equilibrium with silicon nitride or sialon matrix phases, there are still extensive gkss regions in the Y- and Ln sialon systems for which crystallisation behaviour had not been explored. In the present programme, most effort on devitrification of new glass compositions was carried out in the Y-Si-A1-O-N system a high nitrogen contents, and two new phases were identiiled. One of these, designated M, has an approximate composition YSi#d@6,@l.2; the other, designated K, has an approximate composition $Y_2Si_3\text{\textasciitilde}._7O_8N_{1\cdot3}$. Also, further sets of spare X-ray diffraction lines were observed. What is cIear is that in previously unexplored regions of the Y-Si-AI-O-N system (and similar regions in Ln-sialon systems), especially at low (1000- 1200"C) crystallisation temperatures, there are other oxynitride glass ceramic phases available for investigation.

Heat treatments in tube furnace for optimum nucleation temperature determination
The YSi 17G 16 glass composition subjected to different nucleation treatments showed variations in both the volume fraction of crystalline phases and the cnrstd size with nucleation temperature (Figures 4 & 5). The results 'indicate that a maximum amount of crystallisation has occurred for the glass heat treated at Tg+40K. In addition, the crystal size exhibits a minimum at this temperature.
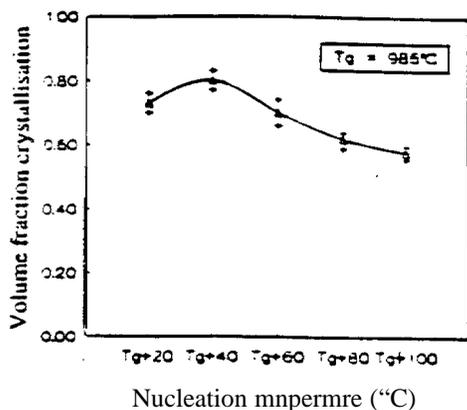

Figure 4: Volume fraction of the crystalline phases as a function of heat treatment temperature.
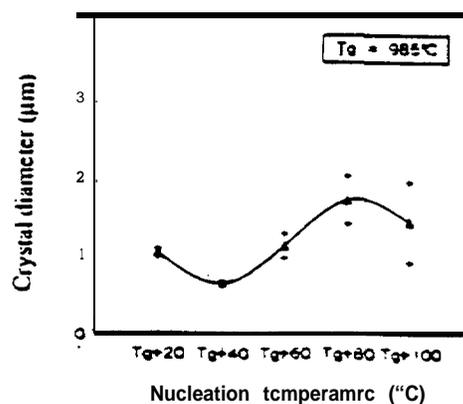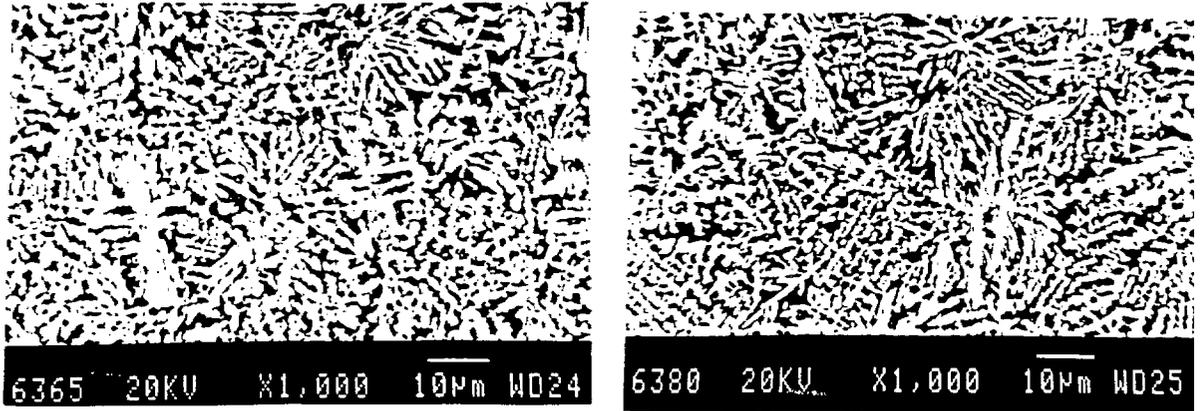
Figure 5: CrystaI size as a function of heat treatment temperature.

(a) Surface morphology   (b) Sectioned morphology

Figure 6: Micrographs of YSi17G 16 gIass obtained following heat trea&ents-at Tg+40K,

Phase assemblage of the heat rreated glass samples identified by XRD reveal yttrium disilicate and silicon oxynitride as the main crystalline phases. Traces of YAG/AlY03 were also noticed. Examination of the cross-sectioned specimens reveals similar morphology to those of surface layers which seems to suggest the occurrence of bulk nucleation in this glass-cerami whereas it had been thought that surface nucleation might be significant. Typical surface and sectioned morphologies for Tg+40K heat treatment are shown in Figure 6.

A sign.iilcant aspect of the phase assemblages on samples heat treated at the optimun nucleation temperature (Tg+40K) for various durations is the transformation of yttriun disilicates horn one form to another with time (Table 2). Analysis of the microstructure in terms of volume fraction crystallised showed maximum crystallisation for the glass held fo 10h at Tg+40K (Figure 7), As the hokling time is increased a decrease in voiume fraction crystallised was observed. This appears to indicate that some of the nuclei formed redissolv on heating to the second stage. Such a phenomena can arise when the growth of the critica sized nucleus becomes unstable with respect to the second stage heat treatment temperature If this is the case, then varying the growth or second stage heat ~atment temperature shoul radically aIter the volume fraction crystailised after a given nucleation heat treatment. This was indeed the case as will be seen below.

Table 2: Crystalline phases observed for the YSi 17G 16 glass heat treated at Tg+40K fo various durations.

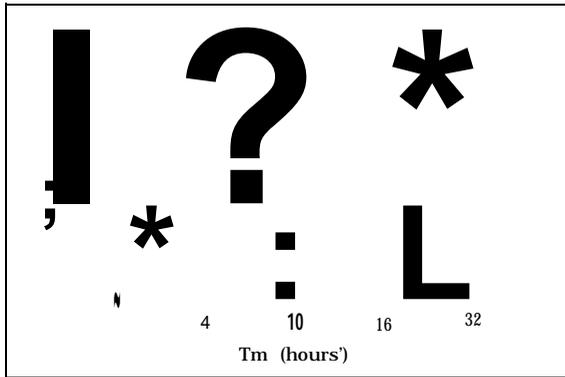| 2l-l	4h	10h	16h	32h
a-Y~Si207	&Y~Si*O~	~-Y~Si~O,	~-YJli~O,	j3- Y~Si*O~
&Y~Si~O~	Cz-YLSi~OT	Ct-Y~Si~O?	&Y~Si~OT	YzSi05
y-YLSi~OT	y-Y~Si~OT*	Si$_2$N$_2$0	Y#i05	Si$_2$N$_2$0*
Si$_2$N$_2$0*	Si$_2$N$_z$O*	YAG*/AIYOJ*	Si~N$_2$0*	& Y#i~@*
			YAG$^{\&}$/AlY0$_3$*	YAG*/AlY0$_3$

  * -+ trace amounts.

Figure 7: Vol. fraction of the crystalline phases obtained as a function of time.
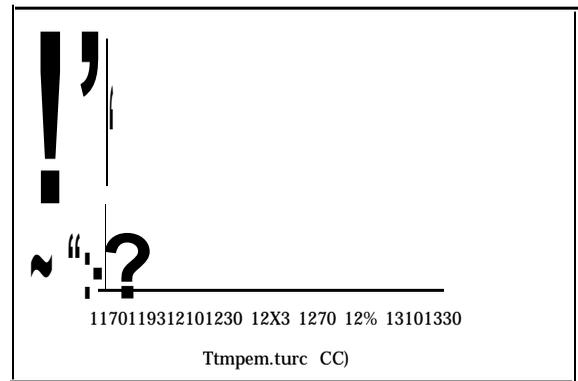

Figure 8: Vol. fkaction of the crystalline phases as a function of growth temperature.

YSi17G 16 gkss specimens were also heat treated at different individual growth temperatures after a nucleation treatment at Tg+40K for 10h. Though all the specimens underwent the same nucleation heat treatments, the number of crystak observed vary sigrdlcant.ly after different growth temperature treatments (Figure 8) which reiterates that some of the nuclei formed dissolve during the second stage heat treatmen~ This also indicates that the number of particles observed after growth treatment does not give a good estimate of the number of nuclei formed at the **lower** temperatures. A second stage treatment at 1210°C corresponding to Tc_2-60K appears to be the optimum crystal growth temperature for this composition.

Heat **treatments using** DTA **for optimum nucleation temperature determination**
DTA experiments were performed on four gk.ss compositions &Si17G4, YSi17G8, YSi17G16 and YSi17G19) to determine the optimum nucleation temperature using a method outlined by Marotta [1982]. Powdered glass samples of particle size 53-106 ym placed in boron nitride lined platinum crucibles with alumina as a reference material and heated at 200 C/minute in a flowing nitrogen atmosphere up to temperatures ranging between Tg and Tg+100K for Ih after which heating was continued at 10°C/minute until the crystallisation peak was observed. The isothermal heat treatment that resulted in the greatest depression in crystallisation temperature is taken as the optimum nucleation temperature. Activation energy for the crystallisation process was determined using the modified Kissinger method outlined by Matusita et al. [1980]. Five different heating rates (5, 8, 10, 15 and 20°C/mirmte) were employed maintaining the same particle size (53- 106 pm).

Table 3 summarises the results of the optimum nucleation temperature determined using the DTA technique for the four glass compositions. As can be seen, Tg varies with composition. As with **Tg,** optimum nucleation temperature aiso varies with composition. As the ahuninium content increases the maximum nucleation occurs close to the glass Eansformation temperature. For YSi 17G 16 glass composition, the optimum nucleation temperature obtained **(Tg+35K)** agrees well with those obtained from the tube furnace (Tg+40K) measurements.

Table 3: **Optimum nucleation temperatures obtained using DTA technique.**

Composition Code	Glass transition temperature (Tg)	Opt. nucleation temperature
Ysi17G4	1017"C	Tg+65K
YSi17G8	1002*C	Tg+60K
YSi17G16	985°C	Tg#OK
YSi17G19	987°C	Tg+20K

To confm whether bulk or surface nucleation is predominant, additional non isothermal DTA runs were carried out on three samples of varying particle sizes (<53pm, 53- 106ym and > 106pm). As can be seen from table 4, the particle size exerts no influence on exotherrnk peak temperature (Tel) for the YSi17G 16 and YSi 17G 19 compositions which indicates that bulk nucleation is dominant.   In contrast, YSi 17G4 and YSi17G8 compositions show considerable influence of particle size on exothermic peak temperature indicating the predominance of surface nucleation.

Table 4: Crystallisation temperatures (Tc 1) obtained for the YSiAION glasses of varying particle size.

Composition	Particle size		
	<53 pm	53-106 pm	>lo6J.un
YSi17G4	1173QC	1185°C	1160°C
YSi17G8	1185°C	1198°C	1170°c
YSi17G16	1189°C	1185°C	1190*C
YSi17G19	1192*C	1190"C	1195*C

Figure 9 shows the activation energy for crystallisation as a function of alwninium content. As can be seen from the figure, the glass composition containing 16 e/oAl (YSi 17G 16) requires considerably higher activation energy for the crystallisation process, which suggests that this is the most stable glass forming composition in the present study.
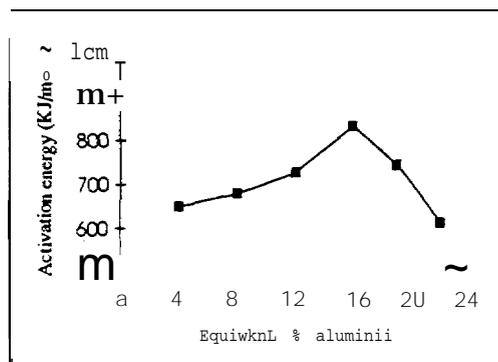

Figure 9: The effect of Al content on the activation energy of the crystallisation process.

Nucleation of Y-Si-Al-O-N glasses using the Ultrasonic Technique
The ultrasonic technique was used to make a detailed study of the frost stage of crystallisation of the Y35Si 17G20 grade. This grade was selected because crystallisation leads to a single phase, the B phase, when heat treatments are limited to temperatures lower than 1100"C. Using the approximation of Voigt and Reuss for a two phase malxrial, the crystdised fraction was linked to the change of Young's modulus with time during isothermal experiments. The change with time of the crystallised fraction is reported in figure 10 for various temperatures. The corresponding ITT diagram is drawn in figure 11.
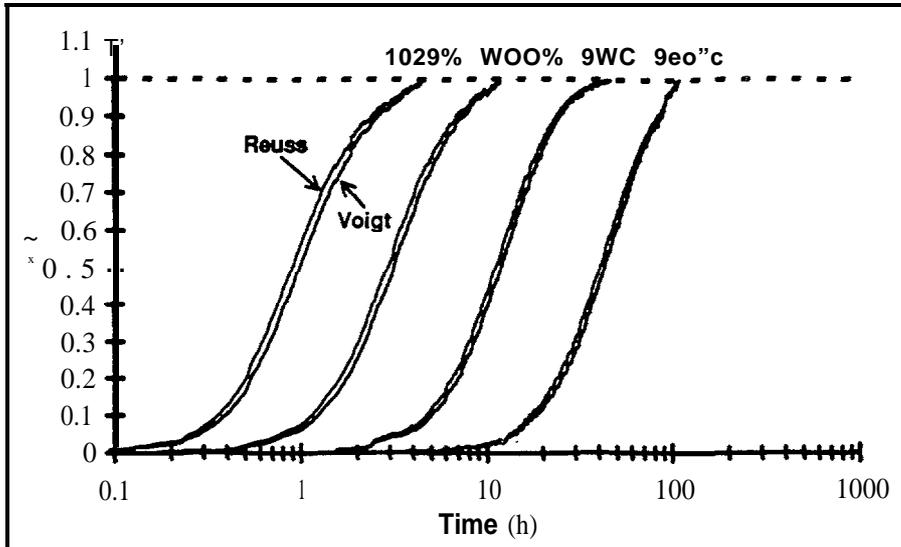
Figure 10: B phase crystallisation kinetics from Voigt and Reuss approximations versus heat treatment temperature.
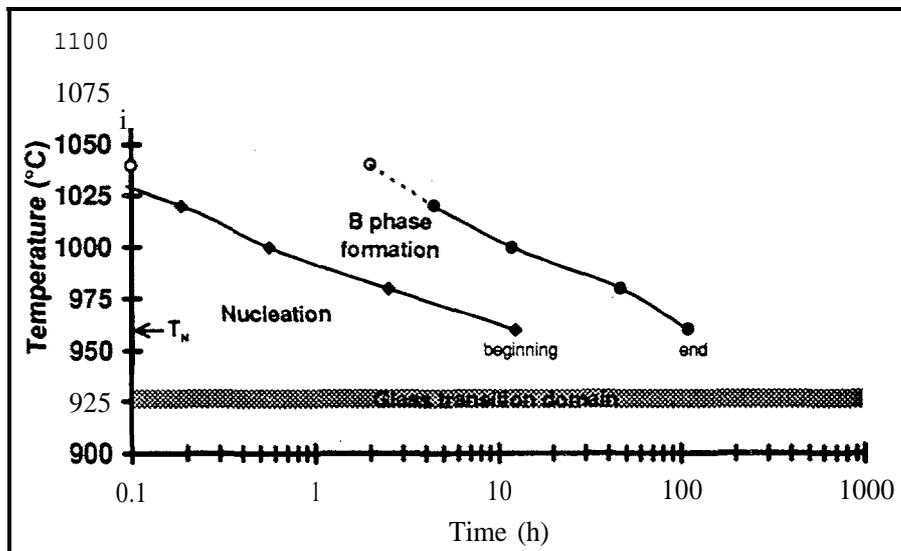
Figure 11: Transformation-Time-Temperature diagram of 35YSi 17G grade.

These results were analysed using the classical Johnson-Mehl-Avrami equation [Avrarni, 1939; Johnson, 1939]:

$$x = 1 - \exp[-(Kt)^n]$$

where x is the volume fraction of crystallised material when the glass is heated isothermally at temperature T for a time t.

The reaction rate K is assumed to have an Arrhenius temperature dependence:

$$K = KO \exp\left(\frac{E,}{RT}\right)$$

The exponent of the JMA relation was found equal to 2.3 that suggests a crystal growth controlled by diffusion with a slightly decreasing nucleation rate. The apparent activation energy E., in this temperature range was found to be 860 kJ/mol.

15

A series **of** non-isothermal runs with different heating rates was analysed using the expression established by Yinnon and Uhhnann [1983] horn the method of Ozawa and Chen.

$$d(\ln(T/ \quad Q) \quad \textbf{E,}$$

$$_+ \ \textbf{d(l i T)} \ _{,=,,} \ ` \quad \textbf{F}$$

where x' is a given crystallised fraction and T the temperature at which this tlaction is obtained for a given heating rate Q. The apparent activation energy was equal to 1025 kJ/mol. It was shown that under these experimental conditions (onset of crystaUisation in the 1020-106O"C temperature range) E. is approximatively the activation energy for crystal growth. This energy is close to the activation energy for viscous flow (960 kJ/mol, determined by creep experiments) that confii the major role of the diffusion in the crystallisation process.

To determine the optimum nucleation temperature, the procedure was sirnikr to that used in DTA experiments. The data analysis was derived from the method proposed by Marotta et al. [198 1]. It was shown that the temperature of the inflexion point in the E(T) curve plays the role of the temperature of the maximum in the DTA curve. A curve that reproduces the change in the nucleation rate with temperature is obtained by plotting (l/Ti)-(I/Ti') versus TN, where T_i is the in.tlexion point temperature on the E(T) curve after a nucleation stage at a temperature TN and T/ is the inflexion point temperature when no nucleation step is included in the temperature schedule. An optimum nucleation temperature of 960*C was obtained (Figure 12).
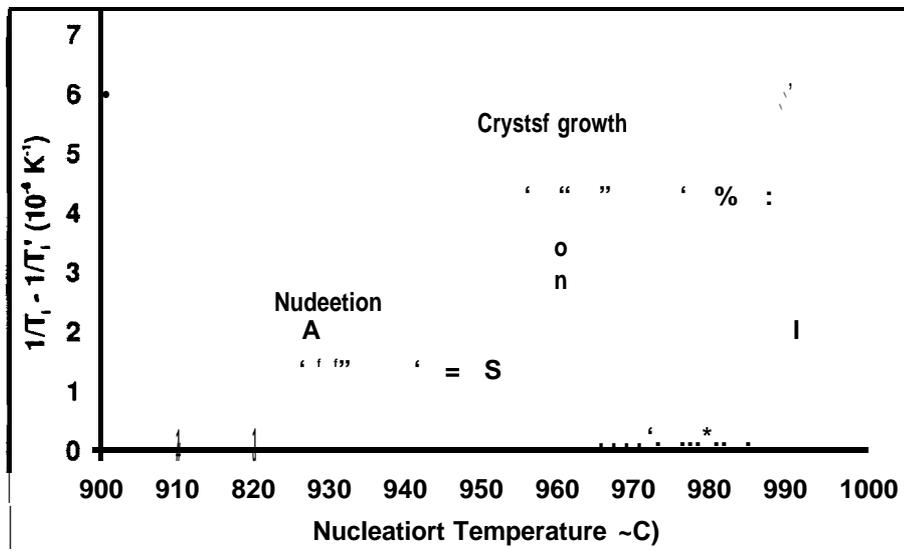

Figure 12: Determination of the optimum nucleation temperature from Marotta's method.

Transmission Electron Microscopy investigations were made on samples treated for different times at 960"C (i.e. maximum nucleation rate and slow crystal growth). It was obsemed that the crystallisation is initiated by a bulk homogeneous nucleation and that crystal growth leads to "rice grain" shaped crystals with a typical grain size of 150 nm.

Characterisation of crystal phases during glass-glass ceramic transformation
A detailed study of crystal~isation in the Y-Si-Al-O-N system at B-phase type compositions as a function of temperature and time, showed that whereas B-phase and then I_w phase crystallised at low (1000- 1200"C} temperatures with some wollastonite (YSi02N j forming, above 1200"C there was a complete change with YAG, nitrogen apatite and yttrium

silicate phases emerging with increasing temperature Clearly, the conditions of the crystallisation make an enormous difference to the type and amount of phases produced. Similar studies carried out for standard cation composition Y-Si-Al-O-N glasses with varying leveIs of nitrogen showed simiIar conclusions but with different phases present. A consistent feature of work on the lower nitrogen content, standard cation glasses is the presence of mixed yttrium silicates, with y-Y2Si207 predominating at 10 e/o nitrogen and mixtures of J3 + 3 predominating at 17 e/o nitrogen.   As a result of these studies there is now a clearer understanding of the predicted occurrence of a particular phase of Y2Si207 for a given set of experimental circumstances.

A disadvantage of the Y-Si-Al-O-N system is that it is difficult to produce a single phase glass ceramic free of second phases. In contrast there are more five-component phases in rare earth sialon systems of lower atomic numbers.

Oxidation resistance of oxynitride glass-ceramics
Glass-ceramics obtained after a thermal processing of gIasses were oxidised in air under various conditions. The influence of the nature and concentration of the formed crystalline phases was studied by diversifying the starting glass composition (Nd-Si-Al-O-N and Y-Si-Al-O-N).

Composition of glass-ceramics plays a determining role during the oxidation in air of these materials. The composition of glass-ceramics studied and the phase assemblage after their subsequent heat treatment is shown in Table 5. In figure 13 are reported the oxidation curves of some glass-ceramics as function of time. The weight gain is calculated using experimental nitrogen content values and by considering the absence of change in the composition during the heat treatment.   Glass-ceramics can be divided into four groups according to their behaviour.

The fust group contains silicates with a residual oxynitride vitreous phase. These samples are obtained by heat treatments at low temperatures or for shorter durations. The presence of this vitreous phase induces a fall in oxidation resistance above 1150°C (Figure 13a, YSi 17C16- 1 and 2).

The second one concerns single phase glass-ceramics formed by quirtary oxynittide phases. Their reactivity with oxygen starts at 1050"C. Moreover, the poor stability of these phases at high temperature (T >1150"C) and their decomposition lead to the release of nitrogen which induces the formation of porosity and cracks in the substrate and accelerates the oxidation of the material (Figures 13b and 13c).

Table 5.: Composition of glass-ceramics and their subsequent heat treatment

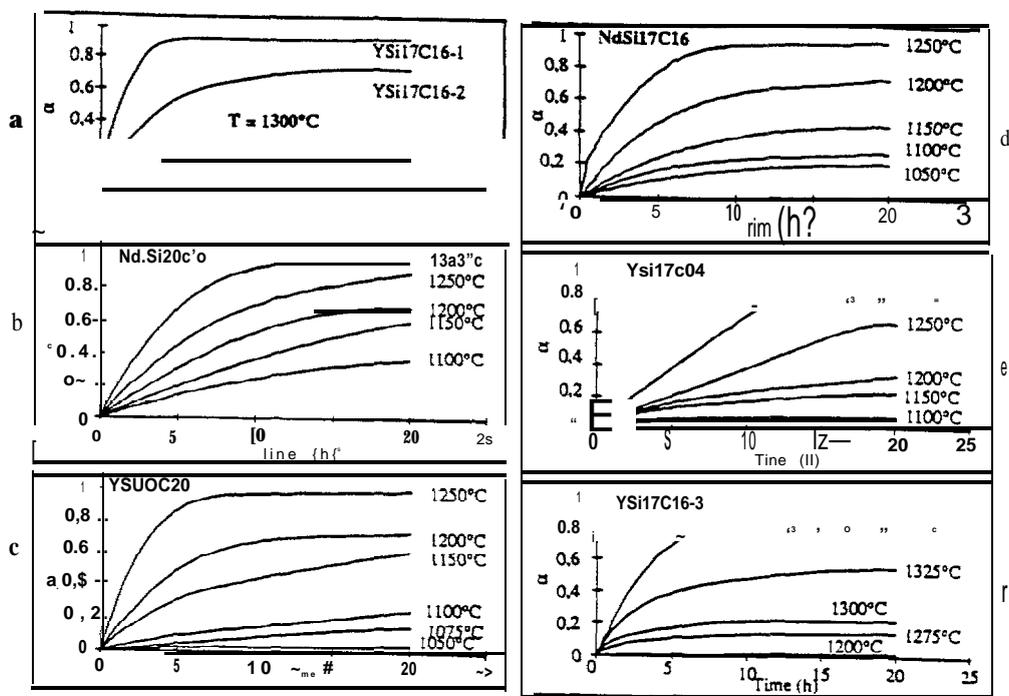| Material	Nucleation	Crystallisation	Crystallisation products
NdSi20C30	-	1150°C-36h	u-phase
YSi20C20	-	1Q40°C-40h	B-Phase, I_w^w
NdSi17C16	950°C-10h	1100°C-36h	Nd&i3012m, W-phase^m, Nd2Si207^w
YSi17C04	1020"C-6h	1150°C-36h	YSi02N^m, i3Y2Si207^m, yY2Si207^m
YSi17C16-1	1020°C-6h	i100°C-36h	yY2Si207^s, 6Y2Si2@^{w}, Y2Si05^w, Amorphous
YSi17C16-2	1020"C-6h	1150°C-2h	Amorphous, yY2Si207^m
YSi17C16-3	1020"C-6h	1150°C-36h	yY2Si207^s, 8Y2Si207^m, Y~Si05^w, YAG^w. SizN?O^w

Figure 13: Oxidation kinetics in air of oxynitride glass-ceramics

The third glass-ceramics group is formed by ternary sdicate, aluminate phases and quaternary or quinary oxynitride phases. The oxidation resistance of these ghs<eramics is 6&er th~ those of the previous ones.   As for single-phase materials, the decomposition of the oxynitride phases inhibits the oxidation resistance (Figures 13d and 13e).

The materials with the highest oxidation resistance contain ternary silicate, aluminate phases and Si2N20 as oxynih-ide phase. The good oxidation behaviour of this phase delays the de~adation of the materials (Figure 13f).

In summary oxygen reacts tirsdy with the residual vitreous phase present in the glass-ceramics, then it oxidises the quatemary or quinary oxynitride phases. The oxidation of silicon oxynitride occurs later.   Materials rich in Si_2N_2O are good candidates for high temperature applications due to their good oxidation behaviour until 1300"C.

Application of Glass-Ceramic Treatments to Nitrogen Ceramics
Previous work has shown that B-phase is undesirable as a grain-boundary phase in sialon ceramics because of its Io w temperature stability and poor oxidation resistance. Both U-phase and W-phase can be produced as a single phase in Lndensified &sialon ceramic% however, in performance these are very similar to &sialon - YAG ceramics in giving better mechanical property retention up to >1300"C than the undevitified, glassy parent materials, but then both oxidation and melting take place, resulting in relatively poor properties at higher temperatures.

The pyroxene phases offer better performance as grain-boundary phases, but these must be used in silicon nitride rather than sialon ceramics. Inevitably the absence of ahmi.nium resuits in more refractory products, but there is the increased problem of densiilcation at 1 atmosphere. Work has shown that it is possible to densify silicon nicide with a combination of $MgO + (Y, Ln]_2O$~ additives designed to give the pyroxene phase as the single grain-boundary phase, but achieving a 1005%0 dense as-freed product is harder than in sizdon systems. Also, the

almost point composition of the LnMgSi$_2$O5N phase makes it harder to avoid either residuai glass or small amounts of other crystalline phases. For varied amounts and *ratios* of M@ + Y2O3 as additives for densifying silicon nitride, the 1:1 molar ratio gave the best performance.

Overall summary

This work has shown that the field of oxynitride glass ceramics is larger than originally thought, and that many new phases exist which merit further exploration. Whereas the properties of the materials explored in the present programme are at least comparable with current oxide glass ceramics, the present results show that fiut.her development of the newer glass ceramics studied in this programxne may be beneficial.

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EXPLOITATION REPORT

X)NTRACT No. BRE2-CT92-0272

BE

PROJECT NO. 5687

HTLE:OP'ITMISATION OF NUCLEATION AND CRYSTALLISATION IN OXYNIT'RIDE GLASSES TO DEVELOP NOVEL GLASS-CERAMICS FOR ADVANCED THERMOMECHANICAL AND OF'IKAL APPLICATIONS.

> R O J E C T

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?ARTNERS: Dr Derek Thompson, University of Newcastie Upon Tyne, UK.
Professor Jean-Louis Besson, E.N.S.C.I., Limoges, France.
Professor Paul Goursat, University of Limoges, Limoges, France.

iTARTING DATE :01.10.92   DURATION:39 MONTHS

COMPLETION DATE: 31-12-95

TITLE: OPTIM3.SATION OF NUCLEATION AND CRYSTALLISATION IN OXYNITRIDE GLASSES TO DEVELOP NOVEL GLASS-CERAMICS FOR ADVANCED THERMOMECHANICAL AND OPTICAL APPLICATIONS
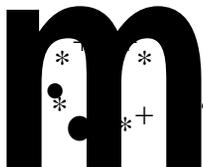
Introduction, Aims **and Objectives**

Glass-ceramics are an important class of materials that are formed by melting, shaping and subsequent controlled crystallisation of glasses.   The possibility of producing glass-ceramics containing refractory oxynitride crystalline phases with particular beneficial properties has led to further studies of oxynitride glass formation and properties. This has complemented more extensive studies of phase equi~bria in M-Si-Al-O-N systems and the effects of vitreous phases on high temperature properties of silicon nitride-based ceramics.

The main aim of the project is a systematic study of nucleation and crystallisation in oxynirnde glasses in order to form suitable novel glass-ceramics for advanced thermomechanical and optical applications. The principal objectives were:

(1)   Study of the formation and characteristics of oxynitride based glasses containing rare earth cations such as Y and Nd;
(2)   Study of the effects of nitrogen and the cations on properties such as gIass transition temperature, Young's modulus, viscosity, etc.;
(3)   Study of the structure of these glasses and the formation of nuclei;
(4)   Study of the optimisation of the controlled crystallisation of these glasses in order to develop novel glass-ceramics with tailored properties.
(5)   Application of these techniques to siIicon nitride-based ceramics to optimise the crystallisation of grain-boundary glasses to effect property improvements.

The roles of the mrtners were as follows:

Partner	Role
University of Limerick, Ireland.	Project Co-ordinator. Preparation of oxynitride glasse: structural changes in glasses by DTA & viscosity; physic: property measurements, optimisation of heat treatments; optic: characteristics of glass-ceramics
University of Newcastle upon Tyne, UK	Preparation/characte fisation of oxynitride **CrYS~ ph=e:** structural study of glasses; application of glass-cerami treatments to nitrogen ceramics
E. N. S. C. I., Limoges, France	Structural study of glasses; ultrasonic investigation-physic property assessment & crystallisation study; high temperatu properties of glass-ceramics
University of Limoges, France.	Oxidation of glasses, crystal phases and glass-ceramics microshuctural studies of glass+ glass-ceramic transformatio application of glass-ceramic treatments to nitrogen ceramics
Cookson Technology Centre, UK.	**Industrial Endorser**
Cthrniques et Composites, France.	**Industrial Endorser**

Description of Results

The glass-forming regions for O, 10, 16 and 22 e/oN in the Y-Si-Al-O-N system have been defined. Limits of glass formation in the La- and Nd- sialon systems have been explored. Comparison of the La-, Nd- and Y-sialon systems showed similar (=38 e/o) maximum Ln/Y content at high (=30 e/o) nitrogen levels, but with the yttrium region narrowing down markedly compared with the other two.

NMR, Neutron diffraction and Rarnan spectroscopy studies were carried out to analyse the local structure of glasses in the Y-Si-Al-O-N system. *'Al NMR spectra indicates that alurninium atoms occupy various sites within the glass structure i.e. it appears to exist in 4, 5 and 6 fold coordination. Nitrogen- 15 spectra demonstrate the [3]-fold coordination of nitrogen by silicon in oxynitride gIasses. The first peak of the total correlation function obtained by neutron diffraction indicates the existence of Si-0, Al-O, Si-N and perhaps Al-N bonds. As the nitrogen content increases there appears to be a change in the nitrogen coordination or in environment or both as revealed by shift in the second peak of the total correlation function. Further studies were carried out using Rarnan spectroscopy to gain insights into the glass network for two complementary series of glasses with either a variable AUY content or a variable AUSi content. The results are correlated with the changes in properties and summarised in table 1.

Series	Al/'y	E (GPa)	G (GPa)	*a* (K-')	Tg ("C)	I'4BO*	c
YSi17G	1 f l 0.1	144 % 137	55 \ 53	7,2 \ 5.4	935 \ f l 925 930	2.8 % 10	V).453 h 0431

Series	A1/Si	E (GPa)	G (GPa)	*a* (K-l)	Tg ("C)	NBO*	c
YYI 7G	0.67 Y 0.27	144 Y 137	56 f l 53	6.2 f l 5.8	932 h 910	1,7 Y 1,6	0441 Y 0.436

Table 1. Changes in Young's modulus (E), shear modulus (G), thermal expansion coefficient (a), ' glass transition temperature (?'g), number of non-bridging anions per silicon atom (NBO*) and compactness (C) with increasing Al/Y ratio through the YSi 17G series and with increasing AUSi ratio through the YY 17G series.

The yttrium aluminosilicate oxynitride glasses have a complex structure. Due to the high cationic field strength of the trivalent yttrium atoms, the Y-O bonds, though the weakest in the structure, are quite strong. This results in high values for Young's modulus, hardness and glass transition temperature. Changing the ratios of the different cations induces only limited variations in the mechanical properties.

At constant yttrium content, the increase of the A1/Si ratio does not modify significantly the degree of polymerisation but resuIts in the replacement of Si-O-Si bridgings by A1-O-Si ones. The number of non-bridging anions increases slightly, though the compactness increases due to a higher number of cations in high coordinated sites. Room temperature Young's modulus, hardness and thermal expansion coefficient increase whereas the glass transition temperature decreases.

At constant silicon content, as the Al/y ratio increases, the polymerisation of the glass network is enhanced by the continuous replacement of two NBO'S by two A1-O-Si Iinkages. The compactness decreases as do Young's modulus, hardness and thermal expansion coefficient.

The comparison of the resuhs obtained for the two series shows that room temperature Young's modulus is controlled primarily by the packing state of the glass structure, that is the quantity of cations [Y, Al(5) or Al(6)] highly coordinated by anions, whereas the thermal expansion coefficient is controlled by the number of non-bridging anions.

Control of nucleation is extremely important in the formation of glass-ceramics. Detailed nucleation and crystallisation studies have been carried out on Y, Nd and La-Si-ALO-N glasses, using a two stage nucleation and growth treatment. Classical and DTA techniques were used for studying the crystallisation process in order to ensure that the optimum heat-treatment schedule is applied. Optimum nucleation and crystal growth temperature and the activation energy for the crystallisation process have been determined and the influence of sample specific-surface on the devitrification mechanisms have been assessed. Aluminium exerts a considerable influence in all these cases. Specimens heat treated in a tube furnace were subjected to microscopical investigation and showed variations in volume fraction of crystalline phases and crystal size with nucleation temperature. The nucleation temperature corresponding to the maximum volume fraction of the crysta.IIine phases and minimum crystal size is consistent with the optimum nucleation temperature determined from DTA. Further, the volume fraction of the crystal phases has been shown to exhibit a maximum with hold times at optimum nucleation temperature and with crystal growth temperature at constant time.

The oxidation behaviour of glasses and glass-ceramics was studied in the 900- 1300°C temperature range and with different oxygen pressures. Various techniques, TGA, XRD, EDAX, Raman Spectroscopy, SEM were used to investigate the composition and the morphology of the oxidised scale. The reaction starts above the glass transition temperature and the progress of the reaction at the intemaI interface is the limiting step. For glass-ceramics obtained after heat treatments under nitrogen, it is shown that multiphase materials in the Y-Si-Al-O-N system exhibit the best oxidation resistance and the results can be used to explain the degradation of Si3Nl sintered with these additives.

With regard to the application of glass-ceramic treatments to nitrogen ceramics, previous work ' has shown that B-phase is undesirable as a grain-boundary phase in sialon ceramics because of its low temperature stability and poor oxidation resistance. Both U-phase and W-phase can be produced as a single phase in Ln-densified 13-sialon ceramics; however, in performance these are very similar to !3-sialon - YAG ceramics in giving better mechanical property retention up to > 1300°C than the undevitrified, glassy parent materials, but then both oxidation and melting take

place, resukingi nrelativelyp oorpropertiesat higher temperatures. Thepyroxene phases offer better performance as grain-boundary phases, but these must be used in silicon nitride rather than sialon ceramics. Inevitably the absence of alurninium results in more refractory products, but there is the increased problem of densification under an atmosphere of 0.1 MPa nitrogen.. Among the vaned amounts and ratios of MgO + Y203 used as additives for densifying silicon nitride, 1:1 molar ratio gave the best performance.

Overall, this work has shown that the field of oxynitride glass ceramics is larger than originally thought, and that many new phases exist which merit further exploration. Whereas the properties of the materials explored in the present programme are at least comparable with current oxide glass ceramics, the present results show that further development of the newer glass ceramics studied in this programme may be beneficial.

Descriptors:
Ceramics, glasses; Composites; Corrosion; Fabrication;

Industrial Applications and Market Analysis

Speciality glasses are being used in modern "high-tech" industrial applications such as optics, optoelectronics, microelectronics, communication technologies, bioengineering and niche areas of the automotive and architectural sectors where their novel functions are being exploited.

Signii5cant markets exist and are being forecast for devices developed using newtypes of glasses in a wide range of industries where applications take advantage of their chemical, biochemical, optical, electronic, thermal, mechanical and magnetic properties.   SWcific activities in other trading blocksn particularly Japan and the U.S.A. show that a significant effort is under way to develop novel glass materials for key industrial technologies.

Oxynitride glasses and glass ceramics are perhaps the latest addition to the range of "new glass" materials and their major areas of application are expected to be in:
. High Temperature Glass Ceramics for Structural Applications
. High Temperature Joining of Ceramics (and Ceramics to Metals)
● Novel Glaze Systems for Refractory Protection
. Passive Coatings on Electronic Substrates

This project was the fwst of its kind in Europe and therefore a market analysis for Oxynitride Glasses in these applications has not been undertaken and the potential for exploitation is largely unknown.

In addition, the results of the work, in terms of understanding the glassy grain boundary phases in silicon nitride ceramics, should provide a major indirect benefit to all silicon nitride manufacturers in Europe. The World market for engineering ceramics is approximately 1400 million ECU with a growth of 10% per annum. The European market is around 350 million ECU but it is not known

what impact the results **of this** project would have on the silicon nitride segment of this market in terms of improved materiais and reliability.

Industrial and Intellectual Property Rights

At the outset, the partners agreed that all new developments on the glass-ceramic process applied to oxynitride glasses, either in terms of any innovations in the thermal treatments or any new materials and their applications, would be protected by taking patents in order to avoid premature disclosure of results which could be commercially exploited. However, no specific patent rights have been considered. The intellectual property obtained from the project is to be considered as "know-how".

Benefits to Partners and Exploitation P1an

Industrial Endorsers: The industrial endorsers of this project are: Ceramiques et Composites (France) and Cookson Technology (UK). The endorsers attended most of the management meetings of the project and the mid-term review meeting in Brussels with the Commission. Generally, the industrialists are well pleased with the results obtained and would be supportive of further research and development on these oxynitride glasses and glass-ceramics in novel applications since they do not foresee immediate exploitation potential.

Value of Project to Cookson:

- Primarily of interest to Cookson Matthey Ceramics (a 50% Cookson owned company).

- Cookson Matthey Ceramics is a major supplier of glass products to the tableware, tile, sanitary ware, cosmetics and automobile industries. Circa. 200,000 tonnes of glass per annum produced by CMC.

- Little information available in literature on oxynitride glasses. New data generated valuabie to CMC data base.

- There may be spin-offs for Vesuvius, Alfa-Frys and Anzon (1007o Cookson companies).

- Vesuvius produce technicai ceramic parts, Alfa-Frys are active in Electronic products (sealing glasses, brazinglsoldering fluxes) while Anzon manufacture flame retardant compounds.

No immediately obvious applications as yet, but possibilities exist in:

- Improving performance of Si nitride-based ceramics through optimisation of grain-boundaiy phases.

- Extending performance capability of oxide glass decoration enamels (CTE, durability, colour), thereby helping to offset loss of Cd, Pb and Ba (due to legislation) in these systems.
- Making a virtue of **a** fault by exploiting the oxidising tendency to generate a "Nitrogen Blanket" for use in flame retmdants or metal brazing applications.

Cookson Technology has commenced a collaboration with the University of Newcastie upon Tyne on "Coloured Oxynitride Glasses" to establish if the addition of nitrogen to standard coloured oxide glasses enlarges the colour space presently available.

Interest from other companies has been generated, initially through an industrial workshop which was arranged by the partners and held in Newcastle in October, i 994. In particular, Cerdec, a company based in Limoges, France took an interest in the glasses for possible applications in electronics coatings and this has led to further collaboration with the University of Limoges. Morgan Matroc (UK) also expressed interest in the results of the project as applied to silicon nitride ceramics.

The industrial workshop also brought the partners into contact with TWI, a major laboratory for welding and joining technologies in the UK. As a result, it is anticipated that the partners will collaborate with TWI in a forthcoming proposal to investigate possibilities for Oxynitride Glass Joining within the framework of a Brite-Euram Thematic Network

Partners: The benefits to the University partners areas follows:

Training of all researchers: **All** the researchers and students involved in the project have participated in the different Management Meetings (Limerick, Newcastle, Limoges, Madrid,, Riccione). They received a good understanding of gkss preparation, glass characterisation techniques and glass ceramics properties. The comparison of different experimental data obtained with various techniques in the different laboratories is also a good training to develop a critical mind and to have more reliable results.

University of Limerick: The project has enabled the Centre in Limerick to build on its previous Brite-Euram experience and collaborations on oxynitride glasses already started with ENSCI, Limoges and to maintain its position as a leading centre in Europe in this field. The researchers involved have spent time undertaking research in the laboratories of the other partners, particularly a number of times in Limoges, and also at the Rutherford Appleton Laboratory (UK) which was a major sub-contractor of the University of Newcastle upon Tyne.

University of Newcastle upon Tyne: The current project has stimulated the research group to enhance its position as a leading centre concerned with characterisation of oxynitride phases. As a follow on, Professor Thompson took the lead in a new proposal under the EU Training and Mobility of Researchers Programme, involving the existing and new partners, to further develop some of the fundamental aspects of the work and provide further opportunities for training of European researchers in this important topic.

University de Limoges: T'hkproject has enabled the group to develop further its expertise in Oxidation of Oxynitide Materials for which it is already a leading authority. During this project, a cooperation with the University of Gothenburg started. As part of this work, Dr J. Sjoberg spent a week at the ISIS-Rutherford Appleton Laboratory and a week at a similar facility in Saclay (Lure).

The group started a cooperation with Cerdec (France) which is involved in glass melting processes and has an interest in glass or glass-ceramics applications.

ENSCI, Limoges: This project enabled the group to further develop the ultrasonics technique to enable crystallisation processes up to high temperatures to be followed. This has put ENSCI at the forefront of this field.

The benefits for the undergraduate researcher, H. Lemercier, in addition to the regular 6 monthly meetings with the other participants, was to have the opportunity to spend two weeks in Limerick to become familiar with the problems of glass elaboration and another two weeks in Paris to perform Raman experiments in the Laboratory of Dr. B. Piriou at the Ecole Centrale de Paris. In addition, he spent one week at Rutherford Appleton Laboratory with Dr. R. Ramesh from Limerick to become initiated into neutron diffraction measurements with the ISIS pulsed neutron **source.**

Exploitation Timescale: At the end of this project, a number of possibilities are available for further exploitation of the results but not yet in an industrial context. The partners were already successful with a TMR proposal on Characterisation of Oxynitride Phases. The partners are currently preparing a Bnte-Euram Thematic Network proposal on Oxynitride Glasses for High Temperature Joining. The partners are also discussing with industrialists the possibility of extending the application area to Silicon Nitride Bearings using different glass additives whichwil.1 not be ready before 1997. Assuming a successful outcome and a further three year RTD project, a further two to three years may be expected to market following successful product development

Communication Strategy and Dissemination of Results

In addition to the regular management meetings at which technical progress was communicated to ail partners and industial endorsers, the partners were involved in joint conference presentations and journal publications and also publications from each individual laboratory. A complete list is given below,

An Industrial Workshop was held in October 1994 at the University of Newcastle upon Tyne, organised by all the partners, in order to communicate results on potential application areas to interested industrialists. The outcome of that Workshop in terms of further potential collaborations has been highlighted in the previous section on Exploitation.

Publications resulting from the Project

1. Hampshire, S., Nestor, E., Flynn, R., Besson, J.L., Rouxel, T., Lemercier, H., Goursat,P., Sebai.,M., Thompson, D.P. and Liddell, K., Yttrium Oxynit.ride Glasses: Properties and Potential for Crystallisation to Glass-Ceramics, (1994)
   J. Euro. Ceram. Sot., ~, 261.

2. Ramesh, R., Nestor, E., Flynn, B., Pomeroy, M.J. and Hampshire, S,, Optimisation of Nucleation in a Y-Si-Al-O-N Glass-Ceramic, (1994) In Ceramic Materials & Components for -, eds. D.S. Yan, X.R. Fu and S.X. Shi (World Scientific, Singapore), 433.

3. Ramesh, R., Nestor, E., Pomeroy, M.J. and Hampshire, S., Optimisation of Heat Treatments for Oxynitride Glass-Ceramics, (1995) In Key Enszineerin~ Materials, eds., S. Hampshire, M. Buggy, B. Meenan & N. Brown (Transtech, Switzerland) 99-100, 211.

4. Ramesh, R., Nestor, E., Pomeroy, M.J. and Hampshire, S., Optimisation of Glass Formation and Crystallisation, (1995) In proceedings of Fourth Euro Ceramics cd., A. Bellosi, g, 271.

5. Sebai, M., Sjoberg, J., Goursat, P., Nester, E., Ramesh, R. and Hampshire, S., Oxidation behaviour of Yttrium and Neodymium Oxynitride Glasses, {1995) J. Euro. Ceram. Sot., E **1015.**

6. Sjoberg, J., Sebai, M., Goursat, P., Nestor, E., Flynn, R. and Hampshire, S., Oxidation of Y-Si-Al-O-N glasses: Microstructural analysis of the reaction products, In proceedings of Fourth Euro Ceramics cd., S. Meriani &V. Serge, j, 439.

7. Ramesh, R., Nestor, E., Pomeroy, M.J., Hampshire, S., Liddell, K. and Thompson, D. P., Potential of NdSiAION Glasses for Crystallisation to Glass-Ceramics - Accepted for publication in J. Non-Cryst. Solids.

8. Nestor, E., Rarnesh, R., Connolly, P. and Hampshire, S., Preparation and Properties of Re-Si-Ai-O-N Glasses - Accepted for publication in the Proceedings of 11th Lrish Materials Forum, Galway, Ireland, Sept. 1995.

9. Lemercier, H., Rouxel, T., Fargeot, D., Besson, J.L. and Piriou, B., Yttrium Oxynitricie Glasses: Structure and Mechanical Properties-Elasticity and Viscosity-Accepted for publication in J. Non-Cryst. Solids.

Publications in preparation

i). Besson, J.L,, Lemercier, H., Rouxel, T. and Trolliard, G., Nucleation and Crystallisation of a Y-Si-Al-O-N glass.

ii). Liddell, K. and Thompson, D. P., Phase characterisation of heat treated sialon phases.

iii). Fang, X. Y., Liddell, K. and Thompson, D. P., Preparation and characterisation of rare-earth nitrogen pyroxenes.

iv). Liddell, K. and Thompson, D. P., Rules governing the crystalline form of $Y_2Si_2O_7$ in heat treated Y-Si-Al-O-N glasses".

v). Ramesh, R.; Nestor, E., Pomeroy, M. J., Hampshire., Yttrium Oxynitride Glasses: Investigation of the G1ass+GIass-Cerarn.ic Transformations.

vi). Sebai, M., Goursat, P., Liddell, K., Thompson, D. P., Ramesh, R. and Hampshire, S., Neodymium Oxynitride Glasses and Glass-Ceramics - Preparation, Properties, Crystallisattion and Oxidation Resistance.

Ptans to publish a book entitled "Oxynitride G1asAes" are in hand and approval from the European Commission has been given. Negotiations with a Potential publisher have commenced.

PRESENTATIONS MADE AT THE FOLLOWING:

Some of the principle scientists involved in the contract have given keynote or overview lectures at various meetings and conferences including:

- Silicon nitride '93, Stuttgart, Germany, Oct. 1993.

- Workshop: Tailoring of High Temperature properties of Si$L Ceramcis, Schlo~-Ringberg, Germany, Oct. 1993.

- 5th International Symposium on Ceramic Materials and Components for Engines, Shanghai, May, 1994.

- 10th Irish Materials Forum Conference, Coleraine, Northern Ireland, September, 1994.

- VIII International Conference on the Physics of Non-Crystalline Solids, Turku, Finland, June-July 1995.

- 1 lth Irish Materials Forum Conference, Galway, September, 1995.

- 4th European Ceramic Society Conference, Riccione, Italy, Oct. 1995.

- Groupe Francais de las C&wniques, Lyon,' 1996.

Poster Presentations

- 3rd European Ceramic Society Conference, Madrid, Spain, Sept. 1995.

- 5th Industrial Materials Technology Conference, Brussels, Belgiurm Dec. 1994.

Doctoral Theses produced/expected from the project

- Herve Lemercier - Verres du system& Y-Si-Al-O-N: Propri&6s, Structure et Gistallisation, Dec. 1995.

- Makdad Sebai - Verres et vitroctkrniques oxyazott?s des systkmes Nd-Si-Al-O-N et Y-Si-Al-O-N: Propri&&s et comportment 41' oxydation, Mar. 1996.

- Liz Nestor - Formation, properties and controlled crystallisation of oxynitride glasses, Sept. 1996.