Effects of nitrogen on phase formation, microstructure and mechanical properties of Y–Ca–Si–Al–O–N oxynitride glass–ceramics

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ABSTRACT

The effect of nitrogen substitution on the crystallisation of an oxynitride glass in the Y–Ca–Si–Al–O–N system has been studied. The appropriate heat treatment temperatures were selected according to the information provided by the differential scanning calorimeter (DSC) measurement. There is a significant increase in T_g and T_c with increasing nitrogen content. X-ray diffraction (XRD) and scanning electron microscope (SEM) analysis demonstrated that, for the oxide glass and oxynitride glasses containing 6 equiv.% and 12 equiv.% nitrogen, crystallisation results in the formation of irregular lath-shaped $Ca_4Y_6O(SiO_4)_6$ and stick-shaped anorthite. As the nitrogen content increases to 18 or 24 equiv.%, irregular plate-like yttrium-aluminium garnet (YAG) is identified as the main crystalline phase. As the nitrogen content increases to 30 equiv.%, microscopic needle-like crystals of $Al_6O_3N_4$ become the only crystallised phase. The best composition, owing to the mechanical properties (e.g. flexural strength of 162 MPa and Vickers hardness of 8.5 GPa), was found to correspond to a nitrogen content of 24 equiv.%.

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1. Introduction

Silicon oxynitride glasses were first discovered as grain boundary phases in silicon nitride based ceramics [1]. Silicon nitride ceramics are usually densified with the aid of various sintering additives (such as MgO, Y_2O_3, etc.). These additives in combination with silicon dioxide, which originates from the furnace atmosphere, or from the dissolution of silicon nitride particles in the melt, cause the formation of a liquid phase that transforms into a glass upon cooling [2]. Since it is very difficult to investigate experimentally the properties of grain boundary phases, research on them in bulk form was initiated [3]. Oxynitride silicate glasses are a branch of high performance glasses, obtained by incorporating nitrogen atoms into silicate or alumino-silicate glasses [4,5]. The unique properties of silicon oxynitride and SiAlON glasses have led to a search for areas of potential application [6–8].

The improvement in physical and mechanical properties when nitrogen is incorporated into silicate or alumino-silicate glasses is also realised in glass–ceramics. As with other silicate or alumino-silicate glasses, oxynitride glasses may be heat treated at the appropriate temperatures to crystallise as glass–ceramics and many studies of crystallisation of these types of glasses have been reported [9–14]. The crystallization improves the mechanical and thermal properties. The specific crystalline phases formed upon heat treatment, and the extent of their formation, determine the properties of the material [15–18]. In general, nitrogen increases the stability of oxynitride glasses. The

conventional process to produce a glass–ceramic involves two steps: a lower temperature heat treatment of glasses, generally just above the glass transition temperature, to induce nucleation, followed by heating to a second higher temperature, the so-called crystallisation temperature, to allow growth of the pre-formed nuclei. The crystalline phases formed depend on both the composition of the parent glass and the heat-treatment process but in many cases, oxide phases form first leaving the residual glass more N-rich [19].

The present work investigates the influence of the nitrogen addition on phase formation, microstructure and mechanical properties of Y–Ca–Si–Al–O–N glass. XRD and SEM were used to study the crystallization behaviour of the glass–ceramics. An understanding of the roles played by nitrogen atom in this system is clearly vital to a coherent approach to improved material performance.

2. Experimental procedure

2.1. Preparation of materials

A base Y–Ca–Al–Si–O oxide glass was prepared with a cation composition (in equiv.%) of 12Y:12Ca:61Si:15Al and 100 equiv.% oxygen. 6, 12, 18, 24 and 30 equiv.% N was substituted for oxygen in order to evaluate the effects of nitrogen on crystallization of oxide glass or oxynitride glasses. Y_2O_3 (99.99%), α-Si_3N_4 (99.8%), SiO_2 (99.9%), $CaCO_3$ (99.9%), and Al_2O_3 (99.9%) were used as raw material powders to prepare Y–Ca–Si–Al–O–N glasses. Dried powders were weighed and performed by mechanical agitation (using an attritor mill), mixed in isopropyl alcohol for 24 h, and then dried again. The mixture was

melted at 1500–1650 °C for 2 h in a graphite crucible lined with BN powder to avoid any sealing between the glass and the crucible. Syntheses were performed in an atmosphere of an inert gas (N_2 or $N_2 + Ar$ gas). Melts were finally poured into a preheated graphite mould and annealed in air at a temperature close to an estimated vitreous transition temperature. After the determination of the effective T_g by DSC analysis, glasses were annealed at T_g for 2 h and slowly cooled to room temperature. Heat treatments of the glass samples to prepare glass–ceramics were carried out in a silicon carbide horizontal furnace in a nitrogen atmosphere after DSC measurement.

2.2. Characterization techniques

2.2.1. Differential scanning calorimeter (DSC)

For DSC analysis, about a 10 mg powder sample was placed in an alumina crucible and subjected to a heating rate of 10 °C/min from ambient temperature to 1400 °C in a flowing high purity argon environment. The onset point of an endothermic drift on the DSC curve corresponding to the beginning of the glass transition range is reported as T_g whilst the peak of the exotherm is taken as T_c. Errors in measurement are ± 5 °C.

2.2.2. Measurement of density (ρ)

The true density (ρ) of the oxynitride glass samples was evaluated by means of a gas pycnometer, operating with He gas on samples in powdered form. The results were averaged on 10 measurements. The experimental error in the measured value was ± 0.01 g/cm^3.

2.2.3. X-ray powder diffraction (XRD)

Crystalline phases in the prepared glass–ceramics were identified by an X-ray diffractometer (D/max 2500 model, Japan) with Cu-$K\alpha$ radiation using an incident wavelength of 0.15406 nm (Cu-K_α). Voltage and current were selected as 40 kV and 50 mA, respectively. Date were collected from $2\theta = 10°$ to 90° at a scanning rate of 8°/min. To identify the crystalline phases, XRD patterns were analysed by jade 6.0 software using ICDD-PDF2 database.

2.2.4. Scanning electron microscopy (SEM)

SEM and environmental SEM imaging were carried out using an FEI Quanta 200 SEM, which was fitted with a Peltier-cooled stage during SEM operation. Energy dispersive X-ray analysis (EDX) was used to obtain a chemical analysis of particular crystals or regions. Before the SEM observations, these glass–ceramic samples were mounted in epoxy resin and polished to 1 μm with diamond slurries. The mirror surfaces of specimens were sputtered with a platinum coating.

2.2.5. Vickers micro-hardness

Vickers hardness was measured using a micro-hardness tester (DHV-1000-CCD, China) with a pyramid shaped diamond indenter. The glass–ceramic surfaces were polished to a 1 μm diamond finish. A load of 2 kg was applied on polished glass–ceramic samples. At least 10 indentations were made on each sample, using the average indentation diagonal length to calculate hardness values in GPa.

2.2.6. Three-point bending strength

Three-point bending strength was measured on a glass bar (4 × mm × 4 mm × 25 mm with accuracy ± 0.02 mm) by using an electronic multipurpose tester (CSS-44100 model, China). The crosshead speed was 0.5 mm/min. The glass–ceramic surfaces were polished to a 1 μm diamond finish. The measurement error for the hardness and the bending strength is within ± 2%.

3. Results and discussion

3.1. Parent glasses

The appearances of the obtained parent glasses were primarily inspected by the naked eye. The prepared oxynitride glass samples are translucent and grey by the naked eye except for samples N0 and N30. Actually, the sample N0 is a high-quality clear colourless glass (with nitrogen-free), whilst the sample N30 is translucent dark. With the influence of nitrogen, the colour of the glasses is observed in the transparent colourless region and shifted to a darker grey region when nitrogen increases. Oxynitride glasses are as a rule less transparent than corresponding oxide glasses.

Measured densities for the determined glass compositions are given in Table 1. The density of the Y–Ca–Si–Al–O–N glasses, as seen in Table 1, is found to have values ranging from 3.02 to 3.24 g/cm^3 and increases slightly with increasing nitrogen content. Addition of nitrogen leads to an increase in density for the silicon oxynitride glasses, which can be attributed to the formation of a significant fraction of three-coordinated N in the glass networks.

To study the crystallization behaviour, the parent glasses were subjected to DSC measurements. The results of DSC curves are shown in Fig. 1. The DSC curve of the glass sample N0 shows well-defined glass transition ranges and two obvious exothermic peaks corresponding to crystallizations of two possible crystalline phases. However, the other glass samples only show one exothermic peak. And it is easy to see that the exothermic peaks of glass samples N6, N12 and N18 are clear and distinct but that of glass samples N24 and N30 become weak or absent. The glass transition temperatures range from 834 ± 5 °C to 941 ± 5 °C and the locations of main exothermic peaks are in the range 1035 ± 5 to 1166 ± 5 °C. It is clearly seen that the crystallization peaks (T_c) are shifted towards higher temperatures with increasing of nitrogen contents and the extracted T_c values are summarised in Table 1. Fig. 1 shows that there is a significant increase in T_g and T_c with increasing nitrogen content. Since an increase in nitrogen content by all accounts increases the cross-linking of the glass network, the T_g and T_c are expected to increase as the nitrogen content of the glass increases. The effect increases with increasing the amount of nitrogen and this may be related to the increase in viscosity of the glass which consequently leads to less mobility of the structural elements in the glass.

Glasses were heat-treated in a resistance furnace under flowing nitrogen with a heating rate of 20 °C/min to near the nucleation temperature, with a hold for 5 h followed by heating at 10 °C/min to >T_c temperature with a hold for 10 h followed by removal from the

Table 1
Composition (in equiv.%), melting temperatures, colour, thermal properties, and density of the Y–Ca–Si–Al–O–N glasses.

Samples no.	Composition (in equiv.%)						Melting temperatures	Colour	T_g (± 5 °C)	T_{c1} (± 5 °C)	T_{c2} (± 5 °C)	Density (± 0.01 g/cm^3)
	Y	Ca	Si	Al	O	N						
N0	12	12	61	15	100	0	1500	Transparent colourless	834	1035	1136	3.02
N6					94	6	1550	Translucent and gray	867	1052		3.04
N12					88	12	1580	Translucent and gray	874	1090		3.07
N18					82	18	1600	Translucent and gray	890	1117		3.13
N24					76	24	1600	Translucent and gray	910	1125		3.16
N30					70	30	1650	Translucent and dark	941	1166		3.24