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Crystallization of $Y_3Al_5O_{12}$ from an Oxynitride Glass Monitored by High-Temperature X-Ray Diffractometry

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Abstract

It is well established that the glassy phase in a β-SiAlON material, with addition of Y_2O_3, can be crystallized to yttrium aluminium garnet ($Y_3Al_5O_{12}$–YAG) by a post-sintering heat treatment. The crystallization of the YAG phase from an oxynitride glass with composition 46·1 wt% Y_2O_3, 26·3 wt% Al_2O_3, 21·6 wt% SiO_2 and 6 wt% Si_3N_4 was studied by means of high-temperature X-ray diffractometry. The kinetics of the crystallization were monitored in terms of the (420)) YAG peak area versus isothermal soaking time at 1150°C during different heat treatments. The crystallization of the YAG phase was found to proceed as a surface crystallization. The results are relevant to developing improved crystallization treatments for glasses with potential for crystallization to YAG-based glass-ceramics and for heat treatments of YAG/β-SiAlON materials. Copyright © 1996 Elsevier Science Ltd

1 Introduction

β-SiAlONs ($Si_{6-z}Al_zO_zN_{8-z}$) are of interest for applications as ceramic components for high-temperature engineering systems because of properties such as high-temperature strength, high hardness, and high oxidation and corrosion resistance. They are usually prepared by dissolution of Al_2O_3 and AlN in α-Si_3N_4 in the presence of an intergranular liquid phase.[1–6] The consequent presence of intergranular glass in sialon ceramics has a strong influence on their mechanical properties and oxidation behaviour. It has been shown that the glassy phase in a β-SiAlON material, with addition of Y_2O_3, can be crystallized to yttrium aluminium garnet ($Y_3Al_5O_{12}$–YAG) by a post-sintering heat treatment at temperatures between 1200 and 1400°C or by slow cooling from the sintering temperature.[7–11] To achieve a perfect β + YAG two-phase structure, it is necessary that as the matrix transforms to YAG, the excess components diffuse into the β phase or precipitate as β of modified composition. Crystallization is promoted by increased polytypoid content (usually 21R which is a structural and compositional variant of the AlN-wurzite structure). Ceramics with high 21R levels crystallize partially during normal process cooling; those with low levels either do not crystallize during a normal (e.g. 5 h) treatment at 1400°C while for longer times additional phases such as yttrium disilicate form. This general trend may be simply interpreted via the ternary oxide liquidus surface and the influence of 21R on liquid composition; i.e. low 21R ceramics have matrix compositions within the eutectic trough in which the liquid is stable above 1300°C and with increased 21R compositions move towards the YAG phase field with increased liquidus temperature.[3,4]

Bonell *et al.*[12] studied YAG crystallization during annealing of a β-SiAlON/YAG ceramic at 1250°C and 1350°C for 40 h. At complete crystallization a very fine film (of the order of 1 to 2 nm) of amorphous phase was found to exist at two-grain junctions and assumed to be a stable configuration. Hohnke and Tien[2] studied YAG crystallization during annealing of β-SiAlON/YAG ceramic at 1200, 1300 and 1400°C for 50 h and found a catalytic effect of Pt added as a nucleating agent. Small amounts of glass retained in grain boundaries and triple points were identified in the microstructure. Bentsen *et al.*[13] investigated the effect of annealing of a β-SiAlON/YAG ceramic on the thermal diffusivity of the material and found a significant increase after an annealing treatment at 1350°C for 20 h.

The aim of the present work was to study the crystallization of the YAG phase from an oxynitride glass by means of high-temperature X-ray diffractometry (HT-XRD). An oxynitride glass composition, prepared in a nitrogen atmosphere

at 1700°C, was subjected to different heat treatments in a high-temperature X-ray diffraction unit. The YAG crystallization from the parent glass was monitored by high-temperature X-ray diffraction during the heat treatment.

2 Experimental

2.1 Glass preparation

Glass with composition 46·1 wt% Y_2O_3, 26·3 wt% Al_2O_3, 21·6 wt% SiO_2 and 6 wt% Si_3N_4[14] was prepared from high-purity Y_2O_3, Al_2O_3, SiO_2 and Si_3N_4 powders (Rhone Poulenc, Alcoa Chemicals, Johnson Matthey Alfa Products and KemaNord Industrikemi). The powders were weighed in a precision balance, and mixed in polyethylene containers on a Siemens roller mill for 10 h using propanol as mixing medium. The alcohol was then evaporated and the powder mixtures were sieved. A batch of approximately 100 g was then compacted into a molybdenum crucible and fired in a nitrogen atmosphere (pressure of 0·17 MPa) at 1700°C for 2·5 h. The heating rate up to the firing temperature was 5°C min^{-1}, the cooling rate from the firing temperature to 1400°C was 20°C min^{-1}, from 1400 to 950°C, 15°C min^{-1}; and from 950 to 500°C min^{-1}. The cooling rate was the natural cooling rate of the furnace (cold wall vacuum/pressure furnace with a graphite heater) after it had been switched off. A mass change of less than 1 wt% was observed.

2.2 Glass and glass-ceramics characterization

The glass transition temperature (T_g) and the temperature of crystallization (T_c) were measured by differential thermal analysis (DTA) on a powdered as-quenched glass sample in a nitrogen atmosphere. An Al_2O_3 powder reference standard and heating rate of 10°C min^{-1} were used.

As a complement to HT-XRD, microhardness and infra-red spectroscopy were also used to study the possible structural changes in the glass during heat treatment. These measurements were carried out on samples heat-treated as follows: 2 g pieces of glass were placed in an Si_3N_4 powder bed in molybdenum boats and heat-treated at temperatures between 900 and 1000°C for 6 h in a static atmosphere of 0·13 MPa N_2 in the cold wall vacuum/pressure furnace with a graphite heater mentioned above. All the samples were weighed on a precision balance before and after the heat treatments to check for mass changes; none were observed. Vickers hardness measurements were performed with a commercial hardness tester (Matsuzawa Seiki Mxt α). A load of 300 g was applied for 15 s on the sample whose surface had been polished with 3 μm spray diamond. At least 10 indentations were made on each sample, the hardness being calculated on the basis of the average length of the indentation diagonals. The infra-red (IR) spectra were measured using a Perkin–Elmer 1760 X Fourier transform spectrometer equipped with a triglycine sulfate (TGS) detector. The measurements were carried out on discs pressed from powdered samples mixed with KBr.

Scanning electron microscopy (SEM) was carried out using a CamScan S4-80DV electron microscope. Room-temperature powder X-ray diffraction was performed on all samples heat-treated as bulk material in the cold wall furnace.

2.3 High-temperature X-ray unit

The high-temperature unit used in this investigation is based on an Anton-PAAR HTK-10 high-temperature chamber. This standard equipment was re-engineered to increase the maximum working temperature to more than 2300 K in an inert atmosphere or in vacuum. The platinum strip which is used as heater in the standard HTK-10 equipment is replaced by a graphite furnace. The basic unit in this system is a Philips powder diffractometer with a vertical goniometer PW 1050/25, graphite monochromater PW 1752/00, proportional counter for reflected beam PW 1711/10 and PW 1730/10 generator. The X-ray diffraction is controlled by a PW 1710 diffractometer control system. The raw data are collected, processed and analysed with PC-APD (PW-1877) software supplied by Philips.

The graphite furnace was coated with silicon nitride by first applying a layer of Si powder to the graphite and then nitriding at temperatures between 1150 and 1450°C. The coating had a thickness of approximately 0·75 mm, a relative density of 0·65 and a pore size of 0·2 μm. It showed good mechanical strength and thermal shock resistance. The voltage required to achieve a given temperature and the resistance of the furnace at that voltage were not significantly affected by the coating. The graphite furnace design and the high-temperature X-ray unit have been described in previous studies by Babushkin *et al.*[15] and Ashkin *et al.*[16]

2.4 Experimental set-up with the HT-XRD unit

Small amounts of as-quenched glass were powdered and the powder was freely compacted to form 8 × 10 × 1·5 mm plate samples. These were put into the coated graphite furnace and subjected to one of two possible heat treatments: (i) a single-stage heat treatment at 1150°C, (ii) a two-stage

heat treatment with various temperatures in a first pre-treatment stage (T_g - 90°C, T_g - 60°C, T_g - 30°C, T_g and T_g + 20°C) for 1 h followed by a second stage at the higher temperature, 1150°C. The first pre-treatment stage was used to cause a partial sintering of the powdered glass sample and consequently to decrease its specific surface area with increasing temperature of the first stage. The heating rate of both heat treatments was 450°C h^{-1}, with the exception of the temperature interval between T_g and 1000°C for which it was 200°C h^{-1} and during which internal nucleation in the glass was expected to occur. The temperature of the sample was measured with a Pt–13% Rh/Pt thermocouple. The heat treatments were conducted in a static atmosphere of 0·13 MPa N_2 (<5 ppm O_2).

During the heat treatment two separate X-ray scans were performed: one over a 2θ range of 31·5 to 35° at a rate of 0·05° s^{-1} in approximately 20 min intervals and a second between 20 and 40° at a rate of 0·05 s^{-1} in 60 min intervals. After the soaking temperature had been reached the scans were performed more frequently (Fig. 5). The first was used to follow the crystallization of the YAG phase [(420) peak at 2θ = 33·5°], the second to check for possible additional phases developing during the heat treatment, mainly δ- and γ-yttrium disilicates.[14] The X-ray generator settings were 50 kV and 30 mA with a Cu-target tube. All the performed high-temperature X-ray runs were repeated twice to ensure reliability of the results. A Marguardt non-linear least-squares algorithm was used to calculate the (420) YAG peak areas in order to obtain a quantitative measure of the amount of crystallized YAG phase. To confirm the nature of phases obtained during the heat treatments in the HT-XRD unit, an additional scan over a 2θ range of 10 to 80° at a rate of 0·02° s^{-1} was performed on the cooled specimens by a room-temperature XRD unit (Philips X-ray diffractometer, Cu K_α radiation).

3 Results and Discussion

3.1 DTA Measurements

Figure 1 shows the DTA chart with an endothermic peak at 943°C corresponding to the glass transition temperature (T_g) and two exothermic peaks at 1075 and 1145°C respectively, corresponding to crystallization processes in the glass. In a previous study[14] it was concluded that different crystal species crystallize from the parent glass at these two different temperatures. The first maximum corresponds to the crystallization of an intermediate phase accompanied by the crystallization of $Y_2Si_2O_7$ and the second one to the crystallization of the YAG phase.

3.2 Microhardness measurements

Figure 2 shows the results of Vickers microhardness measurements performed on bulk glasses heat-treated at 900, 925, 950, 980 and 1000°C for 6 h. These samples were transparent after the heat treatment, amorphous (as indicated by X-ray) and appeared to be homogeneous glasses without any traces of crystalline material when examined by SEM. A change of colour from yellow to light green was observed. However, a weak surface crystallization could be observed on samples heat-treated at 980 and 1000°C. For comparison, two additional microhardness measurements performed on samples heat-treated at 1050 and 1100°C for only 2 h are included in Fig. 2. The microstructures of these two samples contained crystalline material as could be evidenced by SEM observations.

The microhardness of as-quenched glass (without any subsequent heat treatment) was found to be 10·0 ± 0·39 GPa. A decrease of microhardness of samples heat-treated at 980–1000°C can be seen in Fig. 2. This temperature range corresponds approximately to the annealing temperature range

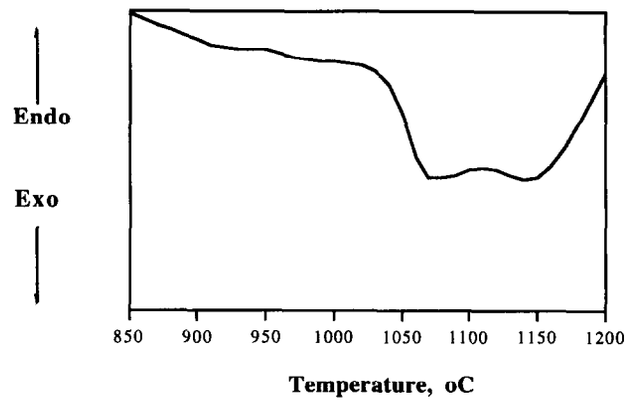

Fig. 1. DTA curve of the glass at a heating rate of 10°C min^{-1}.

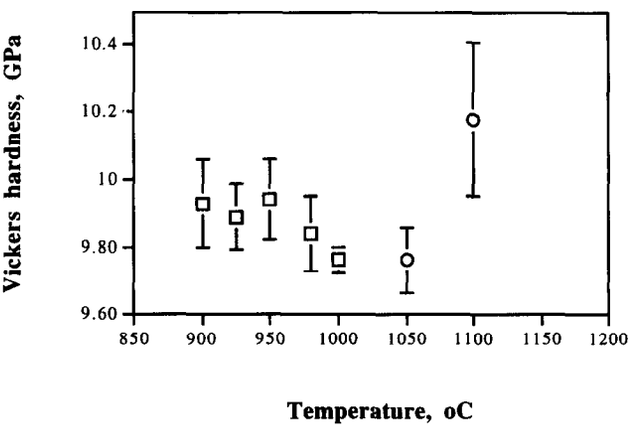

Fig. 2. Hardness of the glass heat-treated for 6 h (□) and 2 h (○).

for this type of glass.[17] Therefore it is believed that the decrease is due to the relaxation processes.[18] The increase of microhardness of the sample heat-treated at 1100°C can be attributed to the increased volume fraction of crystallized material in the parent glass revealed by the X-ray diffraction and SEM observations.

3.3 Infra-red spectroscopy

Figure 3 shows the IR spectra of 4 mg powdered specimens previously heat-treated as bulk glasses at 900, 950 and 1000°C for 6 h. The IR spectra of all three samples were similar with a broad absorption band located around 850–1100 cm^{-1}. The broad absorption is a result of integrated absorption from Si–O and Si–N bond vibrations.[19,20] Figure 3 also indicates a small increase of absorption of the glass heat-treated at 950°C and a large increase of absorption of the glass heat-treated at 1000°C compared with that heat-treated at 900°C. Therefore it can be concluded that some structural changes in the network of the glass took place during the heat treatments at 900–1000°C.

In order to explore the nature of these changes, IR spectra were collected on 1 mg powdered specimens prepared from the same samples as before, as well as on samples heat-treated at 1050 and 1150°C for 2 h and on YAG powder sintered at 1600°C in air. The IRDM deconvolution software included in the Perkin–Elmer equipment was applied to the collected data and after this modification revealed some additional absorption peaks. Thus the evolution of absorption bands related to the YAG phase (790, 730, 695, 565, 515 and 470 cm^{-1}) can be seen in Fig. 4. Since the microstructure of the sample heat-treated at 1150°C contained a large amount of crystalline YAG phase (as evidenced by X-ray powder diffraction), the absorption bands may be related to the developed YAG crystals. This spectrum is very similar to that of the sintered YAG phase. The amount of YAG crystals in the microstructure heat-treated at 1050°C was much less (amorphous when X-rayed) than in that heat-treated at 1150°C. Therefore the IR spectrum of the 1050°C specimen shows less intensity of the characteristic absorption bands attributed to the YAG phase. The microstructure of the sample heat-treated at 1000°C was amorphous with only some surface crystals as observed by SEM. Therefore the weak absorption bands at 790, 730, 695 and 515 cm-l can be attributed mainly to nuclei formed in the glass with the YAG-like structure. The IR spectra of glasses heat-treated at 900 and 950°C did not show any additional peaks after computer treatment, and therefore it was concluded that no nucleation or crystal growth occurred in the glass during the heat treatments at these low temperatures within 6 h.

3.4 Heat-treatments in the HT-XRD unit

Figure 5 shows the crystallization of the YAG phase from the parent as-quenched glass in terms of (420) YAG peak area (hereafter termed intensity) versus isothermal soaking time at 1150°C

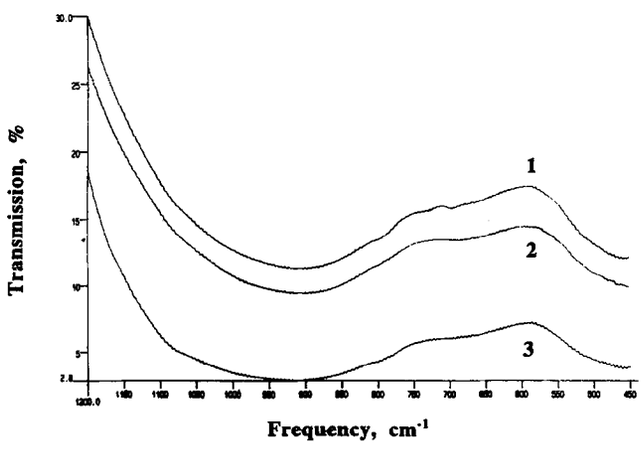

Fig. 3. IR spectra of the glass heat-treated at 900°C (1), 950°C (2) and 1000°C (3).

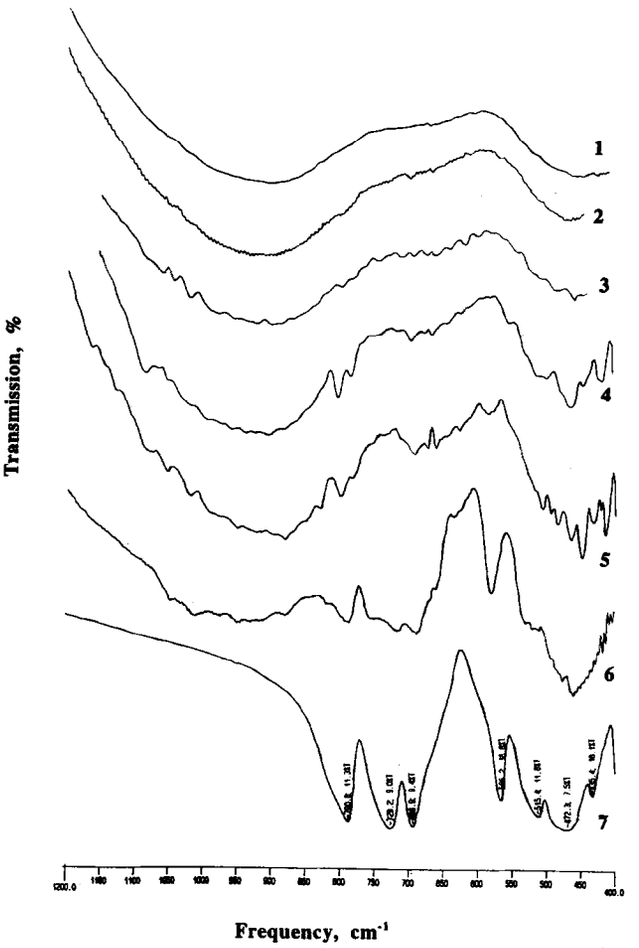

Fig. 4. Deconvoluted IR spectra of the glass as-quenched (1), and heat-treated at 900°C (2), 950°C (3), 1000°C (4), 1050°C (5) and 1150°C (6), and the IR spectrum of the YAG sintered at 1600°C (7).

during different heat treatments in the HT-XRD unit described in the Experimental Section. All the X-ray diffraction patterns collected during heating to the soaking temperature were free of any peaks from crystalline phases. Two groups of data, one low-intensity group (I) and one high-intensity group (II) can be distinguished. Group I included those two-stage heat treatment samples with the first stage treatment at T_g – 30°C and at T_g Group II included the single-stage heat treatment sample and the two-stage heat treatment samples with the first stage treatment at T_g – 90°C and T_g – 60°C. Thus, the crystallization process appears to be influenced by the temperature of the first pre-treatment stage. The intensity of the (420) YAG peak is reduced (group I) when the temperature of the first stage treatment is high enough to cause a partial sintering of the powdered glass within 1 h. This suggests that the crystallization of the YAG phase is influenced by changes of the specific surface area of the powdered glass due to the partial sintering in the first stage heat treatment. According to the IR measurements (Fig. 4) these temperatures are still too low for nucleation in the glass to proceed effectively and consequently the nucleation would occur mainly during heating to the second stage temperature. The influence of the specific surface area indicates that surface nucleation and growth are the dominant mechanisms of crystallization of the YAG phase in the investigated powdered glass. Figure 6 shows a SEM backscattered image of a polished surface of a sample with crystals growing from retained pore surfaces.

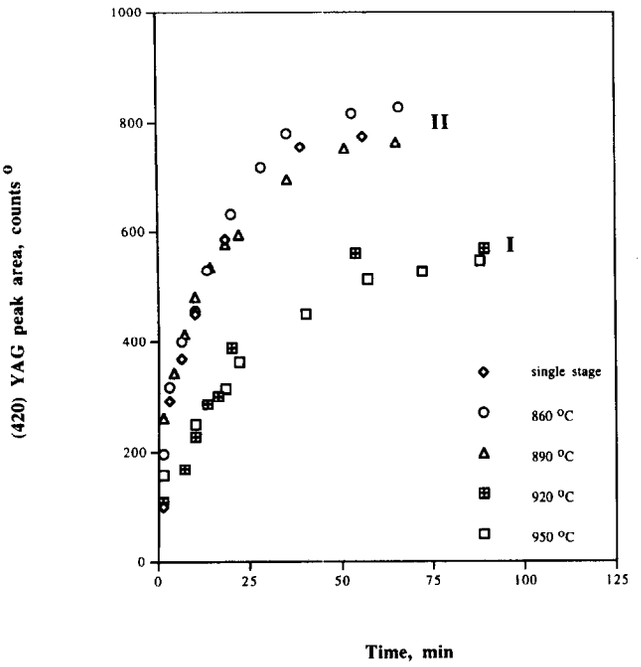

Fig. 5. Kinetics of the YAG crystallization in the glass at 1150°C during a single-stage heat treatment and following an initial pre-treatment at the indicated lower temperatures.

When the temperature of the first stage was increased to T_g + 20°C (≈970°C) and the same procedures were applied, some crystalline peaks started to develop in the X-ray pattern at the end of the initial first stage treatment, i.e. after approximately 40 min at this temperature. This behaviour implies that the nucleation rate in the glass had increased significantly at this temperature and subsequently the developed surface nuclei continued to grow to crystals which could be detected by the X-ray unit (Fig. 7).

The temperature of the first stage treatment also influenced the development of other phases in the microstructure in addition to the YAG phase. Two additional low-intensity peaks appeared in the X-ray patterns of samples heat-treated with the first stage at temperatures close to the T_g (i.e. T_g – 30°C, T_g and T_g + 20°C). These peaks at 2θ = 32·7° and 2θ = 31° correspond to the unidentified intermediate 'silicate' phase observed in previous studies[14,19,21] and to the δ-$Y_2Si_2O_7$ phase, respectively. Inspection of the X-ray patterns indicated that the intermediate phase crystallized from the glass at low temperatures (already around 970°C) and when the temperature was raised it started to transform probably to $Y_2Si_2O_7$ (Fig. 7). Additional peaks were not observed in the X-ray patterns of samples heat-treated with the first stage temperature at T_g – 90°C and at T_g – 60°C or in single-stage treatments. However, SEM observations revealed the presence of $Y_2Si_2O_7$ crystals in the microstructure of these samples (Fig. 8). These observations indicate that the crystallization of the $Y_2Si_2O_7$ phase was enhanced when the specific surface area of the powdered sample and the crystallization of the YAG phase decreased, and consequently that bulk nucleation and crystal growth were the dominant mechanisms of crystallization of the $Y_2Si_2O_7$ phase from the investigated

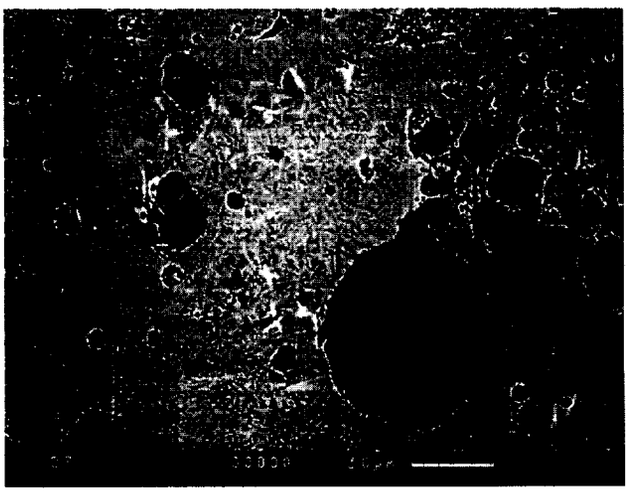

Fig. 6. YAG crystals growing from pore surfaces in the glass during a two-stage treatment with the first stage at T_g – 90°C for 1 h (backscatter image 500x).

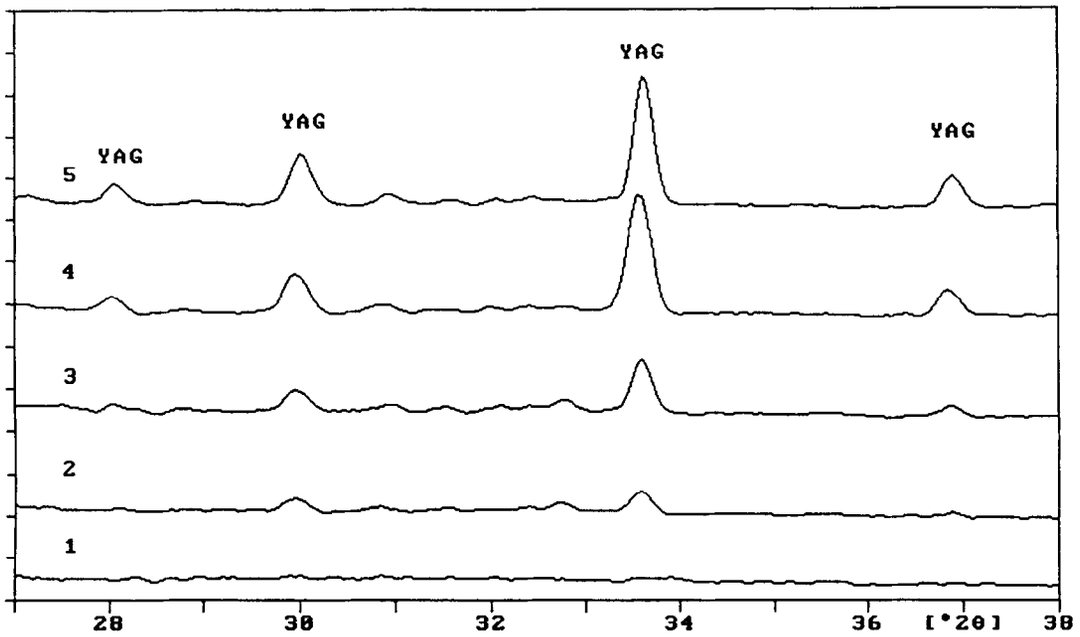

Fig. 7. X-ray patterns of the glass during a two-stage treatment with the first stage at T_g + 20°C (970°C) for 1 h; after 5 min at 970°C (2), after 5 min at 1150°C (3), after 60 min at 1150°C (4) and after 80 min at 1150°C (5).

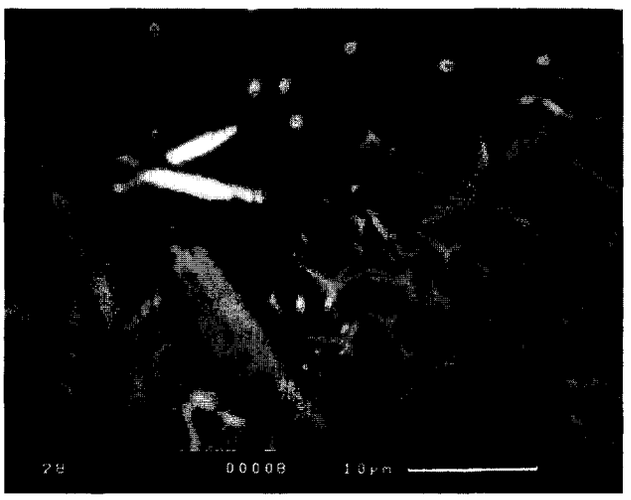

Fig. 8. $Y_2Si_2O_7$ crystals (bright crystals) developed in the microstructure of the glass during a two-stage treatment with the first stage at T_g–60°C for 1 h (backscatter image 2500x).

glass. Since the crystallization of the $Y_2Si_2O_7$ phase proceeded by a bulk process in competition with the surface crystallization of the YAG phase and since the amounts of $Y_2Si_2O_7$ phase crystallizing were small, no kinetic measurements of the $Y_2Si_2O_7$ crystallization were attempted. No oxynitride phase was detected in the microstructure of the glass-ceramics during the heat treatments and therefore it is assumed that the retained glassy phase was enriched by nitrogen.

The suggestion that the main mechanism of crystallization of the $Y_2Si_2O_7$ phase is a bulk process is consistent with results obtained by Ramesh *et al.*[22] using DTA measurements to characterize the crystallization process in a powdered oxynitride glass in the Y–Si–Al–O–N system. In that study the bulk nucleation and growth of the $Y_2Si_2O_7$ phase was identified as the main mechanism responsible for devitrification of the glass. Lewis *et al.*,[10] studying the crystallization of the glassy phase in a YAG/β-SiAlON material, observed that the number of nuclei was restricted and that there was a preference for nucleation of the YAG phase on free surfaces such as microcavities rather than at β-SiAlON/glass interfaces. This was attributed to a compositional influence in addition to the direct effect of surface energy; thus species may be lostto the vapour phase or may surface-segregate, reducing the local viscosity or increasing the driving force for nucleation. Regions of phase separation were also recognized as possible nucleation sites for crystallization of the YAG phase.

4 Conclusions

The crystallization of an oxynitride glass was investigated using high-temperature X-ray diffractometry, IR spectroscopy and microhardness measurements. The crystallization processes were found to begin around 1000°C. The crystallization of the powdered glass at 1150°C was followed in HT-XRD and shown to occur predominantly by YAG formation. The nucleation of the YAG occurred preferentially at free surfaces. A small amount of crystallization occurred by the formation of $Y_2Si_2O_7$ nucleating in the bulk. The results are relevant to developing improved crystallization treatments for glasses with potential for crystallization to YAG-based glass-ceramics and for heat treatment of YAG/β-SiAlON materials.

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