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Influence of ZrO_2 Addition on the Crystallization of Yttrium Oxynitride Glasses to $Y_3Al_5O_{12}$-Based Glass-Ceramics

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Abstract

The influence of a ZrO_2 addition (6 wt%) on the crystallization behaviour of a glass with potential for crystallization to $Y_3Al_5O_{12}$-based glass-ceramics has been investigated. Differential thermal analysis, X-ray diffraction and scanning electron microscopy were used to assess the crystallization process. Vickers hardness was used to monitor changes in the crystallized volume fraction at different heat treatment temperatures. The results indicate that the addition of ZrO_2 to the investigated glass composition promotes the formation of the y-$Y_2Si_2O_7$ and inhibits the crystallization of the $Y_3Al_5O_{12}$ phase. © 1997 Elsevier Science Limited. All rights reserved.

1 Introduction

High-temperature properties of Si_3N_4 ceramics depend on the nature and concentration of the oxynitride glassy phases present at the grain boundaries.[1-5] The principle of heat treating nitrogen ceramics to remove (or minimize) grain-boundary glass and hence improve high-temperature creep performance is well established. In yttria-densified β-sialon ceramics, $Y_3Al_5O_{12}$ (yttrium aluminium garnet, YAG) emerges as the most satisfactory contender. The only viable alternative, $Y_2Si_2O_7$, has five polymorphic forms which in certain cases can cause problems due to phase transformations.[6] The crystallization of YAG in yttria-densified β-sialon ceramics requires either simultaneous Si_2N_2O formation or accommodation of excess Si and N within β-sialon.[3]

A number of investigations of bulk oxynitride glasses with different compositions in the Y–Si–Al–O–N system has been carried out in order to study their properties and crystallization behaviour. It has been shown that the viscosity, glass transition temperature and hardness increase with increasing nitrogen content. A broad range of compositions of the oxynitride glasses has been subjected to different heat treatments and a number of equilibrium and intermediate phases has been found to crystallize from the glasses. The crystallization studies showed that the yttrium disilicate ($Y_2Si_2O_7$) is replaced progressively by YAG with increasing nitrogen content at higher temperatures (>1200°C).[7-13]

Ding *et al.*[7] found that when the amount of SiO_2 in the oxynitride glasses is less than 25 wt%, YAG crystallizes out during an annealing heat treatment at 1200–1400°C and when the SiO_2 content is more than 30 wt%, no YAG crystallizes. Hampshire *et al.*[8] studied the crystallization behaviour of a glass with composition 14·76 wt% SiO_2, 15·05 wt% Al_2O_3, 58·32 wt% Y_2O_3 and 11·87 wt% Si_3N_4 (in eq. % 35Y:45Si:20Al:77O:23N) and observed two completely different phase assemblages after heat treatment above and below 1200°C. The YAG phase was formed at temperatures above 1200°C.

Regarding ZrO_2 additions, it was found that a 6 wt% addition to an oxide glass inhibited the crystal growth of the $Y_2Si_2O_7$ phase at low temperatures (<1100°C).[14] Moreover, a ZrO_2 addition to an oxynitride glass was found to lower the activation energy of crystallization compared to that of the ZrO_2-free parent glass.[15] The lowering of activation energy was associated with a change in the crystallizing species from $Y_2Si_2O_7$ (β- and γ-polymorphs) and $Y_4Al_2O_9$, to yttria-stabilized zirconia. In an ongoing research study,[16] the addition of ZrO_2 to oxide and oxynitride glasses retained in the microstructure of glass-ceramics was found to lower their viscosity and melting temperature.

The aim of the present work was to study the crystallization behaviour of glasses with relatively low SiO_2 content having potential for crystallization to YAG-based glass-ceramics and more importantly to study the influence of a zirconia addition on the YAG crystallization. Two oxynitride glass compositions and one with the addition of 6 wt% ZrO_2 were prepared in nitrogen atmosphere at 1700°C and subjected to different single-stage heat treatments. The glass-ceramics produced were then characterized. It should be emphasized that the objective of the present work was not to bring the crystallization process to completion but to investigate the early stages of the crystallization, focusing on the temperature at which YAG crystallization begins. An investigation of the full crystallization kinetics of YAG from the oxynitride glasses will be reported later.

2 Experimental

2.1 Glass preparation

The fabrication parameters and compositions of all the materials are given in Table 1. In addition to the three oxynitride glass compositions, an oxide composition was prepared. Samples were 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 on 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. Batches of approximately 100 g each were then mechanically compacted into molybdenum crucibles 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, the cooling rate from the firing temperature to 1400°C was around 20°C/min, from 1400 to 950°C, 15°C/min and from 950 to 500, 10°C/min. 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. Mass changes of less than 1 wt% were observed.

2.2 Crystallization of glasses

The heat treatments were carried out using the cold wall vacuum/pressure furnace with a graphite heater under 0·17 MPa nitrogen. Pieces of approximately 1 g (7 × 7 × 4 mm) were placed in a Si_3N_4 powder bed in molybdenum boats and heat-treated at 50°C intervals between 1000 and 1350°C for 2 h with a heating rate of 250°C/h. After the heat treatment the samples were cooled to room temperature at the same cooling rate as described above.

2.3 Glass and glass-ceramics characterization

Powder X-ray diffraction (Phillips X-ray diffractometer, Cu K_α radiation) was performed on the as-melted furnace-cooled specimens to check for crystallization during cooling and on the heat-treated samples to identify crystalline phases. The lower limit of detectability of the technique lies around 2–5 wt% of a given phase. Differential thermal analysis (DTA) was carried out in a nitrogen atmosphere using an Al_2O_3 powder reference standard and a heating rate of 10°C/min from room temperature to 1500°C. Thermogravimetric measurements did not reveal any mass changes during the DTA. Vickers hardness measurements were performed using a commercial hardness tester (Matsuzawa Seiki Mxt α). A load of 300 g was applied for 15 s on sample surfaces polished with 3-μm spray diamond. The mean values of five indentations per sample were determined. Optical microscopy was used to confirm the absence of extensive cracking at the indentation. When extensive cracking occurred, the hardness value was not taken into account. Scanning electron microscopy (SEM) was carried out using a CamScan S4-80DV electron microscope on sectioned and polished samples.

3 Results and Discussion

3.1 Glass formation and glass characterization

Table 1 shows the results of the X-ray analysis of the as-fired materials. The oxide composition did

Table 1. Chemical compositions, fabrication parameters and phases observed after melting

	Composition									*Fabrication parameters*		
Sample designation	Y_2O_3	Al_2O_3 (wt%)	SiO_2	Si_3N_4	*Y*	*Al*	*Si* (eq%)	*O*	*N*	*Firing temp. (°C)*	*Fired in*	*Phases*
Oxide	49	28	23		29·0	36·8	34·2	100	0	1700	N_2	YAG $Y_2Si_2O_7$
A	47·5	27·2	22·3	3	27·4	34·7	37·9	94·4	5·6	1700	N_2	Glass
B	46·1	26·3	21·6	6	25·9	32·8	41·3	89·1	10·9	1700	N_2	Glass
A + 6 wt% ZrO_2										1700	N_2	Glass ZrO_2[a]

[a] Traces evidenced by SEM.

Table 2. Glass transition temperatures (T_g), temperatures of endothermic peaks indicating melting temperatures (T_L) and Vickers hardness (300 g, 15 s) of investigated glasses

Composition	T_g (°C)	T_L (°C)	*Vickers hardness (GPa)*
A	930	1434, 1433	9·63 ± 0·14
B	943	1371, 1422	10·00 ± 0·39
A + 6 wt% ZrO_2	930	1391, 1445	9·68 ± 0·17

not produce glass but a green mixture of the two crystalline phases, YAG and β-$Y_2Si_2O_7$ confirming that this composition lies outside the glass-forming region in the Y–Al–Si–O system.[8,17,18] Compositions A and B formed homogeneous glasses which were yellow to light green in colour. This coloration was quite different to the grey colour of nitrogen-free glasses produced in a previous study.[19] Weidner *et al.*[20] suggested that two phenomena influence the coloration of oxynitride glasses namely light absorption by nitrogen which increases with nitrogen content and leads to a yellow tint and secondly scattering from inclusions <1 to 20 μm in diameter such as bubbles and metallic inclusions (i.e. iron) which leads to a grey-black coloration. Composition A + 6 wt% ZrO_2 formed a slightly opaque green-grey glass with a low fraction of small dendritic ZrO_2 crystals not detectable by X-ray diffraction but observed in SEM examination.

The results from DTA and Vickers hardness measurements on as-melted glasses are given in Table 2. Glass B possesses the highest value of glass transition temperature (T_g) and hardness consistent with its higher nitrogen content as reported elsewhere.[1,8,10–12,21] All the DTA charts show two endothermic peaks. No mass changes in association with the endotherms occurred and therefore they were interpreted as representing melting reactions. The eutectic temperature in the compatibility triangle which includes the oxide composition was previously determined by O'Meara *et al.*[22] to be 1505°C. The lowest endotherm detected here indicates that this eutectic is lowered to 1434°C by the small addition of Si_3N_4 in composition A, to 1371°C by an increased addition of Si_3N_4 in composition B and to 1391°C in composition A + 6 wt% ZrO_2 by the combined addition of Si_3N_4 and ZrO_2.

3.2 Crystallization of glasses

3.2.1 DTA analysis

Figure 1 shows the DTA charts with exothermic peaks corresponding to the crystallization processes in the glasses. The results of the 2 h heat treatments at different temperatures are summarized in Table 3 in terms of phases formed and hardness. The onset and maximum of the exothermic reaction for glasses A and A + 6 wt% ZrO_2 are located at approximately the same temperature namely 1000°C and 1055°C, respectively. This implies that the ZrO_2 addition does not influence the early stages of the glass crystallization in terms of temperature. The existence of two maxima in the exothermic peak for glass B at 1075°C and 1145°C implies that two different crystal species crystallize from the glass at these two different temperatures. According to Table 3, Fig. 3 and SEM investigations the first maximum corresponds to the crystallization of an intermediate phase together with the $Y_2Si_2O_7$ phase while the second corresponds to the crystallization of the YAG phase. The onset of the exothermic reaction is shifted to a higher temperature (1040°C) compared to the A glasses presumably because of the higher nitrogen content.

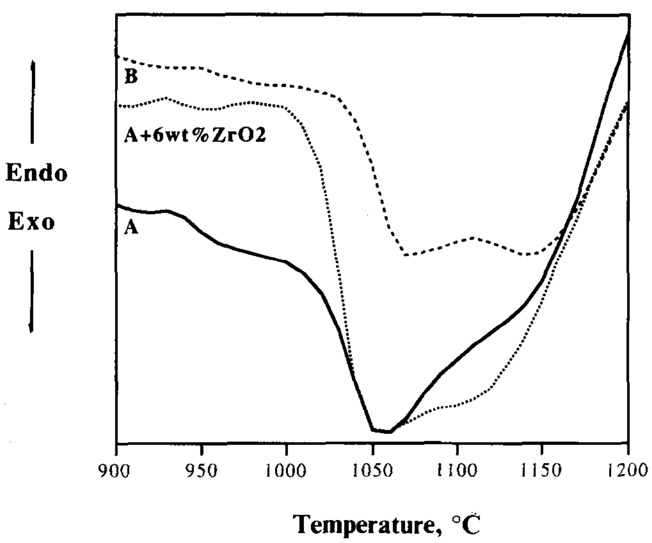

Fig. 1. DTA curves of the investigated glasses at a heating rate of 10°C.

3.2.2 Vickers hardness measurements

Table 3 summarizes the results of the hardness measurements. For composition A the highest hardness value was reached for the heat treatment at 1250°C and for compositions A + 6 wt% ZrO_2 and B at 1200°C. Ramesh *et al.*[23] found when investigating the crystallization behaviour of a glass with composition 28Y : 56Si : 16Al : 83O : 17N in eq% using two-stage heat treatment that some of the nuclei formed during the nucleation treatment redissolve on heating to the second (growth) stage. It was concluded that such a phenomenon can arise because the critical sized nuclei become unstable with respect to the second-stage heat treatment temperature. Consequently, varying the second-stage heat treatment temperature can alter radically the volume fraction crystallized after

Table 3. Results of single-stage 2 h crystallization heat treatments at different temperatures and Vickers hardness (300 g, 15 s) of produced glass-ceramics

Composition	*Heat treatment temperature (°C)*	*Crystalline phases*	*Vickers hardness (GPa)*
A	1100	$Y_3Al_5O_{12}$, IP[a]	9·86 ± 0·13
	1150	IP, $Y_3Al_5O_{12}$, y-$Y_2Si_2O_7$	10·79 ± 0·19
	1200	$Y_3Al_5O_{12}$, y-$Y_2Si_2O_7$, IP, δ-$Y_2Si_2O_7$	11·06 ± 0·16
	1250	y-$Y_2Si_2O_7$, $Y_3Al_5O_{12}$, δ-$Y_2Si_2O_7$, IP	11·62 ± 0·66
	1300	$Y_3Al_5O_{12}$, y-$Y_2Si_2O_7$, δ-$Y_2Si_2O_7$	11·41 ± 0·20
	1350	$Y_3Al_5O_{12}$, δ-$Y_2Si_2O_7$	10·89 ± 0·37
B	1100	$Y_3Al_5O_{12}$, IP, y-$Y_2Si_2O_7$	10·18 ± 0·23
	1150	$Y_3Al_5O_{12}$, IP, y-$Y_2Si_2O_7$	11·88 ± 0·23
	1200	$Y_3Al_5O_{12}$, y-$Y_2Si_2O_7$, δ-$Y_2Si_2O_7$	12·10 ± 0·27
	1250	$Y_3Al_5O_{12}$, y-$Y_2Si_2O_7$, δ-$Y_2Si_2O_7$	11·66 ± 0·10
	1300	$Y_3Al_5O_{12}$, y-$Y_2Si_2O_7$, δ-$Y_2Si_2O_7$	11·47 ± 0·34
	1350	$Y_3Al_5O_{12}$, δ-$Y_2Si_2O_7$	11·45 ± 0·22
A + 6 wt% ZrO_2	1100	IP, $Y_3Al_5O_{12}$, y-$Y_2Si_2O_7$, ZrO_2	9·74 ± 0·21
	1150	IP, $Y_3Al_5O_{12}$, y-$Y_2Si_2O_7$, ZrO_2	10·46 ± 0·29
	1200	y-$Y_2Si_2O_7$, IP, $Y_3Al_5O_{12}$, δ-$Y_2Si_2O_7$, ZrO_2	11·64 ± 0·92
	1250	y-$Y_2Si_2O_7$, IP, $Y_3Al_5O_{12}$, δ-$Y_2Si_2O_7$, ZrO_2	11·37 ± 0·47
	1300	y-$Y_2Si_2O_7$, $Y_3Al_5O_{12}$, δ-$Y_2Si_2O_7$, ZrO_2	10·79 ± 0·28
	1350	$Y_3Al_5O_{12}$, δ-$Y_2Si_2O_7$, y-$Y_2Si_2O_7$, ZrO_2	10·26 ± 0·28

[a] Intermediate phase.

a given nucleation heat treatment. Therefore optimum heat treatment schedules for Y–Si–Al–O–N glass-ceramics consist of an optimum combination of nucleation and crystal growth treatment. In the present study the soaking temperature was reached in 5 h, so nucleation took place during heating. The maximum in hardness for all the compositions can be explained by the phenomenon described by Ramesh *et al.* assuming that the hardness of the glass-ceramics increases with increasing crystallized volume fraction.[24] This observation was also confirmed by the metallography.

3.2.3 *X-ray diffraction and scanning electron microscopy*

Devitrification of the A and B glasses produced green-coloured glass-ceramics. The A + 6 wt% ZrO_2 glass formed reddish-coloured glass-ceramics. The results of X-ray diffraction analysis after the 2 h heat treatments in terms of crystallization products are summarized in Table 3 and the X-ray intensities of the crystalline phases are illustrated in Figs 2, 3 and 4. All the X-ray diffraction patterns for composition A + 6 wt% ZrO_2 contained peaks of cubic (yttria-stabilized) ZrO_2. Al_2O_3 was detected in compositions A and A + 6 wt% ZrO_2 in small amounts. Both oxides are however omitted from Table 3 and the intensity plots. An intermediate phase which could not be identified using the JCPDS tables was detected for heat treatments below 1250°C for compositions A and A + 6 wt% ZrO_2 and below 1150°C for composition B. This phase had the same X-ray diffraction pattern as the intermediate phase detected in two previous studies[14,19] of nitrogen-free yttria–alumina–silica glasses. It is noteworthy that this intermediate phase appears to crystallize from the glass at low temperatures, probably already at 1000–1050°C. Dinger *et al.*[25] observed an intermediate phase with composition $YSi_2AlO_4N_2$ crystallizing from a glass with a normalized composition of $Y_{0.26}Si_{0.30}Al_{0.11}ON_{0.11}$ and proposed that the crystallization of this phase follows the crystallization of y-$Y_2Si_2O_7$ species (impurity stabilized) which requires the rejection of Al, Si, O and N to the glass phase ahead of the glass / crystal interface. It was also stated that the solubility of Al in

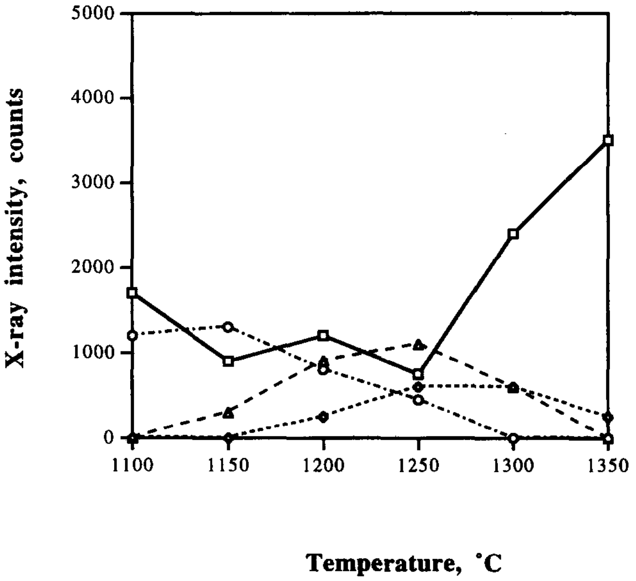

Fig. 2. Crystallization products following 2 h heat treatments of glass A. (□-YAG, ◇-δ-$Y_2Si_2O_7$, △-y-$Y_2Si_2O_7$, O-intermediate phase).

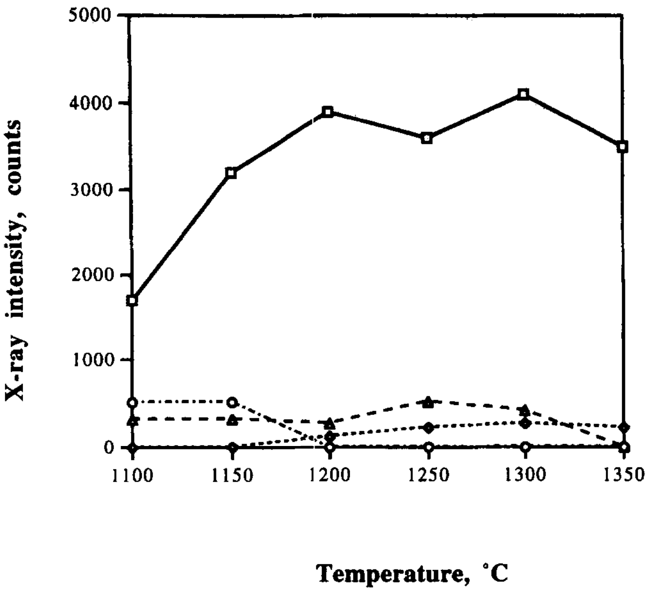

Fig. 3. Crystallization products following 2 h heat treatments of glass B. (□-YAG, ◇-δ-$Y_2Si_2O_7$, △-y-$Y_2Si_2O_7$, O-intermediate phase).

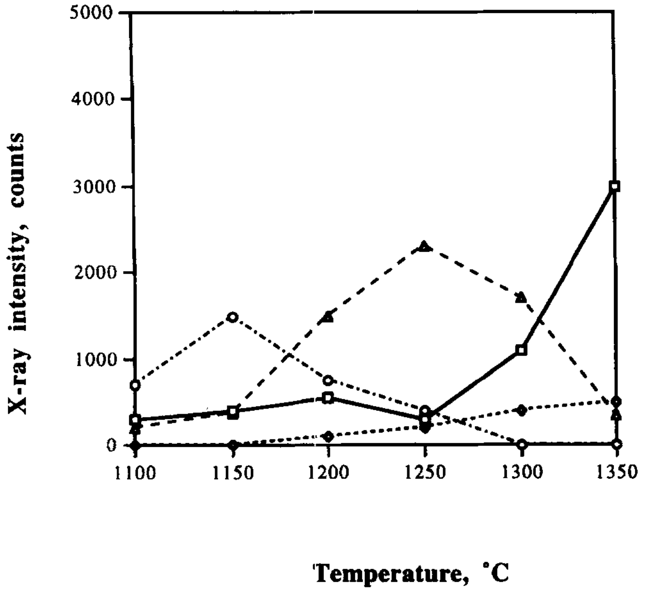

Fig. 4. Crystallization products following 2 h heat treatments of glass A + 6 wt% ZrO_2. (□-YAG, ◇-δ-$Y_2Si_2O_7$, △-y-$Y_2Si_2O_7$, O-intermediate phase).

Fig. 5. Micrograph of composition A heat treated at 1250°C for 2 h (backscatter image-1000*x*).

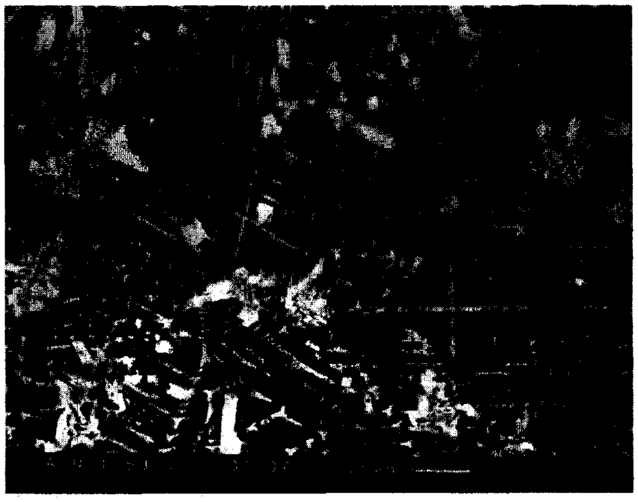

Fig. 6. Micrograph of composition B heat treated at 1250°C for 2 h (backscatter image-1000*x*).

the y-$Y_2Si_2O_7$ phase decreases with increasing crystallization temperature. In the present study the $Y_2Si_2O_7$ phase appeared as y and δ polymorphs. Kumar and Drummond[26-28] found that the quench rate of melts is a significant variable in the crystallization of $Y_2Si_2O_7$ from the glass in terms of the type of $Y_2Si_2O_7$ polymorph. They also suggested that the δ polymorph is impurity stabilized. The results of the present investigation indicate (Figs 2 and 4) that ZrO_2 promotes the crystallization of the y-$Y_2Si_2O_7$ polymorph at temperatures higher than 1150°C. This is somewhat surprising in the light of the previous study[14] on the role of ZrO_2 as a nucleating agent in an yttria–alumina–silica glass where it was concluded that the ZrO_2 addition inhibited growth of the $Y_2Si_2O_7$. It has to be emphasized however that the earlier investigation was carried out at temperatures below 1100°C when the diffusion rates of the ions involved were still very slow.

Micrographs of the glass-ceramics produced at 1250°C are shown in Figs 5, 6 and 7. The microstructure of the A glass-ceramic (Fig. 5) consists of $Y_2Si_2O_7$ and the dendritic YAG phase. The A + 6 wt% ZrO_2 microstructure (Fig. 7) consists mainly of the $Y_2Si_2O_7$ phase (bright platelet-like crystals). The yttria-stabilized zirconia (small very bright crystals) can also be seen in the microstructure. The amount of YAG in the A + 6 wt% ZrO_2 microstructure is much lower than in the A glass-ceramic. Composition B (Fig. 6) shows the crystallization of dendritic YAG phase.

The results confirm the earlier reports [7-13] that with increasing nitrogen content the proportion of YAG increases at the expense of the $Y_2Si_2O_7$ polymorphs. Thus in the A composition the

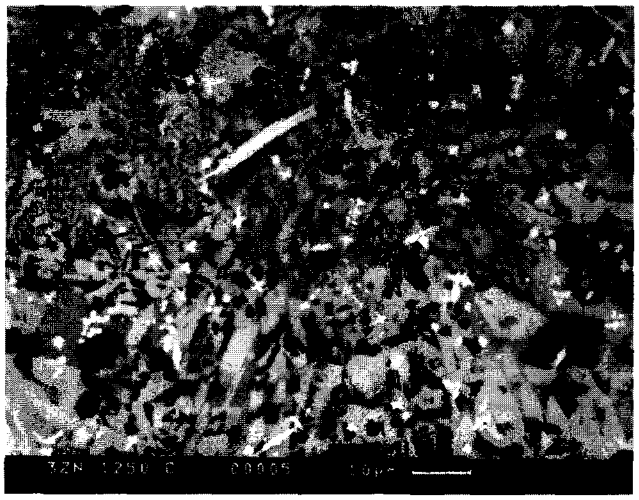

Fig. 7. Micrograph of composition A + 6 wt% ZrO_2 heat treated at 1250°C for 2 h (backscatter image-1000*x*).

crystallization of YAG begins to dominate only above 1250°C while in the B composition it dominates from the onset of crystallization around 1100°C.

The effect of zirconia addition on the crystallization of the investigated oxynitride glass at temperatures <1300°C is evidently to promote the crystallization of the $Y_2Si_2O_7$ phase (y-polymorph). The presence of the y-$Y_2Si_2O_7$ polymorph in the A + 6 wt% ZrO_2 glass-ceramics at temperatures higher than in the ZrO_2-free compositions is probably a result of the stabilization of the y-$Y_2Si_2O_7$ by the Zr^{4+} cation as reported elsewhere.[29] Because of this stabilization and because a significant crystallization of the y-$Y_2Si_2O_7$ occurs during heating to the soaking temperature the crystallization of the YAG phase, which requires higher temperature,[30] is suppressed. At temperatures between 1300 and 1350°C the YAG phase is the dominant phase in the microstructures of both the A and the A + 6 wt% ZrO_2 glass-ceramics and ZrO_2 has little influence on the morphology.

4 Conclusions

The results of this study indicate that the addition of 6 wt% zirconia to the investigated oxynitride glass promotes the formation of the y-$Y_2Si_2O_7$. Consequently, the crystallization of the YAG phase is inhibited. The glass composition designated B was found to crystallize primarily to the YAG phase above about 1100°C. This composition will therefore be selected for the investigation of kinetics of YAG crystallization from oxynitride glasses relevant to the heat treatment of β-sialon/YAG materials.

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