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Influence of ZrO_2 Addition on Melting Kinetics of a YSiAlO Glass-Ceramic

P. Vomacka[a] & D. S. Wilkinson[b]

[a]Department of Engineering Materials, Luleå University of Technology, S-951 87 Luleå, Sweden
[b]Department of Materials Science and Engineering, McMaster University, Hamilton, Ontario L8S 4L7, Canada

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Abstract

A ZrO_2-free YSiAlO glass of composition 27Y: 42Si:31Al in equivalent % and one with the addition of 6 wt% ZrO_2 were prepared in a nitrogen atmosphere at 1700°C. These glasses were treated in a nitrogen atmosphere at a controlled rate, during which the glass partially crystallizes to form a glass-ceramic. Under continued heating melting occurs. This behaviour was monitored by differential thermal analysis, scanning electron microscopy and X-ray diffraction. The original dendritic appearance of the crystallized microstructures changed to a blocky one in the early stages of the melting process. The ZrO_2 addition was found to increase the kinetics of the phase transformations occurring during the melting. Copyright © 1996 Elsevier Science Ltd

1 Introduction

Yttria–alumina–silica glasses have motivated numerous investigations over the past 20 years due to their potential for forming glass-ceramic materials and also due to the use of Y_2O_3 and Al_2O_3 as sintering additives in the production of structural ceramics such as silicon nitride (Si_3N_4).[1-4] A review of the crystallization studies on Y_2O_3–Al_2O_3–SiO_2 glasses was reported previously.[5] Oxide and oxynitride glasses in this system are generally considered as self-nucleating,[6] which has been confirmed in recent studies using ZrO_2 as a nucleating agent.[7,8] However, there are indications that the addition of zirconia influences the devitrification reactions in these glasses and in (Y_2O_3 + Al_2O_3)-fluxed sintered Si_3N_4.[9,10] In a previous study on yttria–alumina–silica glasses with zirconia additions,[11] two endothermic reactions were observed by differential thermal analysis (DTA) at temperatures exceeding 1400°C. Since the thermogravimetric measurements showed no mass changes these two endotherms were interpreted as representing melting reactions, assuming a formation of two immiscible liquids by a monotectic reaction.

The aim of the present work is to investigate the influence of ZrO_2 addition to a YSiAlO glass on the melting of YSiAlO glass-ceramics.

2 Experimental Procedure

A ZrO_2-free YSiAlO glass of composition 27Y: 42Si:31Al (eq. %), and one with the addition of 6 wt% unstabilized ZrO_2,[7] were prepared from mixtures of high purity yttria, alumina and silica (Rhone Poulenc, Alcoa Chemicals and Johnson Matthey, respectively) in the appropriate proportions. The equivalent% method representation of composition has been reported elsewhere.[12] The powders were mixed in polyethylene containers on a Siemens roller mill for 10 h using propanol, dried and sieved. Batches of approximately 100 g each were then mechanically compacted into molybdenum crucibles, melted under 0·17 MPa nitrogen pressure at 1700°C for 2·5 h, and furnace cooled. 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, 10°C min^{-1}. This rate was dictated by the natural cooling of the furnace (cold wall vacuum / pressure furnace with a graphite heater) after it had been switched off. Chemical analysis on as-received glasses was performed using X-ray fluorescence (Philips PW 3510, Rh tube), to verify the final composition of the glasses.

DTA (Netzsch STA instrument) was performed on 0·2 g powdered glass samples (particle size of approximately 50–90 μm) mechanically compacted into Al_2O_3 crucibles. The measurements were carried out in a nitrogen atmosphere using an Al_2O_3 powder reference standard and a heating rate of 5°C min^{-1}. The DTA runs were interrupted abruptly at the temperatures indicated in Table 1

Table 1. Compositions of the studied glasses, experimental conditions and phases identified by X-ray diffraction after cooling to room temperature (v.s., very strong; s., strong; m., medium; w., weak; v.w., very weak)

Sample designation	*Compositions (as-batched)*								*Max. temp. of DTA scan (°C)*	*Phases*
	eq %				*wt %*					
	Y	*Si*	*Al*	*O*	Y_2O_3	Al_2O_3	SiO_2	ZrO_2		
A	27	42	31	100	46·9	24·3	28·8	0	1370	β-$Y_2Si_2O_7$ (s.) mullite (v.w.) YAG (v.w.)
									1420	β-$Y_2Si_2O_7$ (s.) mullite (v.w.) YAG (v.w.)
									1430	β-$Y_2Si_2O_7$ (s.) YAG (m.) γ-$Y_2Si_2O_7$ (v.w.)
A + 6 wt% ZrO_2					44·1	22·8	27·1	6	1370	β-$Y_2Si_2O_7$ (s) mullite (v.w.) YAG (v.w.) Al_2O_3 (v.w.) ZrO_2 (v.w.)
									1400	β-$Y_2Si_2O_7$ (s.) mullite (v.w.) YAG (v.w.) Al_2O_3 (v.w.) ZrO_2 (v.w.)
									1420	β-$Y_2Si_2O_7$ (m.) YAG (s.) Al_2O_3 (s.) ZrO_2 (v.w.)

by switching the DTA furnace off and allowing the specimens to cool in the furnace. The cooling rate of the DTA furnace was approximately 20°C min^{-1} between the maximum temperature and 1000°C. The cooling rate was assumed to be high enough to avoid significant additional crystallization on cooling. Samples obtained in the DTA furnace were cut and polished with a dispersion of 1 μm diamond in kerosene as a final step. X-ray diffraction (Siemens diffractometer, CuK_α radiation) was performed on the specimens to identify crystalline phases after the heat treatments. Scanning electron microscopy (SEM) investigations were carried out using a Philips 515 scanning electron microscope with attached energy dispersive X-ray detector (EDX).

3 Results and Discussion

3.1 Glass preparation

Both compositions formed homogeneous glasses on melting without any traces of crystalline phases in the X-ray diffraction patterns. However, SEM examination of the as-received glasses revealed a very small amount of ZrO_2 precipitates in the microstructure of the ZrO_2-containing glass. These precipitates are believed to have either survived the melting or precipitated from the parent glass on cooling from the melting temperature. The latter is possible due to the limited solubility of ZrO_2 in the yttrium aluminosilicate liquid. The results of the chemical analysis of as-received glasses by X-ray fluorescence are summarized in Table 2. These results indicate a compositional shift, compared with the as-batched compositions, into the $Y_2Si_2O_7$–Al_2O_3–$Y_3Al_5O_{12}$ (YAG) compatibility triangle with the eutectic temperature of 1505°C,[3] caused probably by losses of some of the constituents (Al and Si) during melting of the glass.

3.2 Differential thermal analysis

Figure 1 shows typical DTA traces of the ZrO_2-free and ZrO_2-containing glasses at a temperature interval of 800–1550°C. An exothermic peak was detected at 1100 and at 1093°C for the ZrO_2-free

Table 2. Chemical analysis of as-received glasses

Sample	Y_2O_3	Al_2O_3	SiO_2 *(wt%)*[a]	ZrO_2	*Std deviation (wt%)*
A	56·5	18·8	24·7	0	0·2
A + 6 wt% ZrO_2	52·2	17·6	22·8	7·4	0·2

[a] Detectability limit 0·01%.

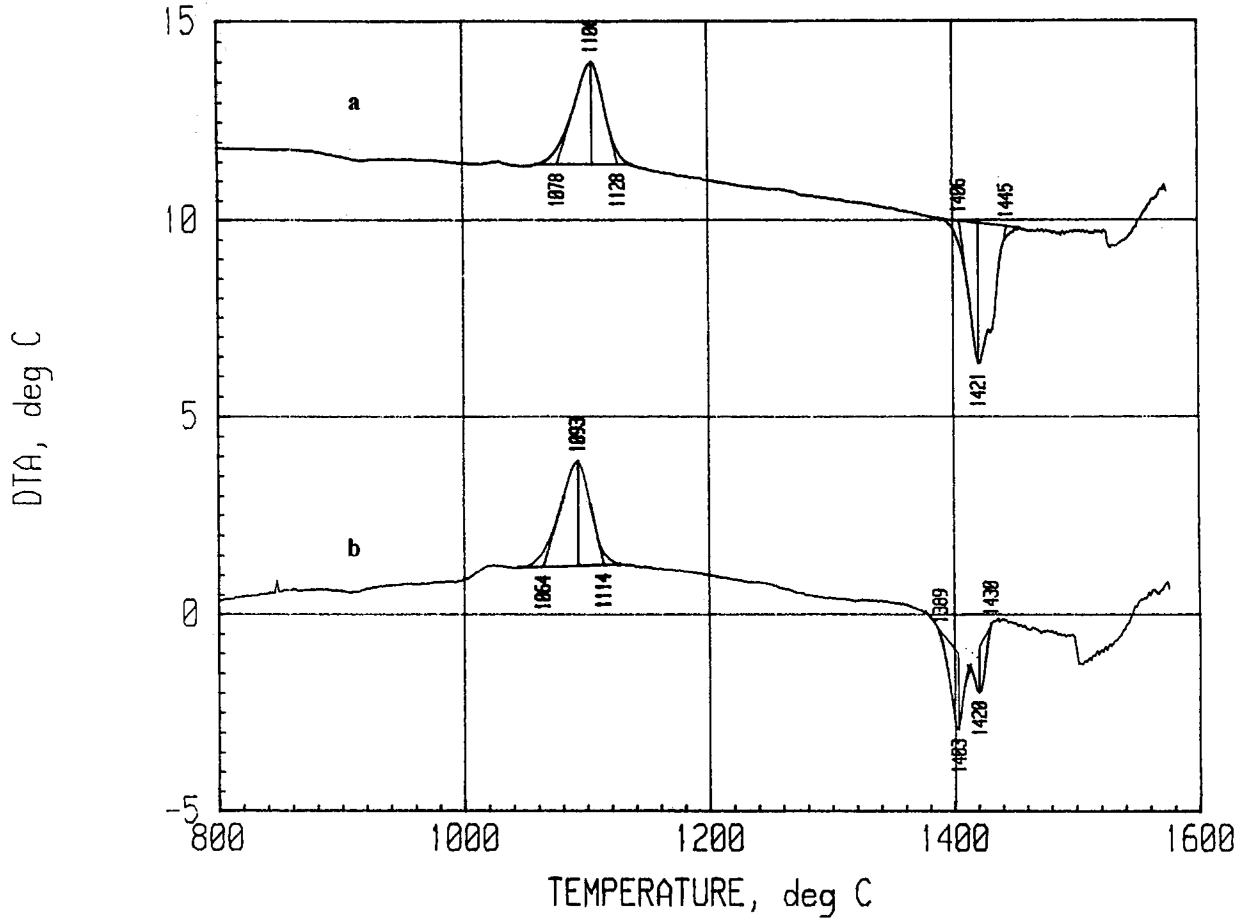


Fig. 1. DTA traces of the as-received glasses A (a) and A + 6 wt% ZrO_2 (b).

and the ZrO_2-containing glass, respectively, indicating crystallization of the glasses to form glass-ceramics. Three endothermic peaks can be distinguished on the curve of the ZrO_2-containing glass while the second endotherm appears only as a weak endothermic shoulder on the ZrO_2-free curve. Three DTA scans were carried out for each composition. The first one was interrupted for both compositions at 1370°C before the onset of the endothermic reactions. The second and third scans were interrupted at temperatures corresponding to the peak temperatures of the first and second endothermic reactions (at 1420 and 1430°C for the ZrO_2-free composition, and at 1400 and 1420°C for the ZrO_2-containing composition, respectively) as indicated in Table 1 and Fig. 1.

3.3 Phase identification and microstructure

The crystalline phases identified by X-ray diffraction analysis, following heat treatment in the DTA rig, are listed in Table 1 for both compositions and all the maximum temperatures. The phases detected are in general agreement with those expected from the equilibrium ternary phase diagram,[3] namely $Y_2Si_2O_7$, Al_2O_3 and YAG. However, some small amount of non-equilibrium mullite was also detected for both compositions. A cubic yttria-stabilized zirconia was observed additionally in the X-ray diffraction patterns of the A + 6 wt% ZrO_2 glass-ceramics.

Since the starting material was a glass powder with a significant specific surface area and due to a non-isothermal heat treatment, it is assumed that nucleation of the crystallization occurs predominantly at the surfaces. Figure 2 shows the microstructure of the glass-ceramics after the DTA scans were interrupted at 1370°C. The microstructures consist mainly of dendrites of the β-$Y_2Si_2O_7$ phase. β-$Y_2Si_2O_7$ side branches are seen to develop from the larger β-$Y_2Si_2O_7$ dendrites. A small amount of glassy phase remains in the microstructures. The A + 6 wt% ZrO_2 composition also contains small precipitates of the yttria-stabilized zirconia phase.

When the DTA scans were interrupted at temperatures corresponding to the first endothermic peak (at 1420 and 1400°C for A and A + 6 wt% ZrO_2, respectively), the dendritic morphologies of both microstructures have given way to a blocky morphology with a grain size of approximately 3–10 μm (Fig. 3). The X-ray diffraction patterns showed the same phases as for the heat treatment to 1370°C (see Table 1). The amount of glassy phase however increased slightly. (This could not

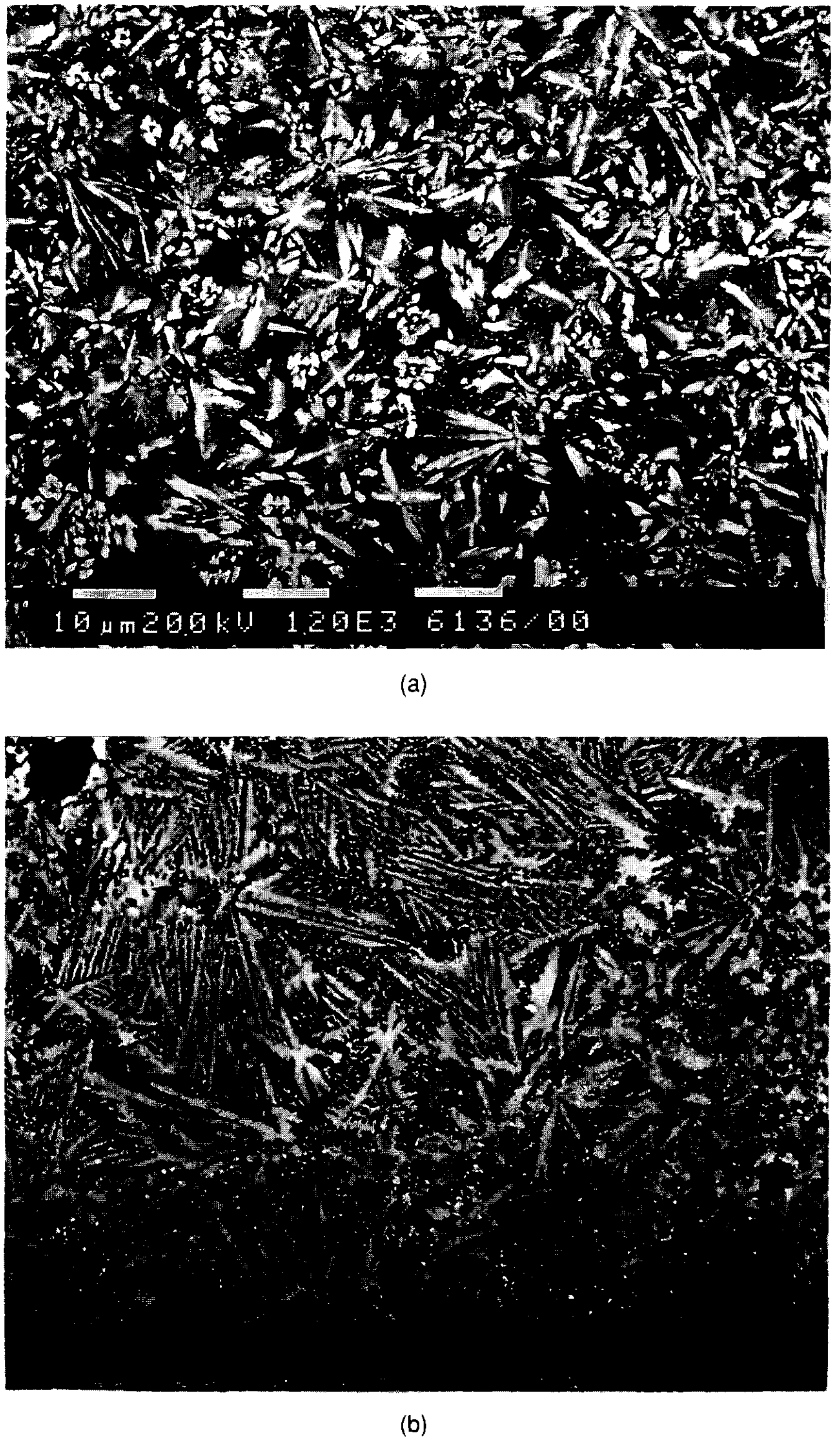
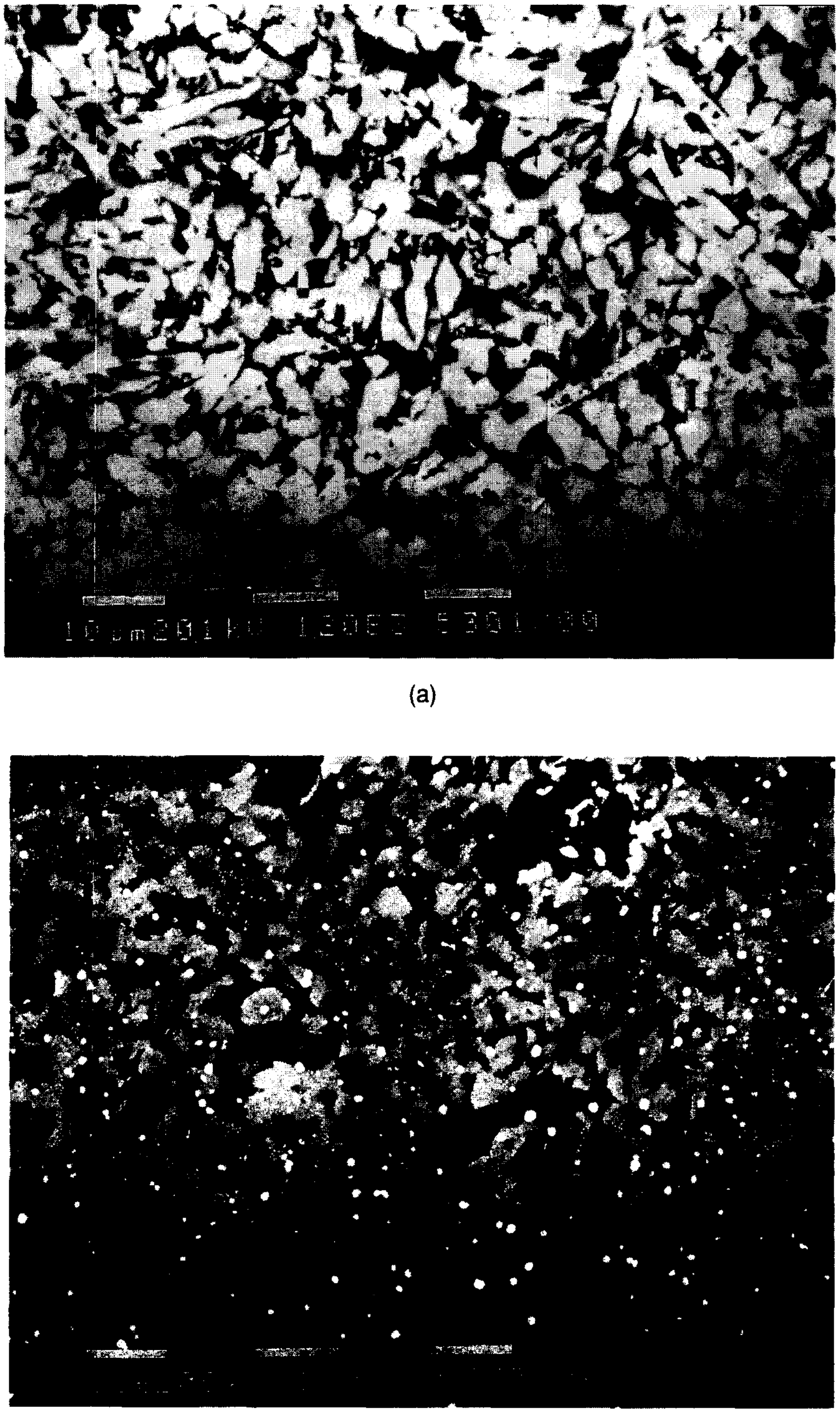


Fig. 2. Micrographs of the glass-ceramics A (a) and A + 6 wt % ZrO_2 (b) at 1370°C-backscatter image of β-$Y_2Si_2O_7$ dendrites in a glassy matrix. Small bright crystals in (b) are the yttria-stabilized zirconia.

be detected by X-ray diffraction but was measured by careful analysis of the microstructure using SEM and the point counting method.) Thus, the appearance of the first endotherm is attributed to the partial dissolution of a very small amount of the β-$Y_2Si_2O_7$, and other non-equilibrium phases present. The crystallization of both glasses involves large compositional changes when the crystalline phases crystallize out from the parent glass. Therefore diffusion of ions over large distances is required in order to achieve the equilibrium phase content. The viscosity of the retained glass in the microstructure controls the diffusion rates. At the end of crystallization, the retained glass in the glass-ceramics A and A + 6 wt% ZrO_2 is rich in SiO_2 and Al_2O_3 because of the crystallization of the β-$Y_2Si_2O_7$. This involves the rejection of Si, O, Al (and Zr for the A + 6 wt% ZrO_2 composition) ahead at the glass/crystal interphase.[13] The viscosity of the retained glass at the temperature approaching the onset of the endothermic reaction is low enough to cause the change of the morph-



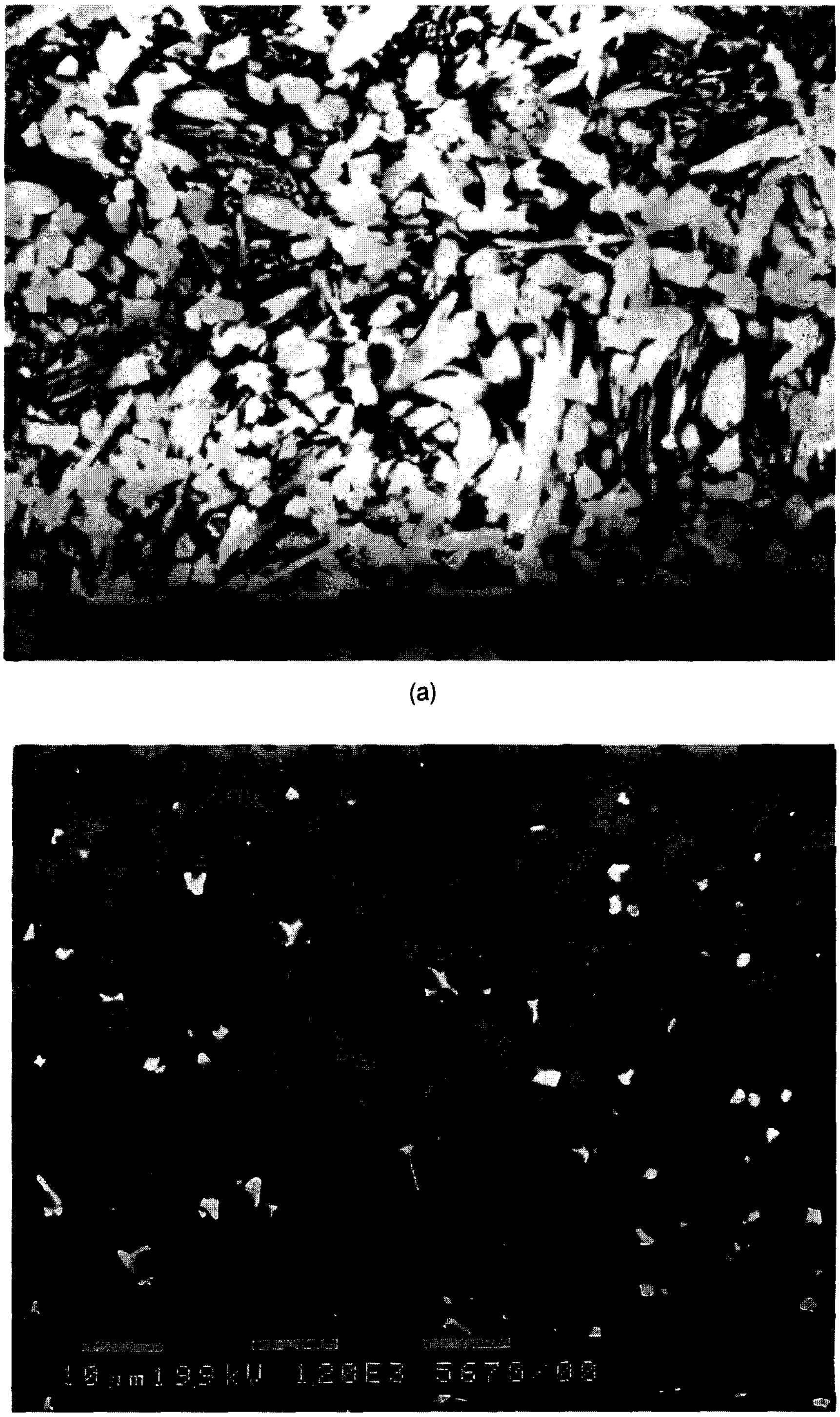
(a)

(b)

Fig. 3. Micrographs of the glass-ceramics A (a) and A + 6 wt% ZrO_2 (b) at the temperature of the first endothermic peak-backscatter image.

ology. The thermodynamic driving force for this change is lowering of the surface energy as the dendritic crystals with high specific surface area are continuously transformed into a microstructure with a lower specific area. The onset temperature of the first endothermic reaction is lowered by approximately 20°C for the A + 6 wt% ZrO_2 composition compared with the A composition. This can be attributed to the influence of the Zr^{4+} cation which acts as a glass-network modifier and decreases the viscosity of the retained glass at this high temperature. The heat of reaction (proportional to the area bounded by the endothermic peak and the DTA base line) of the first endothermic reaction is lower for the A + 6 wt% ZrO_2 glass, probably due to an additional exothermic crystal growth of the yttria-stabilized zirconia crystals in the microstructure.

The phase assemblage observed at the second endothermic peak temperature (1430 and 1420°C for A and A + 6wt% ZrO_2, respectively) indicates a partial dissolution of the β-$Y_2Si_2O_7$ phase and


(a)

(b)

Fig. 4. Micrographs of the glass-ceramics A (a) and A + 6 wt% ZrO_2 (b) at the temperature of the second endothermic peak-backscatter image of a mixture of β-$Y_2Si_2O_7$, YAG and yttria-stabilized zirconia crystals.

crystallization of the YAG phase. Micrographs of the samples at the temperatures of the second endothermic reaction are shown in Fig. 4. The intensity of the YAG peaks in the X-ray pattern of the A + 6 wt% ZrO_2 composition was much higher than in the A composition. EDX analysis confirmed a much higher content of the YAG phase in the A + 6 wt% ZrO_2 microstructure. Although no noticeable Al_2O_3 crystallization was detected by X-ray diffraction of the A composition, a small amount could be observed when examined by EDX. γ-$Y_2Si_2O_7$ could be detected in small amounts for the A sample due to the high temperature. (The equilibrium transformation temperature of β-$Y_2Si_2O_7$ to γ-$Y_2Si_2O_7$ is 1445°C in the binary Y_2O_3-SiO_2 system.[14]) An increase of the Al_2O_3 amount and the glassy phase content was noticed for the A + 6 wt% ZrO_2 composition. The significant YAG and Al_2O_3 crystallization as well as the crystal growth of the yttria-stabilized zirconia, which are probably exothermic reactions, lower the overall endothermic heat of reaction of the A + 6 wt% ZrO_2 composition. The effect of zirconia on lowering the viscosity of the retained glassy phase (or more accurately liquid phase) is more obvious at this high temperature of the second endothermic reaction. The kinetic rates of the phase transformations occurring during melting are increased due to the presence of a larger amount of the liquid phase. Consequently, Al_2O_3 and a larger amount of the YAG phase can precipitate out from the liquid phase in the A + 6 wt% ZrO_2 composition.

A third endothermic peak could be seen on the DTA charts at 1530 and 1500°C for A and A + 6 wt% ZrO_2, respectively. Due to cracking of the Al_2O_3 crucibles at higher temperatures than 1500°C, samples of both compositions were prepared at 1500±20°C in a conventional furnace of the same type as used for the glass preparation. The same atmosphere and heating rate were applied as in the DTA furnace. For the A composition the YAG phase was the major phase detected, accompanied by γ-$Y_2Si_2O_7$ and a smaller amount of β-$Y_2Si_2O_7$. The A + 6 wt% ZrO_2 composition formed a homogeneous glass with some ZrO_2 crystals precipitated in the microstructure. This observation and the DTA results imply that the last crystalline phases dissolve into the liquid at 1530 and 1500°C for the A and the A + 6 wt% ZrO_2, respectively.

3.4 Zirconia in an oxynitride glass-ceramic

The same DTA scans as described above were performed on oxynitride and ZrO_2-containing oxynitride glasses with the same Y:Si:Al ratio with 10 eq% of nitrogen incorporated into the glass structure by adding an appropriate amount of silicon nitride powder (Kema Nord Industrikemi) to the oxide mixtures prior to firing at 1700°C. The same tendency of lowering the onset temperature of the endothermic reaction could be observed for the composition containing 6 wt% of zirconia.

4 Conclusions

The influence of ZrO_2 addition on the melting behaviour of a YSiAlO glass-ceramic has been assessed. ZrO_2 lowers the viscosity of the retained glassy phase in the glass-ceramic and consequently increases the kinetics of the phase transformations occurring during melting. The onset temperature of the endothermic reaction representing melting is lowered by approximately 20°C. The overall heat of reaction of the endothermic reaction is also lowered. The same influence of ZrO_2 addition was observed in the oxynitride glass-ceramic with the same Y:Si:Al cation ratio and 10 eq% of nitrogen.

References

1. Hyatt, M. J. & Day, D. E., Glass properties in yttria–alumina–silica system. *J. Am. Ceram. Soc.*, **70**[10] (1987) C-283–7.
2. Leng-Ward, G. & Lewis, M. H., Crystallisation in Y–Si–Al–O–N glasses. *Mater. Sci. Eng.*, **71** (1985) 101–11.
3. O'Meara, C., Dunlop, G. L. & Pompe, R., Phase relationship in the system Y_2O_3–Al_2O_3–SiO_2. In *Proc. World Congress on High Tech. Ceramics* (6th CIMTEC), Milan, Italy, ed. P. Vicenzini. Elsevier Science Publishers, Amsterdam, 1986, pp. 265–70.
4. Lewis, M. H., Crystallization of grain boundary phases in silicon nitride and sialon ceramics. *Key Eng. Mater.*, **89–91** (1994) 333–8.
5. Arita, I. H., Wilkinson, D. S. & Purdy, G. R., Crystallisation of yttria–alumina–silica glasses. *J. Am. Ceram. Soc.*, **75**[12] (1992) 3315–20.
6. Hampshire, S., Oxynitride glasses and glass ceramics. *Mater. Res. Soc. Symp. Proc.*, **287** (1993) 93–103.
7. Vomacka, P., Babushkin, O. & Warren, R., Zirconia as a nucleating agent in an yttria–alumina–silica glass. *J. Eur. Ceram. Soc.*, **15** (1995) 1111–17.
8. Vomacka, P., Ramesh, R. & Hampshire, S., Influence of zirconia addition on the crystallization kinetics of a YSiAlON glass. *J. Eur. Ceram. Soc.*, in press.
9. Braue, W., Wotting, G. & Ziegler, G., Devitrification effect of grain boundary phases on high-temperature strength of sintered Si_3N_4 materials. In *Proc. 2nd Int. Symp. On Ceramics and Components for Engines*, Lubeck-Travemunde, 14–17 April 1986.
10. Thomas, G., Ahn, C. & Weiss, J., Characterization and crystallisation of Y–Si–Al–O–N glass. *J. Am. Ceram. Soc.*, **65**(11), (1982) C-185–8.
11. Vomacka, P. & Babushkin, O., Yttria–alumina–silica glass with addition of zirconia. *J. Eur. Ceram. Soc.*, **15** (1995) 921–8.
12. Hampshire, S., Nestor, E., Flynn, Besson, J. L., Goursat, P. & Thompson, D., Yttrium oxynitride glasses: properties and potential for crystallization to glass-ceramics. *J. Eur. Ceram. Soc.*, **14** (1994) 261–73.
13. Dinger, T. R., Rai, R. S. & Thomas, G., Crystallization behaviour of a glass in the Y_2O_3–SiO_2–AlN system. *J. Am. Ceram. Soc.*, **71**[4] (1988) 236–44.
14. Kumar, S. & Drummond, C. H. III, Crystallization of various compositions in the Y_2O_3–SiO_2 system. *J. Mater. Res.*, **7**[4] (1992).