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Crystallization behaviour and hardness of glass ceramics rich in nanocrystals of ZrO_2

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Abstract

This research is mainly directed toward the development of hardness of glass ceramic by adding different amounts of ZrO_2 to the glass and by applying different heat-treatments. Differential thermal analysis (DTA), X-ray diffraction (XRD) and Scanning electron microscope (SEM) were used to study the crystallization behaviour of the glass samples. The only observed crystalline phases were tetragonal and monoclinic zirconia. Hardness was found to increase by increasing time and temperature of heat-treatment due to the formation of monoclinic phase as a result of the martensitic reaction. This transformation opposes crack opening.

Keywords: C. Hardness; D. Glass ceramics; D. ZrO_2; Nanocrystal

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1. Introduction

Glass-ceramic materials, prepared by controlled crystallization of glasses, have a variety of established uses due to their uniform reproducible fine-grain microstructures, absence of porosity and wide-ranging properties which can be tailored by changes in composition and heat-treatment. In recent years, new compositions, processing methods and applications have begun to emerge. Among the recent developments considered are new phosphate-based compositions, the use of sol–gel processing, glass ceramic matrix composites, glass ceramics in microelectronics packaging, glass ceramics bonded to metals and as joining media, high-strength and high-toughness materials, and machineable compositions [1].

In general, glasses are brittle materials which are very sensitive to flaws or cracks as expressed by their low fracture toughness (K_{IC}) values smaller than $1\ \mathrm{MPa\,m^{1/2}}$. When converting glass into glass ceramics, the fracture toughness usually increases to K_{IC} values between $1–2\ \mathrm{MPa\,m^{1/2}}$, but these materials remain sensitive to flaws. By precipitating crystalline phases which are known to be tough or are easily cleaved, it is possible to substantially reduce the sensitivity of glass ceramics to flaws [2].

To improve glass-ceramic toughness, several methods have been successfully employed. These include the formation of surface compressive stresses through ion exchange [3–5], fibre reinforcement using both brittle [6,7] and ductile [8] fibres, and the addition of Ti particles to bioactive glass ceramics [9]. Zirconia-toughened glass ceramics have also been investigated [10–20] following toughness improvements realized in conventionally processed ceramics [21–25].

In general, ZrO_2-containing glass ceramics have become of interest because of their high fracture toughness which has been attributed to the stress-induced transformation of tetragonal ZrO_2. Tetragonal and cubic ZrO_2 were observed to precipitate during the crystallization together with other crystalline compounds [26].

The goal of the work described in this article is to study the effect of ZrO_2 on the crystallization behaviour and

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hardness of borosilicate (Na_2O, B_2O_3, and SiO_2) glass ceramic.

2. Experimental procedure

2.1. Preparation of materials

Chemical composition of base glass used is 11.03 Na_2O, 24.79 B_2O_3 and 64.18 SiO_2 in wt% and ZrO_2 were added gradually till complete solubility at 26%. Increasing the percentage of ZrO_2 over 26% causes undesirable precipitation of ZrO_2 in the formed glass. The particular composition was chosen keeping in mind two criteria: (1) in borosilicate systems transparent glasses may be produced with ZrO_2 content up to 26 wt% and (2) the composition was chosen in order to crystallize ZrO_2 alone and only after an additional thermal treatment in which time and temperature control the process.

After well mixing 100 g of batch, materials were melted in a Pt crucible in an electrically heated Globar furnace at 1500 °C for 3 h with occasional swirling every 30 min to ensure homogenization. The melt was then cast onto hot steel moulds in the form rods (10 cm × 1 cm × 1 cm) which were then rapidly transferred to a muffle furnace for annealing, adjusted at 550 °C for 1 h and then switched off to obtain strain-free and transparent glass samples. For simplicity, samples were coded as N_x, where x is ZrO_2%.

2.2. Analytical methods

Differential thermal analysis (DTA) (Shimadzu, DTG-50/50H) was utilized to determine the glass transition temperature (Tg) and crystallization temperature (Tc) of the glass samples. The DTA measurements were performed using ~35 mg of powdered glass samples (of 90–250 μm grain size), in a ceramic crucible under dry N_2 atmosphere using powdered alpha Al_2O_3 as a reference material.

Identification of crystalline phases was carried out by X-ray diffraction (XRD, Rigaku Miniflex with graphite monochrometer, Cu Kα radiation). Each measurement in the 2θ range 27–33° was the sum of three runs, corresponding to 6 s per step of 0.01°.

The crystallization of zirconia was given by sum of the integrated intensities of (1 1 1) tetragonal phase (T) and (1 1 1) + (−1 1 1) monoclinic phase (M), while the relative percentages of the two phases were evaluated following the Toraya et al. method [27]. The integrated intensities were obtained using a computer program of Rigaku Miniflex. The program permits the performance peak separation, Kα_2 elimination and background subtraction.

The surfaces of glass-ceramic samples were examined by the scanning electron microscope (SEM, JEOL JSA-840A, Electron Probe Microanalyzer, Japan), after etching by 1:1 of 5% HNO_3 and HF acid for 60 s, then coating with gold.

Microhardness was measured on the polished glass-ceramic samples using a microhardness testing machine (Mitutoyo, HM-100 series), and by application of 0.2 kg (1.961 N) load.

3. Results and discussion

3.1. Differential thermal analysis

Fig. 1 shows the DTA curves of the base glass and glass containing various ZrO_2 amounts, Table 1 gives a summary of the results of the differential thermal analysis, glass transition temperature (Tg), onset crystallization temperature (Tc), the peak temperature of crystallization (Tp), and the end temperature of crystallization peak.

Adding ZrO_2 has a marked shift on the DTA effects to higher values, which is evidenced by shift the endothermic peaks and crystallization peaks to higher temperatures. This effect increased with increasing the amount of ZrO_2 and may be related to the increase in viscosity of the glass which consequently leads to less mobility of the structural elements in the glass [28]. Also, a clear increases in the intensity of crystallization peak were observed by adding ZrO_2, with respect to base glass, which was due to the precipitation of zirconia phases that increased with increasing ZrO_2 percent.

The heat-treatments were performed at 700, 720 and 740 °C for different times according to the onset of crystallization obtained.

3.2. X-Ray diffraction analysis

We are concerned here with samples N26 which have the maximum solubility of ZrO_2. Heat-treatment at 700, 720 and 740 °C showed that the only observed crystallized phase was zirconia in its polymorphous phases monoclinic (M) and tetragonal (T) (Figs. 2–4).

In general, the crystallization of zirconia increased with time and temperature. The crystallization started after 8 h at 700 °C and after 1 h at 720 °C and 740 °C. It is obvious that tetragonal phase increase with minor amount of monoclinic with increasing time of heat-treatment up to 10 h, after that the tetragonal phase slightly decreases while monoclinic phase was more developed specially at 740 °C.

3.2.1. Fraction of transformed ZrO_2

The fraction of transformed, i.e. monoclinic, zirconia for N26 calculated from the X-ray integrated intensities of the

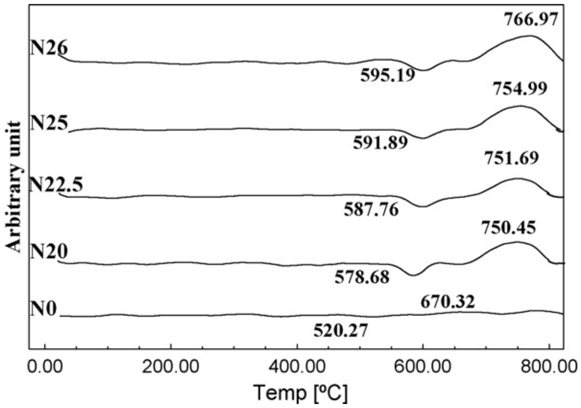

Fig. 1. DTA patterns of glass with different amounts of ZrO_2%.

Table 1
Characteristic temperature of glass specimens (°C)

Sample	Tg	Tc	Tp	End of crystallization
N0	520.27	–	670.32	–
N20	578.68	679.43	750.45	800
N22.5	587.76	682.73	751.69	801
N25	891.89	684.80	784.99	818
N26	595.19	683.97	766.97	826.84

m-ZrO_2 (−1 1 1) and (1 1 1) peaks and from the t-ZrO_2 (1 1 1) peak is plotted versus time of heat-treatment in Fig. 5.

In general the fraction in sample heat-treated at 740 °C is higher than that at heat-treated at 720 °C. By increasing time of heat-treatment, the fraction of transformed ZrO_2 is small up to 10 h then sharply increased. This is explained by the above discussion mentioned in Section 3.2.

3.2.2. Total intensity of ZrO_2

The crystallization kinetics has been studied by evaluating the sum of the integrated intensities of (1 1 1) tetragonal and (1 1 1) and (1 1 −1) monoclinic diffraction lines (Eq. (1)) [26].

$$I(\text{total}) = I(T) + 0.80\,I(M) \qquad (1)$$

Fig. 6 shows the total intensity *I* (total) of N26 as a function of the heat-treatment time at 720 and 740 °C. The total intensity increases with increasing the time of heat-treatment and the temperature as discussed before.

3.3. Scanning electron microscope

SEM of sample heat-treated at 700 °C/10 h (Fig. 7a) shows uniform ultrafine grain microstructure with grain size 285 nm of almost tetragonal form (according to X-ray data Fig. 2). Increasing heat-treatment temperature to 720 °C/10 h leads to more chance for transformation from t to m form due to decrease in viscosity. Fig. 7b shows the coexistence of stars like tetragonal phase and the well developed monoclinic crystals (diamond like crystals) that are in consistence with XRD results. Fig. 7c shows SEM of sample heat-treated at 740 °C/10 h which revealed more crystallization of zirconia forms especially m-ZrO_2.

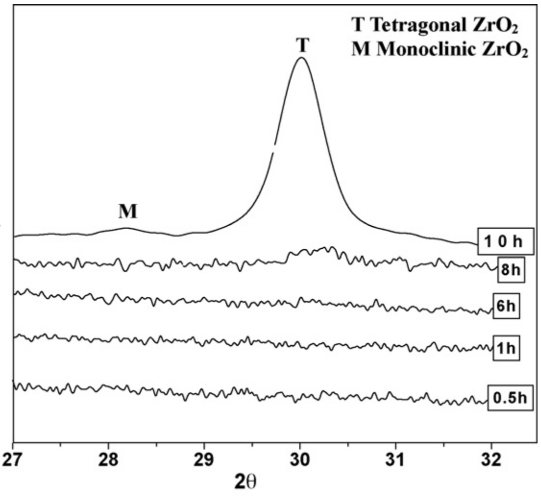

Fig. 2. XRD patterns of N26 heat-treated at 700 °C.

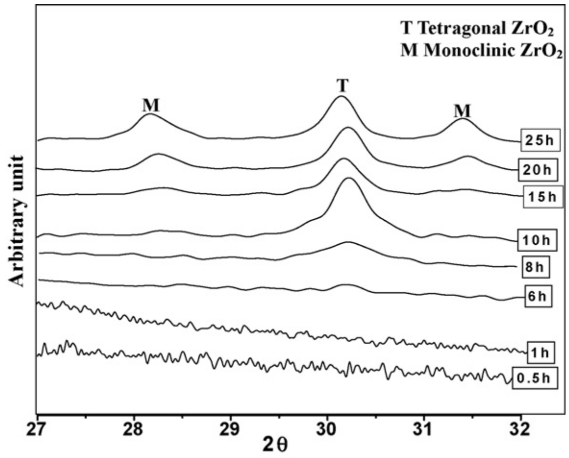

Fig. 3. XRD patterns of N26 heat-treated at 720 °C.

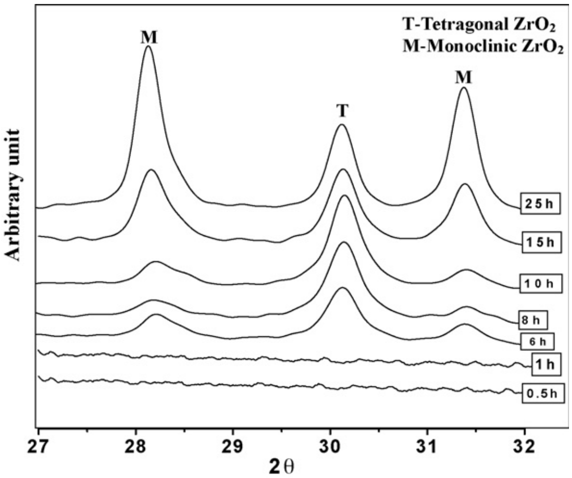

Fig. 4. XRD patterns of N26 heat-treated at 740 °C.

3.4. Hardness

Fig. 8 reports hardness of N26 heat-treated at 740 °C versus time of heat-treatment,

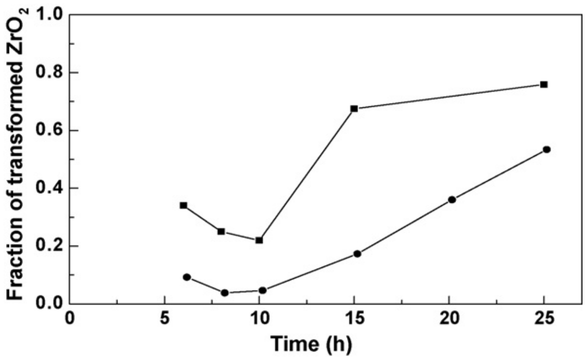

Fig. 5. Fraction of transformed, i.e. monoclinic, ZrO_2 versus treatment time for N26 at 740 °C (■) and 720 °C (●).

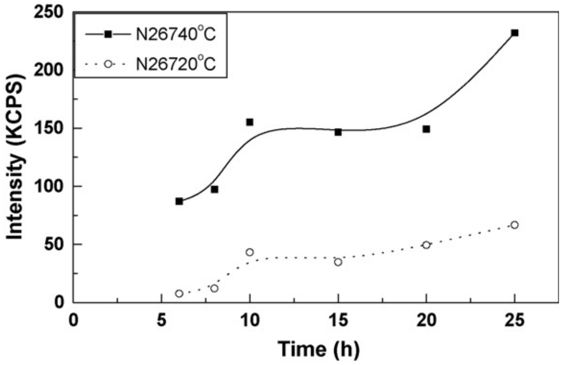

Fig. 6. XRD total intensity I (total) versus heat-treatment times for N26 at 740 and 720 °C.

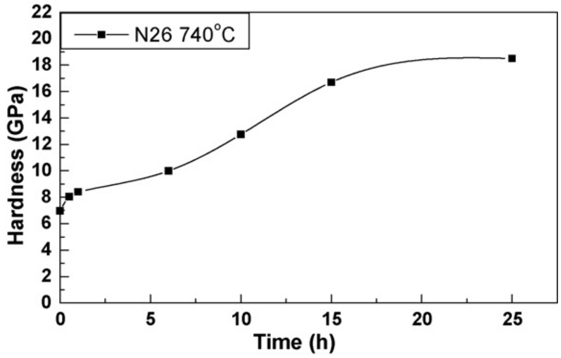

Fig. 8. Vickers hardness of N26 heat-treated at 740 °C versus heat-treatment time (h).

There is a limited increase in hardness values at the short time of heat-treatment (till 6 h), but at longer time sharp increase could be observed till stability occurred from 20 h. This result can be explained by Stevens [29], through the transformation temperature from tetragonal phase to monoclinic ($T_{t \rightarrow m}$); the volume expansion of 3–5% occurring in the ZrO_2 particles causes tangential stress around the transformed particle, which induces microcracks in the matrix (Fig. 9). These by their ability to extend in the stress field of a propagating crack, caused by hardness, can absorb or dissipate the energy of such cracks, thereby increasing the toughness of the glass ceramics. The optimum conditions are met each other when the particles are large enough to transform but still small enough to cause limited microcrack development.

The volume change and the shear strain developed in the martensitic reaction were recognized as opposing the opening of the crack and therefore acting to increase the resistance of the glass ceramic to crack propagation [30].

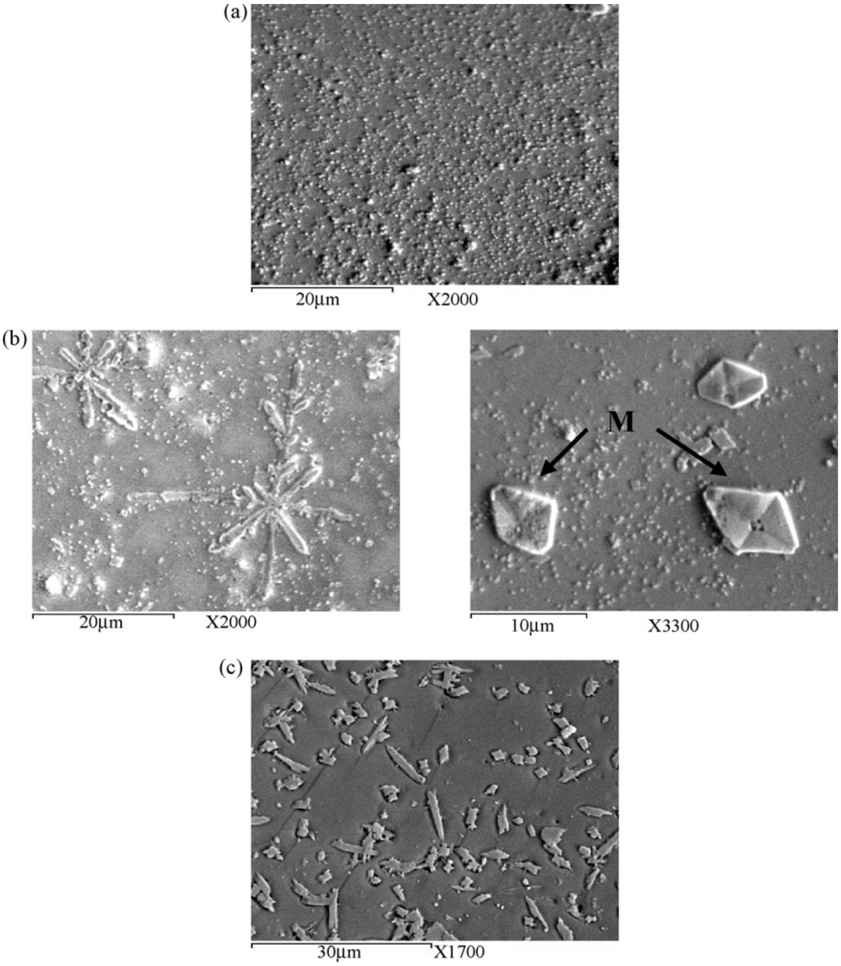

Fig. 7. SEM of sample N26 heat-treated at (a) 700 °C/10 h, (b) 720 °C/10 h and (c) 740 °C/10 h.

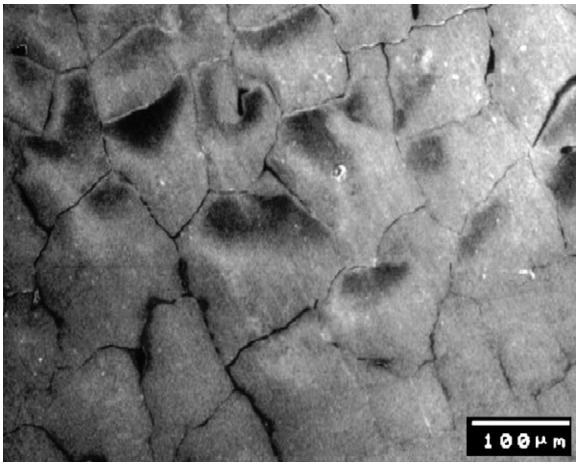

Fig. 9. SEM of sample N26 heat-treated at 740 °C/25 h.

4. Conclusion

Glass ceramic containing ZrO_2 with maximum solubility 26 wt% was prepared. The composition was chosen carefully to precipitate tetragonal and monoclinic zirconia phases only. Tetragonal ZrO_2 was transformed to Monoclinic by increasing heat-treatment parameters leading to cracks formation. Hardness of the prepared glass ceramic was found to increase with the time of heat-treatment due to hindering microcrack development.

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