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Ceramics International 38 (2012) 1523–1527

CERAMICS
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Sintering, crystallization and mechanical properties of a gel-cast cordierite glass–ceramic body

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Received 27 August 2011; received in revised form 18 September 2011; accepted 19 September 2011
Available online 22 September 2011

Abstract

Gel-cast bodies based on cordierite glass–ceramics were prepared by sintering route. Effect of monomer and cross-linker values as well as sintering temperatures on bending strength of dried and sintered bodies were investigated. While the bending strength of dried gel-cast bodies was increased with the percentage of the polymers, bending strength of sintered bodies was changed conversely with them. Therefore, it was concluded that the least amount of monomer acrylamid (3 wt.%) and moderate amount of cross-linker (~0.75 wt.%) guarantees the required dried and fired bending strengths. The optimum sintering temperature was about 1270 °C and specimens that was fired at this temperature showed a maximum bending strength of about 200 MPa.

Keywords: D. Cordierite; D. Glass ceramics; Gel-casting

1. Introduction

Gel-casting is a relatively simple and near-net-shape forming technique for ceramic components in which ceramic fluid slurries containing a solution of monomers can be transformed into rigid and non-porous cavities without liquid removal [1]. Due to the internal gelation of this solution at a certain temperature, the ceramic particles fix together and form as the mold. Finally, the body is dried and sintered, after being extracted from the mold [2].

Using a relatively small amounts of polymers (2–6 wt.%) and catalyst is one of the main characteristic of this method [3]. These materials have no detrimental effect on solid particles and do not leave considerable impurities after burnout. Furthermore, this technique is used for vast ranges of ceramic and even metal powders [3–7]. Green bodies prepared by this process show a relatively high strength (3–4 MPa) and can be machined at considerable cost saving [8].

Glasses and glass–ceramics are normally shaped by melt casting methods. However, when a glass or a glass–ceramic based composite is desired or it has a complex shape, melt casting will not be applicable. At these conditions one should profit by powder based shaping methods, e.g. pressing, extrusion, injection molding, slurry casting, gel-casting, etc., and sintering of shaped specimen.

Cordierite based glass–ceramics which cannot be excluded from the above-mentioned rules can be prepared by a simultaneously sintering and crystallization of its compacted glass powder [9]. The above-mentioned reasons convinced the present authors to apply the gel-casting for shaping of this glass–ceramic and investigate the influence of polymers and their ratio on the drying and sintering behaviors of the formed specimens.

2. Experimental procedure

The glass composition which was used contained SiO_2 49.02 wt.%, Al_2O_3 33.35 wt.%, MgO 13.19 wt.%, V_2O_5 2.96 wt.% and BaO 1.5 wt.% [10]. The raw materials used to make the glass were acid washed silica sand (with purity more than 99.8%) and reagent grade aluminum hydroxide (BDH 3059090), magnesium oxide (Applichem A2387.1000), vanadium oxide (Merck 8240250) and barium carbonate (Merck 1714), respectively. The thoroughly mixed materials were melted in an alumina crucible at 1630 °C in electric kiln

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doi:10.1016/j.ceramint.2011.09.036

for 1 h. The molten glasses were then quenched in cold distilled water.

The frit obtained was ground in a planetary mill for various times until its particle size distribution lied exactly within the Andreasen range. The particle size distribution of glass powder was determined by a laser particle size analyzer (Analysette 22, Fritch, Idar-Oberstein, Germany). The crystallization temperature of the glasses was determined by differential thermal analysis (STA, model 1640, Polymer Laboratories, Amherst, MA) using 10 mg of glass powders in a platinum crucible and in air atmosphere at a heating rate of 10 °C min^{-1}.

Acrylamide (AM) (Merck Prolabo 79-06-1), N′,N-ethylene bisacrylamide (MBAM) (Merck Prolabo 110-26-9), ammonium per sulfate (APS) (Merck 1.01201.0500) and tetra methyl ethylene diamine (TEMED) (Merck 1.10732.0100) were used as monomer, cross-linker, reaction initiator and catalyst, respectively.

Slurries were prepared by dispersing of 70 wt.% glass powder in water-based solution of the monomers and dispersant, and were completed with adding of the initiator and the catalyst.

The slurries were stirred for 5 min and then were cast into a polyethylene container and remained there for 24 h to ensure a complete polymerization. After that, the samples were removed and dried naturally in room temperature for 48 h and then in an electric dryer at 80 °C for 24 h. The flexural strength of specimens was determined by three point bending test on specimens of 50 mm × 10 mm × 5 mm in size, at a span of 46 mm and cross head speed of 0.6 mm min^{-1}.

3. Results and discussion

3.1. Thermal behaviors of specimens

Fig. 1 shows the STA thermographs of a cordierite-based gel-cast glass specimen containing 5 wt.% AM, 2.5 wt.% MBAM and 0.4 wt.% initiator. Accordingly, the polymers are exhausted at about 350 °C, which is associated with a small exothermic peak in the DTA trace and a weight loss in the TG thermograph, respectively. To identify the responsible reactions for arising the second and the third exothermic peaks in the DTA trace, the gel-cast specimens were heated at 850 and 930 °C for 2 h. Fig. 2 depicts the X-ray diffraction patterns of the fired specimens. Based on these results, formation of μ-cordierite and its conversion to α-cordierite are responsible for the second and the third exothermic peaks, respectively. These two fired samples were completely porous; therefore, they were fired at higher temperatures, between 1020 and 1320 °C for 2 h. Fig. 3 shows the X-ray diffraction patterns of the resulted samples. Based on these results, cordierite ($2MgO\cdot2Al_2O_3\cdot5SiO_2$) is the sole crystalline phase that has been precipitated gradually with increasing firing temperature.

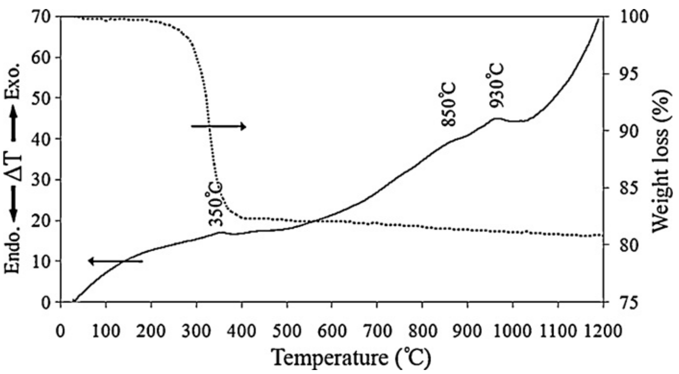

Fig. 1. STA thermographs of the powdered gel-cast green body.

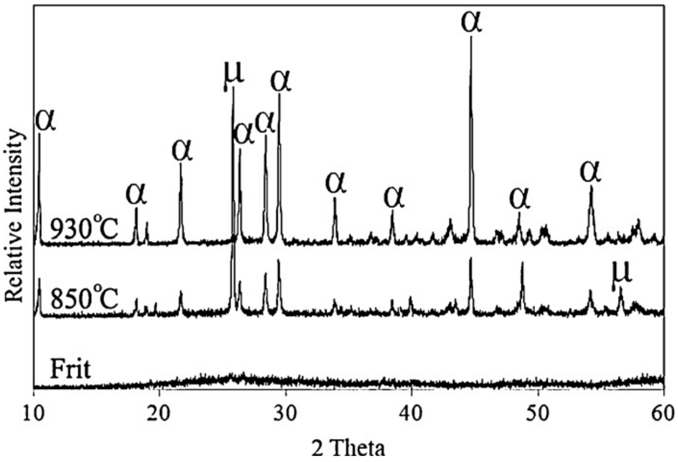

Fig. 2. X-ray diffraction patterns of the gel-cast samples after heat treatment for 2 h at 850 °C and 930 °C, (α) α-cordierite; (μ), μ-cordierite.

Fig. 4 shows the relative densities of the above-mentioned sintered specimens. As it was expected, the relative density of each specimen increased gradually to its optimum value with increasing of firing temperature. This temperature (about 1270 °C) is quite above the crystallization peak temperature of the glass. According to previous report [10], about 92 wt.% cordierite was precipitated when the glass was heat treated at its crystallization peak temperature. Generally, this widespread crystallization will increase the viscosity of glass and retards viscous flowing of residual glass phase [11–13], which is necessary for its densification. Therefore, the glass specimen compulsorily was densified at higher temperatures.

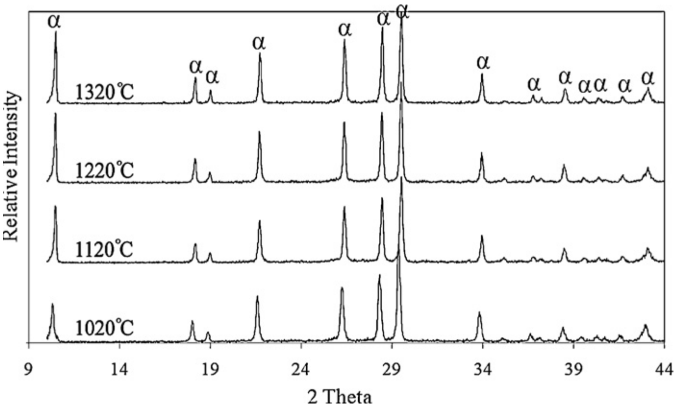

Fig. 3. X-ray diffraction patterns of the samples after firing at different temperatures with a heating rate of 10 °C min^{-1}, (α), α-cordierite.

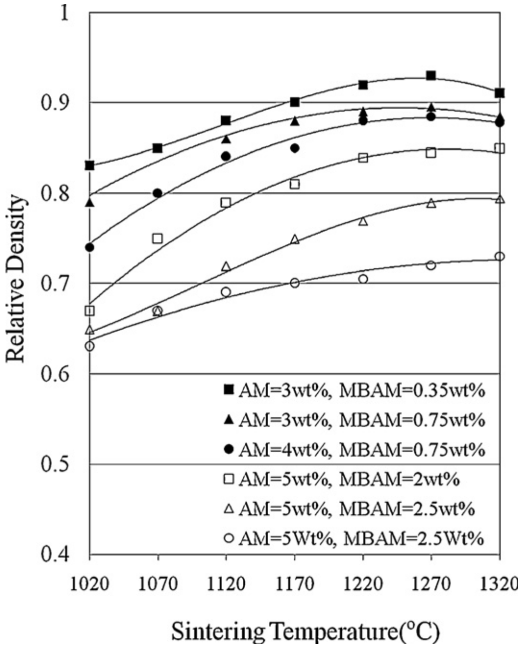

Fig. 4. Variations of relative density of gel-cast samples as a function of sintering temperature and amounts of the polymers.

Besides, it can be seen that the sinterability of the specimen is a polymer-dependent function and decreases with increasing the amounts of the used polymers. The variation of linear shrinkage of each specimen with firing temperature is also shown in Fig. 5. It can be seen that specimens with less polymers experience a lower firing shrinkage to acquire its maximum densification.

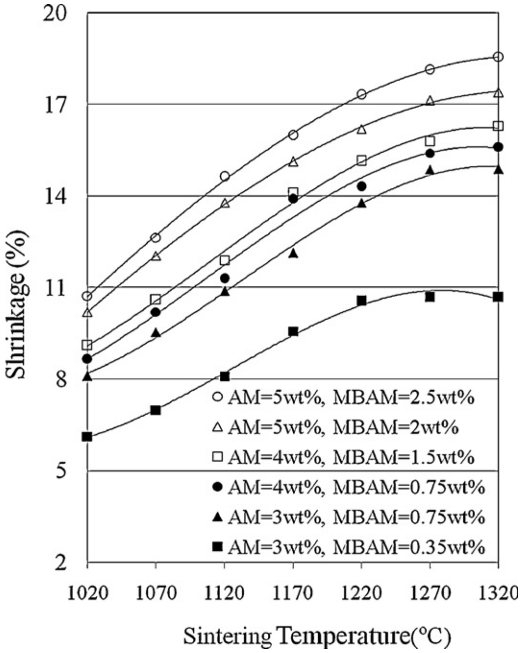

Fig. 5. Variations of linear shrinkage of various gel-cast samples as a function of firing temperature.

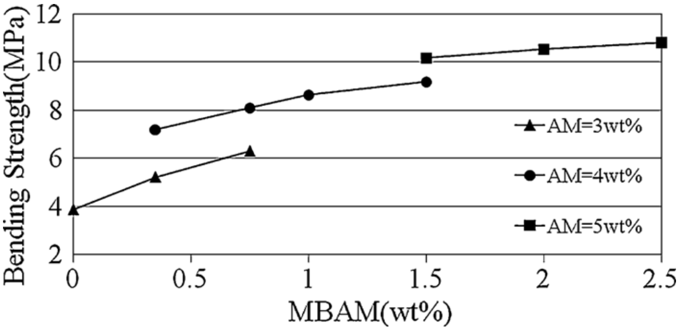

Fig. 6. Variations of green bending strength of gel-cast samples as a function of monomer and cross-linker containing 0.4 wt.% initiator.

3.2. Bending strengths

Fig. 6 shows the role of polymers on the bending strength of the dried gel-cast specimens. It is clear that more extensive polymerization which is associated with more amounts of polymers AM and MAMB, separately and jointly, brings about a higher dried bending strength [14,15]. The dried bending strength of a sample containing 5 wt.% AM and 2.5 wt.% MAMB has reached to about 11 MPa which is absolutely high and inaccessible via other shaping methods. However, as it was

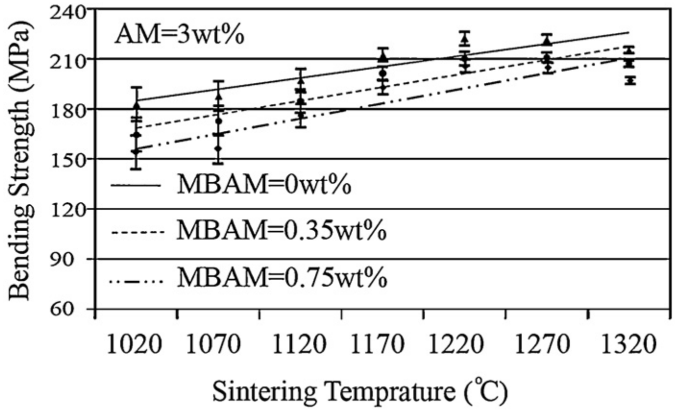

Fig. 7. Three-points bending strength of heat treated samples with thermal rate of 10 °C $\min^{-1}$ containing 3 wt.% monomer and 0.4 wt.% initiator.

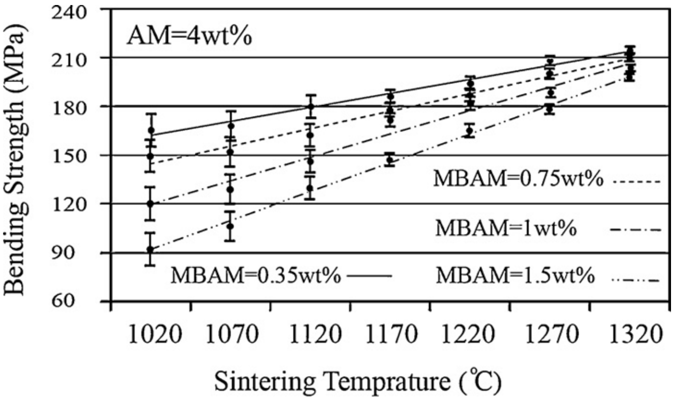

Fig. 8. Three-points bending strength of heat treated samples with thermal rate of 10 °C $\min^{-1}$ containing 4 wt.% monomer and 0.4 wt.% initiator.

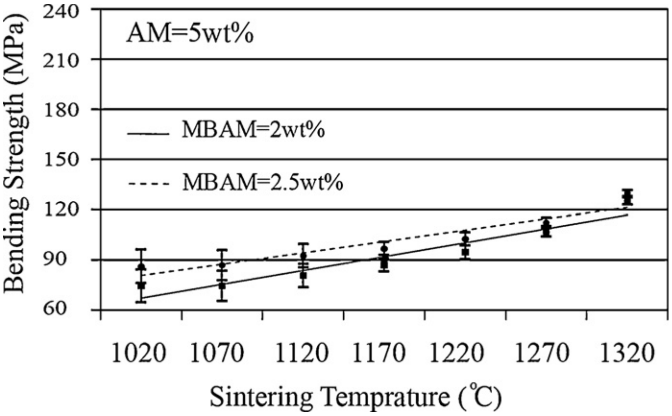

Fig. 9. Three-points bending strength of heat treated samples with thermal rate of 10 °C $\min^{-1}$ containing 5 wt.% monomer and 0.4 wt.% initiator.

expected from Figs. 4 and 5, polymers affect the bending strength of fired samples inversely (Figs. 7–9) as they residue a high volume percent porosity during burnout. Nevertheless, the bending strength of the samples which contain a low amount of polymer AM (Fig. 7) is high enough (about 200 MPa) and unexpectedly stronger than the same composition that obtained through melt casting technique [10]. Accordingly, the amount of polymers which is used in gel-casting process must be reduced to what extend that only guarantees enough polymerization and hence a safe handling of cast body.

Figs. 10 and 11 demonstrate the microstructure of the gel-cast body containing 3 wt.% AM, 0.75 wt.% MBAM and 0.4 wt.% initiator, at two different magnifications, after sintering at 1270 °C for 1 h and remaining at 970 °C during its cooling for 1 h. Based on Fig. 10, it can be concluded that the body is not yet pore – free. In spite of a relatively high firing temperature, fine crystals of α-cordierite are also visible in this sample whose dimensions are smaller than 0.5 μm (Fig. 11).

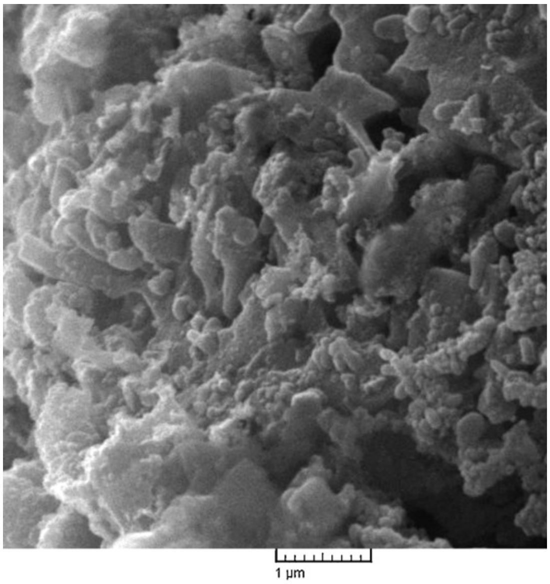

Fig. 10. Microstructure of sintered sample after firing at 1270 °C for 1 h and then heat treated during cooling at 927 °C for 1 h, magnification 25,000×.

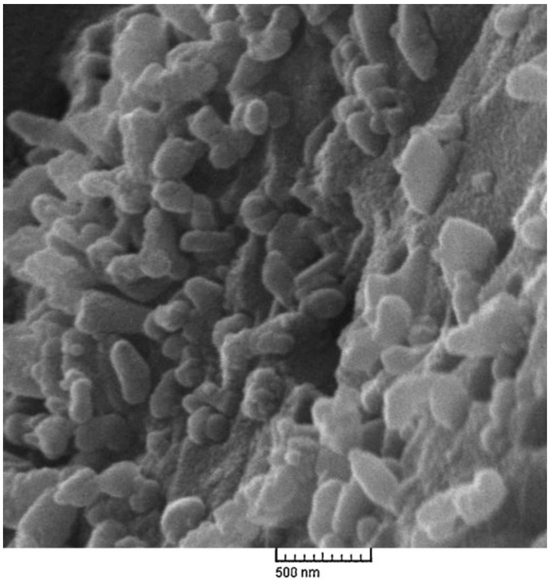

Fig. 11. Microstructure of sintered sample after firing at 1270 °C for 1 h and then heat treated during cooling at 927 °C for 1 h, magnification 50,000×.

4. Conclusion

According to the STA thermographs, elimination of organic materials of the gel-cast bodies was performed completely at 350 °C.

Enhancing the percentage of polymers of the gel-cast slurries led to increase of porosity and so decreasing the relative density of fired specimen.

Bending strength of the bodies depended strongly on the amounts of used polymers. Increasing the amount of monomer and arising the cross-linker monomer ratio led to increase of dried strength of gel-cast bodies.

Firing of the optimum sample at 1270 °C caused a mean relative density equal to 94% and a three-point bending strength of about 210 MPa.

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