Acta Materialia 130 (2017) 347–360

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

Microstructure and mechanical properties of nucleant-free Li_2O-CaO-SiO_2 glass-ceramics

Gisele G. Santos [a], [*], Francisco C. Serbena [b], Vladimir M. Fokin [a], [c], Edgar D. Zanotto [a]

[a] Vitreous Materials Laboratory, Department of Materials Engineering, Federal University of São Carlos (UFSCar), 13565-905, São Carlos, SP, Brazil
[b] Department of Physics, State University of Ponta Grossa (UEPG), 84.030-900 Ponta Grossa, PR, Brazil
[c] Vavilov State Optical Institute, ul. Babushkina 36-1, 193171 St. Petersburg, Russia

ARTICLE INFO

Article history:
Received 10 November 2016
Received in revised form
4 March 2017
Accepted 6 March 2017
Available online 30 March 2017

Keywords:
Crystallization
Glass-ceramic
Mechanical property
Lithium metasilicate
Wollastonite

ABSTRACT

An attractive characteristic of the Li_2O-CaO-SiO_2 glass-forming system is the possibility of obtaining internally nucleated crystal phases – $CaSiO_3$ and Li_2SiO_3 – having elongated morphologies that can potentially lead to tough glass-ceramics. Another great advantage of this system is that it does not need a nucleating agent to crystallize internally. In this research work, three glasses with systematic compositional variations within the range of 30–50 mol% $CaSiO_3$/70-50 mol% Li_2SiO_3 were prepared, heat-treated and their microstructures and mechanical properties evaluated. Heating cycles were applied in two-stage treatments. The temperatures were selected based on previous DSC analyses. The crystallized samples were characterized by XRD and SEM to examine the nature, size and morphology of their crystals. The effect of microstructure on the Vickers hardness (H_v) and indentation fracture toughness (K_c) of the glass-ceramics was determined. Elastic modulus (E), biaxial strength (σ_m) and fracture toughness (K_{DTIC}) were determined from nanoindentation, ball-on-three-balls and double torsion tests, respectively. The level of internal residual stresses was evaluated by X-rays diffraction. The best mechanical properties were exhibited by a composition containing 44 mol% $CaSiO_3$ heat-treated at 498 °C for 24 h for nucleation and at 700 °C for 2 h for crystal growth. This composition resulted in a glass-ceramic with the following microstructural features and properties: average Li_2SiO_3 (LS) crystal size of 8.5 µm, wollastonite (CS) phase surrounding the LS crystals with approximately 50% LS crystallized volume fraction, $K_{DTIC} = 2.3 \pm 0.5$ MPa $m^{1/2}$, $\sigma_m = 270 \pm 20$ MPa, $H_V = 8.4 \pm 0.7$ GPa and $E = 146 \pm 8$ GPa. These are exciting mechanical properties for glass-ceramics intended for load bearing applications.

1. Introduction

Glass-ceramics are polycrystalline materials produced through the controlled internal crystallization of certain glasses, and contain one or more crystalline phases embedded in a residual glass phase. These materials are obtained by subjecting the parent glass to controlled heat treatments that favor internal nucleation followed by crystal growth [1]. The advantages of glass-ceramics over sintered ceramics is their negligible or even zero porosity, easier microstructural design and control, greater uniformity, possibility of rapidly producing complex shapes using fast glass-forming techniques, and reproducibility [2]. The chemical composition influences their glass forming ability, their ability for nucleus formation and growth, and the nature of their crystal phase, while the microstructure is a key factor for most properties [3].

With respect to mechanical properties, the performance of glasses is usually inferior to that of ceramics. However, this disadvantage is overcome by the possibility of designing and producing pore-free glass-ceramic microstructures that enable the development of new materials with unusual combinations of properties. Therefore, the study of the crystallization behavior of glass-forming systems and the evaluation of their properties epitomize a significant field in glass technology for developing new materials and products [4]. As a matter of fact, a recent study by Mauro and Zanotto [5] demonstrated that the most frequent keyword in the past 200 years of glass research history is "crystallization"!

Surprisingly few studies about Li_2O-CaO-SiO_2 glasses have been published so far, despite the possibility of obtaining glass-ceramics displaying high strength and toughness. Previous works on this system include the identification of the crystalline phases and a

---

[*] Corresponding author.
E-mail address: giseleguis@gmail.com (G.G. Santos).

http://dx.doi.org/10.1016/j.actamat.2017.03.010
1359-6454/

study of the ternary and pseudo-binary diagrams (Fig. 1) by A.R. West [6], a study of some properties and the influence of liquid phase separation, by J.E. Shelby and S.R. Shelby [7], and a study of the influence of the addition of certain components, such as MgO, SrO, Al_2O_3 and ZnO, on the properties of glass-ceramics, by S. M. Salman et al. [8–10].

More recently, some of us studied the kinetics of nucleation and crystallization of non-stoichiometric glasses of the $Li_2SiO_3 - CaSiO_3$ system [11]. Compositions containing 35, 47, 50, 60 and 66 mol% of $CaSiO_3$ were analyzed to determine their nucleation rates, crystal growth rates, crystal shape and size. Glasses containing 35 mol% of $CaSiO_3$ showed the highest nucleation rates among the studied compositions, whereas the nucleation rates decreased as the molar content of $CaSiO_3$ increased. In the second part of the paper [12], the same authors described the influence of the residual liquid composition on the crystallization process. They found that, because Ca ions are less mobile than Li ions, wollastonite crystallization is delayed compared to that of the lithium metasilicate phase in glasses of the LS-CS system. Consequently, only the formation of LS is observed in the initial stages of crystallization. This shifts the composition of the residual melt towards calcium metasilicate until the latter reaches the composition corresponding to the metastable liquidus temperature. LS crystals remain in equilibrium with the residual melt until CS crystals form by heterogeneous nucleation and growth, which again leads to changes in the composition of the residual liquid and the resumption of LS crystallization, until the material eventually crystallizes completely.

In this work, we study the microstructural development of $Li_2O - CaO - SiO_2$ glasses in response to heat treatments aimed at obtaining glass-ceramics containing elongated $CaO \cdot SiO_2$ (wollastonite) or $Li_2O \cdot SiO_2$ crystals inside the glass, without using nucleating agents. Calcium silicate glasses are known to have low nucleation rates and to undergo mostly surface crystallization [13]. On the other hand, pure lithium metasilicate (LS) glasses show extremely high nucleation rates ($10^{25}\ m^{-3}\ s^{-1}$, according to the estimations by Fokin et al. [11]), which are comparable to values reported for some metallic alloys. In the current LS - CS glasses, lithium metasilicate nuclei form spontaneously in response to appropriate heat treatment, and remain embedded in the residual glassy matrix with a composition approaching that of wollastonite during the growth of LS crystals [11,12]. Upon further heat treatment, the CaO-rich glassy matrix crystallizes around the lithium metasilicate crystals or at the LS/melt interphase, inducing internal crystallization of wollastonite. Therefore, both LS and CS crystals are formed inside the glass.

That being said, the core goal of this article is to explore the possibility of developing new CS-LS glass-ceramics with controlled microstructures, using the high spontaneous nucleation rates of lithium metasilicate to obtain a material with outstanding mechanical properties, such as high toughness, K_{IC}, and elastic modulus, E, due to the good mechanical properties of both wollastonite and LS.

2. Experimental

Compositions from 30 to 50 mol% of $CaSiO_3$ (the remainder consisting of Li_2SiO_3) were studied, more specifically formulations containing 32, 44 and 47 mol% of $CaSiO_3$ (47 mol% $CaSiO_3$ being the eutectic, according to Fig. 1). These compositions are hereinafter referred to as B32, B44 and B47, respectively. We chose to work within this compositional range because we believed it could generate crystallized samples with adequate combinations of the two crystal phases having good mechanical properties, while simultaneously maintaining reasonable internal nucleation rates without using a nucleating agent. This idea was based on our previous fundamental studies on the crystallization mechanism and kinetics of this system [11,12].

Calcium carbonate (98%, J. T. Baker), lithium carbonate (99%, Synth) and fumed silica (99.8%, Sigma-Aldrich) were weighed, mixed, deposited in an alumina crucible and subjected to a preheat treatment (800 °C for 20 h) to facilitate the release of carbon dioxide. The weights before and after the pretreatment were monitored. The mixed reagents were then fused in a platinum crucible at about 1400 °C, poured 3 times and remelted to promote homogenization, cast onto a flat steel plate and annealed at a temperature 60 °C below the T_g of each glass for 3–6 h.

Monolithic samples weighing about 20 mg were analyzed by DSC (differential scanning calorimetry, NETZSCH 404) at a heating

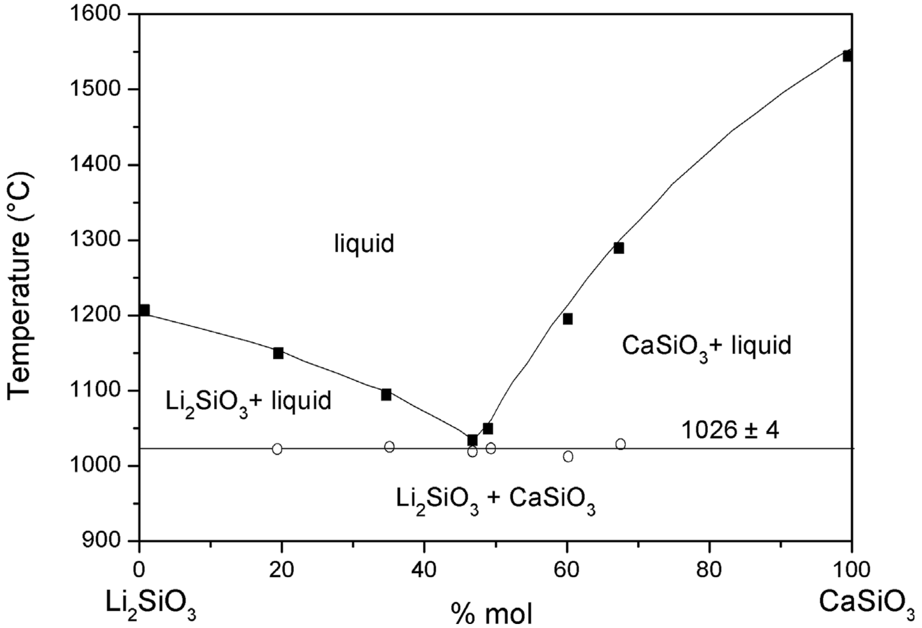

Fig. 1. Phase equilibrium diagram of the binary $Li_2SiO_3 - CaSiO_3$ system. The lines were taken from Ref. [6]; the data points were estimated from DSC curves in Ref. [11].