Materials Chemistry and Physics 170 (2016) 246–250

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

Effect of the thermal history of glass melts on crystallization in lithium and sodium disilicate glasses doped with platinum as a nucleating agent

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HIGHLIGHTS

- Pt-doped Li_2O–Na_2O–$2SiO_2$ glasses were produced.
- Glasses were synthesized by holding melts at various temperatures.
- Crystallization behaviors of glasses with different thermal histories were examined.
- Crystal particles increased in number as the holding temperature decreased.
- Melt structure was estimated from crystallization depending on holding temperature.

ARTICLE INFO

Article history:
Received 3 May 2015
Received in revised form
30 October 2015
Accepted 19 December 2015
Available online 31 December 2015

Keywords:
Glasses
Crystallisation
Optical microscopy
Microstructure

ABSTRACT

The crystallization behavior of Li_2O–Na_2O–$2SiO_2$ glasses with different thermal histories was examined. The glass melts were doped with 0.005 wt% platinum, held at various temperatures ($>T_L$) and then water-quenched, and glasses were obtained. Measurements revealed distinctly different crystallization tendencies between glasses whose melt was held at just above the liquidus temperature and glasses whose melt was held at a higher temperature. After double-stage heat treatments, the glasses were crystallized, and needle-like crystals ($Li_2O \cdot SiO_2$) and spherical crystals ($Li_2O \cdot SiO_2$) formed. In particular, platinum-derived nuclei promoted the generation of $Li_2O \cdot SiO_2$ crystal. Microscopic observations showed that both crystal particles precipitating in the interior of the crystallized glasses increased in number as the holding temperature decreased. The exothermic crystallization peak of the glass held at a lower temperature appeared earlier than that of the glass with a higher holding temperature in the profile of differential thermal analysis. Additionally, the precipitated amount of $Li_2O \cdot SiO_2$ obtained from X-ray diffraction measurement increased with decreasing holding temperature. These results suggest that the distribution of platinum colloids in glass melts varies depending on the holding temperature.

1. Introduction

When quenching several molten slags, different amounts of crystals form in the as-quenched products depending on the temperature of the slag melt [1]. Consequently, as a hypothesis of a liquid model, it has been suggested that any liquid should contain crystal embryos at temperatures even above the melting point or liquidus temperature, and the number density of the embryos should decrease with a rise in temperature [1].

Morey [2] stated that, according to the devitrification phenomena of glasses, no components of a glass melt dissociate into oxides, and molecular compounds or molecular species form depending on the glass composition and temperature. The rate of formation of the complex molecular species increases with a decrease in temperature. Additionally, the molecular species have a dynamic form, in that they incidentally form and disappear and do not have a persistently stable structure. The possibility that these kinds of molecular species occur statistically depending on temperature is considered. This corresponds to the idea of imaging the existence of an instantaneous molecular arrangement similar in structure to crystals, and has a general resemblance to the above mentioned liquid model.

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http://dx.doi.org/10.1016/j.matchemphys.2015.12.045
0254-0584/

Table 1
Glass composition, liquidus temperature, and holding temperature for $x\text{Li}_2\text{O}\cdot(1\text{-}x)\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ glasses.

Glass composition	Liquidus temperature/°C[a]	Holding temperature/°C
0.55 L ($x = 0.55$)	859	865, 1350
0.6 L ($x = 0.6$)	890	895, 1000, 1150, 1350
0.65 L ($x = 0.65$)	917	920, 1350

[a] ref. [10].

We have studied the crystallization behavior of alkali silicate glasses with different thermal histories. The glass that is produced by quenching a melt held at a temperature will preserve the melt structure in the molten state to a certain extent; temperature-dependent structures form in the glass. The examination of the variation of crystallization in glasses melted at different temperatures could substantiate the liquid model, and the following experiments were conducted. For a lithium disilicate ($T_m = 1033$ °C [3]) composition that gives rise to homogeneous nucleation, the number and size of crystals precipitated in the interior of crystallized glass that was melted at 1035 °C were larger than those of crystals precipitated in the interior of crystallized glass that was melted at 1300 °C [4–6]. In the case of sodium disilicate ($T_m = 874$ °C [7]) having heterogeneous nucleation, the amount of surface crystallization increased with a decrease in the temperature at which the glass melt was held [8]. Obvious differences between glasses held at lower and higher temperatures were also found in terms of crystallization not only by isothermal treatment but also by elevated-temperature treatment such as differential thermal analysis (DTA) [9].

To accelerate and control the crystallization of glasses of heterogeneous nucleation, various nucleating agents are often introduced to the glass. Noble metals such as Pt, Au, Ag and Cu have been found to play an important role in nucleation. From the view of the liquid model, it is of extreme interest to find whether finely dispersed metal particles or colloids in a glass melt are affected by the thermal history of the melt. The present study examined the crystallization kinetics of Pt-doped lithium and sodium disilicate ($\text{Li}_2\text{O}{-}\text{Na}_2\text{O}{-}2\text{SiO}_2$) glasses with different melting thermal histories. The relationship between the amount of precipitated crystal and the distribution of Pt colloids was discussed on the basis of the

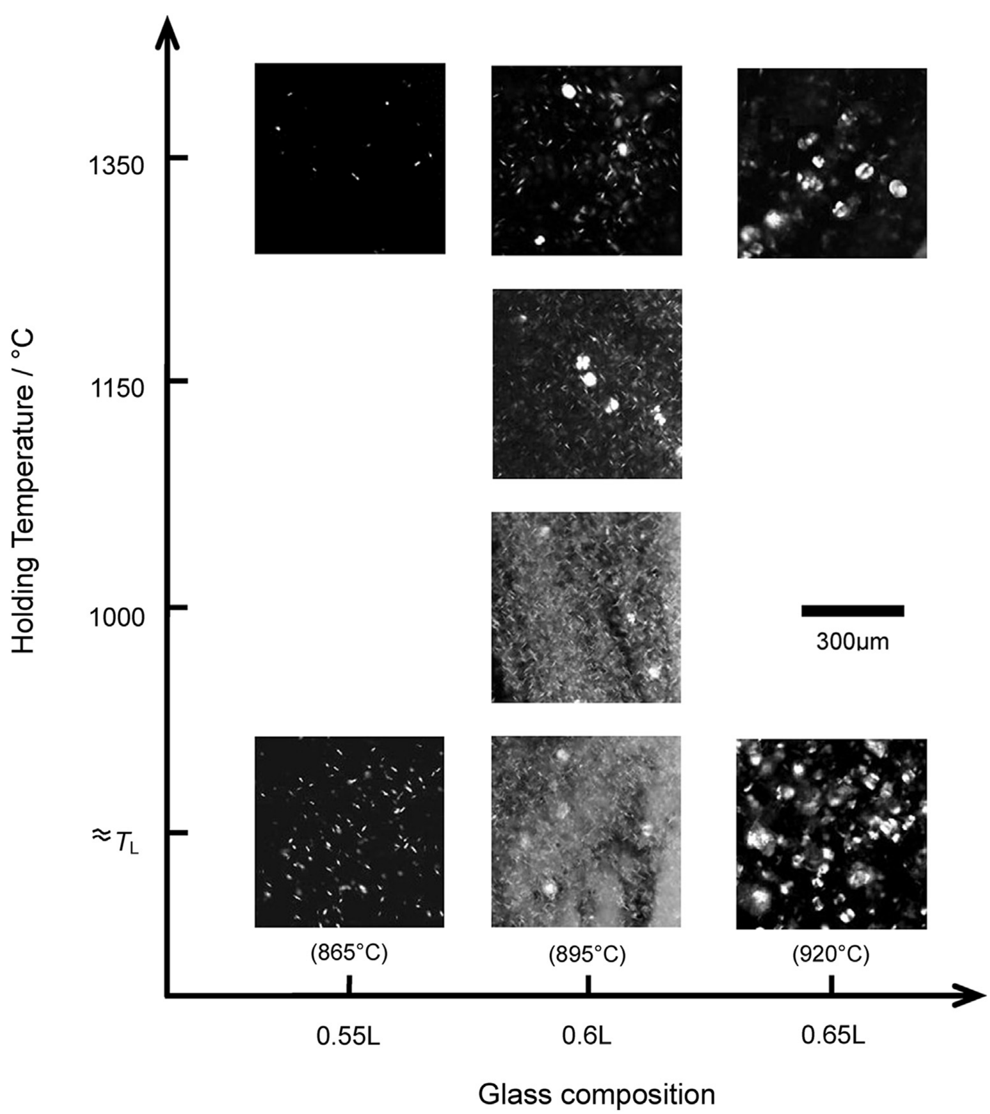

Fig. 1. Optical micrographs of crystal particles precipitated in crystallized glasses melted at various holding temperatures. Heat treatment: 450 °C for 30 min and 600 °C for 60 min for 0.55 L and 600 °C for 30 min for 0.6 L and 0.65 L.