Journal of Non-Crystalline Solids 427 (2015) 152–159

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Effect of molybdenum and tungsten oxides on nucleation and crystallization behaviors of $MgO–Al_2O_3–SiO_2$ glasses

Kei Maeda *, Atsuo Yasumori

Asahi Glass Co., Ltd., Research Center, 1150 Hazawa-cho, Kanagawa-ku, Yokohama 221-8755, Japan

ARTICLE INFO

Article history:
Received 23 April 2015
Received in revised form 23 July 2015
Accepted 24 July 2015
Available online 6 August 2015

Keywords:
Glass-ceramics;
Cordierite;
Enstatite;
Molybdenum;
Tungsten

ABSTRACT

To investigate the effect of novel nucleating agents, this study investigates the crystallization behavior of a $MgO–Al_2O_3–SiO_2$ glass with molybdenum or tungsten oxide addition. Under a reducing condition, crystals formed in the bulk of the supercooled liquids, whereas melting in air yielded only surface crystallization. The first crystalline phase precipitated inside the glass was enstatite and Mg–petalite in glasses doped with molybdenum and tungsten oxides, respectively, whereas the surface precipitate was cordierite. Molybdenum oxide yielded a finer microstructure of the glass-ceramic than tungsten oxide. Some fractions of the nucleating agents were considered to be reduced to metallic states and dispersed through the glasses, providing heterogeneous nucleating sites for enstatite and Mg–petalite.

1. Introduction

Crystallization is a well-recognized practical means of improving the brittleness of glass. Many glass-ceramics have been investigated, and some have been incorporated into practical materials [1,2].

Glass-ceramics in the $MgO–Al_2O_3–SiO_2$ (MAS) system have attracted much interest on account of their superior mechanical and thermal properties, i.e., high strength and stability at high temperatures [3,4]. These properties have been enhanced by incorporating MAS glass-ceramics into fiber-reinforced composite materials [5,6]. However, the glass-ceramics in fiber-reinforced composites are made from glass powders along with fiber materials such as SiC or Si_3N_4, which diminishes the formability of glass. Consequently, glass formed by these techniques cannot be pressed or drawn out. From this perspective, bulk-crystallized glass-ceramics are advantageous in various practical applications.

Chemical compositions and properties of typical bulk crystallized MAS glass-ceramics are shown in Table 1 [3,9]. Cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) glass-ceramic is characterized by high strength and low thermal expansion. Corning code 9606 possesses excellent electrical properties at microwave frequencies in this system, and has been developed into a successful commercial product [7]. Cordierite glass-ceramics doped with NiO were also investigated recently, aiming at a new infrared radiation application [8]. Conversely, enstatite ($MgSiO_3$) glass-ceramic is one of the toughest glass-ceramics, with a fracture toughness of 5 MPa $m^{1/2}$ and a high Young's modulus (140 GPa) [9]. The toughness of this material is comparable with that of natural stone jade, one of the toughest known minerals [10,11].

TiO_2 and/or ZrO_2 are the most commonly used nucleating agents in bulk crystallization of MAS glass-ceramics. These nucleating agents promote the phase separation of the parent glass and precipitate either as solid $ZrO_2–TiO_2$ or $MgO–2TiO_2–Al_2O_3 \cdot TiO_2$ or as a single component oxide such as tetragonal ZrO_2 ($t\text{-}ZrO_2$) or TiO_2, which usually constitutes the first crystalline phases [3]. In recent years, Dargaud et al. investigated the kinetics of the nucleation of MAS glass doped with ZrO_2 by a new approach, based on the in-situ XANES technique [12].

The toughening mechanism of enstatite-precipitated MAS glass-ceramics appears to occur by the transformation of enstatite crystal; in particular, fine-grained twinned crystal has been implicated in crack deflection [9]. However, the interpretation of the toughening mechanism is confounded by the presence of another toughening agent, $t\text{-}ZrO_2$, in the glass-ceramics [13]. Although enstatite-precipitated MAS glass-ceramics have also been nucleated by TiO_2 [14], the resulting materials failed to attain the high fracture toughness of glass-ceramics nucleated by $t\text{-}ZrO_2$ described in [9], probably because the enstatite precipitated in small quantities.

Thus, a nucleating agent that yields high toughness at small concentrations would enable a better interpretation of how the physical properties relate to those of the main crystal. Furthermore, such nucleating agents would improve the performance of glass-ceramics.

As is well known, some metallic particles provide heterogeneous nucleating sites in glass [15,16]. Since metal is relatively insoluble in silicate glass, heterogeneous nucleating sites should be initiated by only a small amount of metal. In fact, β-wollastonite ($CaSiO_3$) has been

* Corresponding author.
E-mail address: kei-maeda@agc.com (K. Maeda).

http://dx.doi.org/10.1016/j.jnoncrysol.2015.07.040