Effect of molybdenum and tungsten oxides on nucleation and crystallization behaviors of MgO–Al₂O₃–SiO₂ glasses

Kei Maeda *, Atsuo Yasumori
Joshi Glass Co., Ltd. Research Center, 1150 Hinao-cho, Konagawa-ku, Yokohama 221-8555, Japan

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–Al₂O₃–SiO₂ (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 Si₃N₄, 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 · 2Al₂O₃ · 5SiO₂) glass-ceramic is characterized by high strength and low thermal expansion. Corning code 9608 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 NbO were also investigated recently, aiming at a new infrared radiation application [8]. Conversely, enstatite (MgSiO₃) glass-ceramic is one of the toughest glass-ceramics, with a fracture toughness of 5 MPa m¹/₂ and a high Young's modulus (140 GPa) [9].

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The toughness of this material is comparable with that of natural stone jade, one of the toughest known minerals [10,11]. TiO₂ and/or ZrO₂ 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 ZrO₂–TiO₂ or MgO–ZrO₂–TiO₂–Al₂O₃–SiO₂. As a single component oxide such as tetragonal ZrO₂ (t-ZrO₂) or TiO₂, 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 ZrO₂ by a new approach, based on the in-situ WAXS 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 confused by the presence of another toughening agent, t-ZrO₂ in the glass-ceramics [13]. Although enstatite-precipitated MAS glass-ceramics have also been nucleated by TiO₂ [14], the resulting materials failed to attain the high fracture toughness of glass-ceramics nucleated by t-ZrO₂ 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 the physical properties of glass-ceramics. 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 (CaSiO₃) has been