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Effect of TiO_2 content on the crystallization behavior and properties of $CaO-Al_2O_3-SiO_2$ glass ceramic fillers for high temperature joining application

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ABSTRACT

The effects of TiO_2 content on the crystallization behavior, microstructure, microhardness, coefficient of thermal expansion (CTE) and softening temperature of $CaO-Al_2O_3-SiO_2$ glass ceramic fillers were investigated. The results show that the crystallization activation energy (E) firstly decreases and then increases with the TiO_2 addition from 10 wt% to 20 wt%. The microstructure and phase composition of glass ceramics importantly depend on the content of TiO_2. Low TiO_2 content results in formation of Ti-contained crystals ($CaTiSiO_5$) due to phase separation. In contrast, high TiO_2 concentrations lead to precipitation of small titanium oxide crystals that act as nuclei, facilitating the development of $CaAl_2Si_2O_8$. Furthermore, the formation of crystalline phases is beneficial for improving the microhardness and refractoriness of glass ceramics. The $CaO-Al_2O_3-SiO_2$ glass with 15 wt% TiO_2 addition exhibits the highest crystalline volume fraction possibly due to the lowest activation energy of crystallization. As a result, its microhardness and softening temperature can reach as high as 898.2 HV and 1027 °C, respectively. However, its CTE slightly decreases from $7.44 \times 10^{-6}/°C$ to $6.35 \times 10^{-6}/°C$ after crystallization treatment because of the formation of $CaTiSiO_5$.

1. Introduction

Alumina ceramics have many specific properties, such as excellent heat resistance, corrosion resistance, high strength and low density, which enable them to be used in aerospace, transport, energy and industrial manufacture fields [1,2]. However, owing to the intrinsic brittleness and poor workability of structural ceramics, complex shaped and large-sized components are often fabricated by joining technology [3,4]. Among all the joining techniques for ceramic materials, the use of glass or glass ceramic filler is very desirable due to the excellent chemical compatibility between the glass and ceramics, tailorable coefficient of thermal expansion (CTE) and low cost [5]. Several glass ceramics fillers have been used to join alumina ceramic [6–8]. Especially, The $CaO-Al_2O_3-SiO_2$ glass with eutectic composition exhibits excellent wettability and flowability on the surface of alumina ceramic at relatively low temperature [8]. However, low crystallinity of glass ceramic fillers can lead to poor refractoriness of joints. Therefore, it is necessary to further optimize the composition of glass ceramic filler for promoting crystallization and then improving the refractoriness of joints.

A common approach to promote crystallization is adding nucleating agents into the basic glass. Literature reviews suggested that the wide varieties of chemicals, like TiO_2, CaF_2, ZrO_2, P_2O_5, Cr_2O_3, La_2O_3, MoO_3 can be used as nucleating agents [9–13]. Among that, TiO_2 is the most commonly used nucleating agent in many silicate glass systems. This oxide is believed to encourage the liquid-liquid phase separation and then promote the following nucleation and crystallization process [14,15]. The effect of TiO_2 content on the crystallization behavior of $34SiO_2-43Al_2O_3-23CaO$ glass ceramic has been investigated by Mukherjee et al. [16]. However, the maximum additive amount of TiO_2 was limited to 12 wt%. McMillan [17] has pointed out that the solubility of TiO_2 in glass melt can reach to 20 wt%. Moreover, the CTE of glass ceramics before and after crystallization has not been reported. It is well known that crystallization of glass ceramic not only can improve the softening temperature but also can change its CTE [18]. Therefore, it is essential to control the phase composition of glass ceramic filler in order to obtain compatible CTE with the alumina

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Table 1
Chemical composition of the glass ceramic fillers (in g).

	CaO	Al_2O_3	SiO_2	B_2O_3	K_2O	Na_2O	TiO_2 (% excess)
CAST-1	21.43	13.71	56.86	2	3	3	10
CAST-2	21.43	13.71	56.86	2	3	3	15
CAST-3	21.43	13.71	56.86	2	3	3	20

substrate on the premise of high crystallinity.

In this paper, glass ceramic fillers based on the $CaO\text{-}Al_2O_3\text{-}SiO_2$ eutectic composition were developed. However, the CTE of $CaO\text{-}Al_2O_3\text{-}SiO_2$ glass with eutectic composition ($5.5 \times 10^{-6}/°C$ [8]) is mismatched with that of alumina ceramic ($7.4 \times 10^{-6}/°C$ [19]). Therefore, a small quantity of Na_2O, K_2O and B_2O_3 were added into the glass to increase its CTE [20]. At the same time, high content of TiO_2 was used as nucleation agent to promote crystallization and control the phase composition of the glass ceramics. The effects of TiO_2 content on the crystallization kinetics, microstructure, microhardness, CTE and softening temperature of $CaO\text{-}Al_2O_3\text{-}SiO_2$ based glass ceramic fillers were investigated in details.

2. Experimental procedure

Reagent grade chemicals of CaO, Al_2O_3, SiO_2, B_2O_3, Na_2O, K_2O, and TiO_2 (purchased by Sinopharm Chemical Reagent Co.) with higher than 99.9% purity was used as raw materials for glass preparation. Table 1 shows the chemical composition of the different glass batches. The chemicals were weighed by using electronic balance and then mixed in a pestle mortal. The well-mixed powder was melted in a Pt crucible at 1500 °C for 2 h. After that, one part of the melt was quenched by pouring it into a copper mould, followed by annealing at 700 °C for 2 h to remove the residual stress. The remaining part of the melt was poured into cold water. After rinsing and drying, the quenched glass frits were ball milled for 3 h in ethanol with agate as the milling media. The glass was sieved after the milling to obtain powders with an average particle size of about 10 μm.

Glass transition temperature (Tg) and crystallization peak temperature (Tp) were measured by using a differential scanning calorimetric (DSC, STA 409C/CD; Netzsch, Germany) with α-Al_2O_3 powder as reference material. The glasses were heated at the rate of 5, 10, 15 and 20 °C/min during the DSC trace, to study the kinetics of crystallization and also to calculate the activation energy and the Avrami parameter.

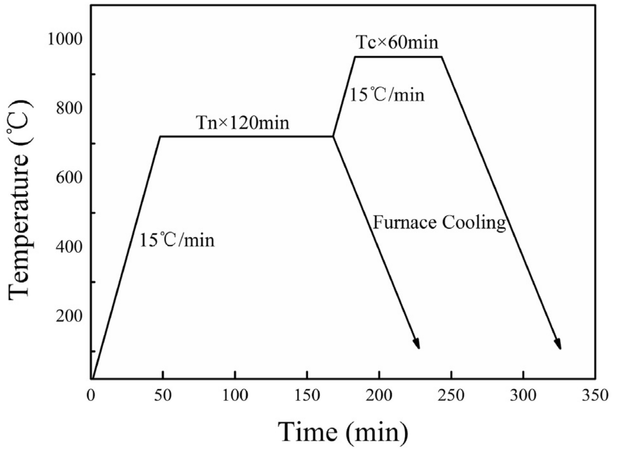

Fig. 1. Heating treatment schedule of the disc-shaped glasses (Tn: nucleation temperature, Tc: crystallization temperature).

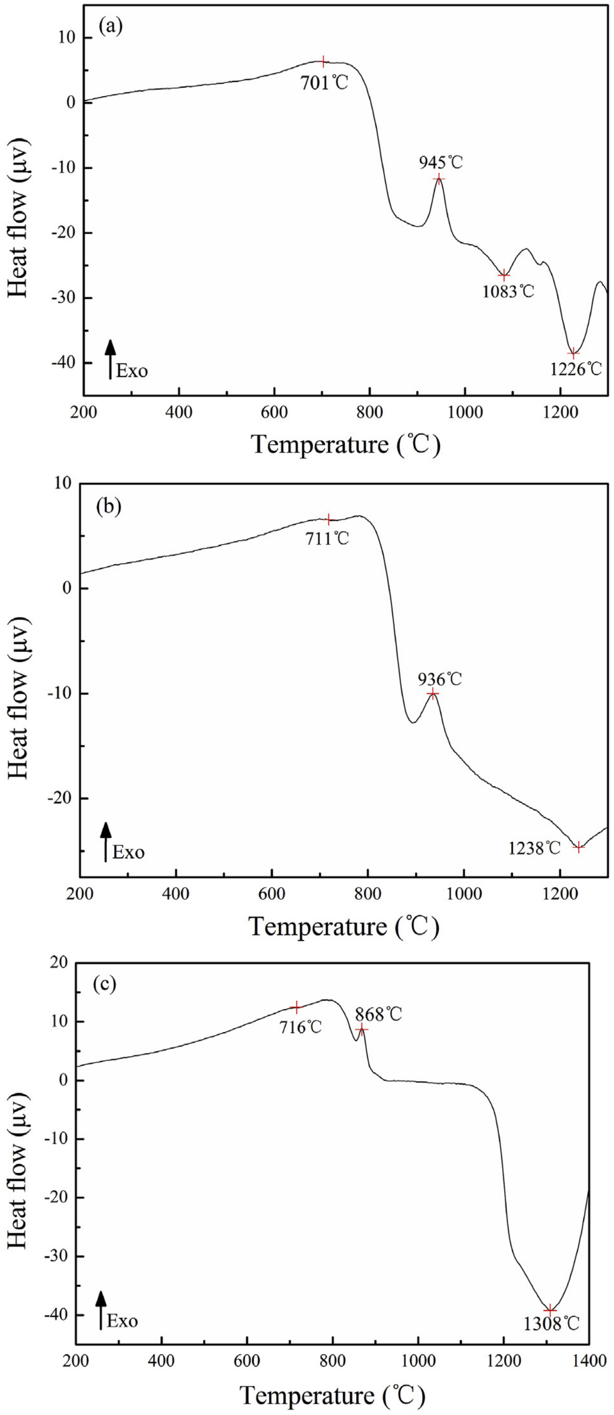

Fig. 2. DSC curves of the glass specimens, (a) CAST-1, (b) CAST-2, (c) CAST-3.

The bulk glass was cut by using a diamond saw to yield disc-shaped samples (10 × 10 × 0.5 mm) for controlled crystallization experiments. The heat treatment schedule was shown in Fig. 1. Partial specimens were cooled from nucleation temperature and others from crystallization temperature. The nucleation temperature and crystallization temperature were chosen according to the DSC results. Nucleation temperatures were chosen at about 20 °C higher than the glass transition temperature (Tg). Crystallization temperatures were chosen at the crystallization peak temperature (Tp).