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Short communication

Can crystalline phases be self-healing sealants for solid oxide fuel cells?

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ABSTRACT

The poor thermodynamic and thermal stability of self-healing glass sealants restrict their applications in planar solid oxide fuel cells (SOFCs). In this paper, a calcium borate crystalline is prepared by melting-quench and a subsequent crystallization. The crystalline phases include CaB_4O_7 and CaB_2O_4. The in situ observation reveals that the micro-indentation on the surface of such crystalline can be healed when heating from room temperature to 840 °C at a heating rate of 40 °C min^{-1}. Combining with the improved thermal stability, the crystalline sealant with desired self-healing property, at the operational temperature of SOFCs (e.g., 700–900 °C), provides additional solution for the sealing challenge of SOFCs.

1. Introduction

Solid oxide fuel cells (SOFCs) provide a promising solution for the worldwide energy shortage because of their high electric conversion efficiency, environmental compatibility, and system flexibility. However, the sealing challenge is one of the important factors intervening the SOFCs, especially for planar design [1], in which an overall efficiency of about 80% can be achieved [2,3].

A variety of different joining and sealing techniques have been developed for planar SOFCs, including brazing, glass and glass–ceramic sealing, thermal spraying and sol–gel deposition [4,5]. In the last decade, much attention has been focused on the viscous glass–ceramics seals, which releases the thermal stress in the cell stacks by the viscous flow of residual glass in the operational temperature range (e.g., 700–900 °C) of SOFCs [6–8]. In particular, the glasses without crystallization or with very slow crystallization, i.e., self-healing glasses, are highly desired for the long-term operation of SOFCs, for example, at 800 °C for 40,000 h.

However, the self-healing glasses are prone to crystallize under the SOFCs operational condition, due to their thermodynamic instability [6]. Some processing on the surface, e.g., polishing, also accelerates the crystallization of glasses, which imposes additional uncertainty on their self-healing properties [9]. Moreover, the notorious volatility of some components in glass matrix, such as B_2O_3, also impairs the thermal stability of such materials, especially under the operational environments of SOFCs [10]. A recent work of our group has found that the volatility of borate-containing glasses in the operational environments of SOFCs, e.g., in wet forming gas at 800 °C for 20 days, decreases from 6.6 to 2.5 g cm^{-2} as the borate content increases from 20 to 30 mole%. It is worth noting that the formation of borate-containing crystalline phases, e.g., $Sr_3B_2O_6$, reduces the vitreous B_2O_3 content in glasses matrix, which leads to the great improvement of thermal stability of resulting glasses–ceramics [11]. Therefore, the crystalline sealants, such as borate-containing species, are more attractive due to their better thermodynamic as well as thermal stabilities compared with that of amorphous analogues, if such materials can also possess the sealing-healing properties in the operational temperature range of SOFCs.

In this paper, a glass with high borate content (67 mole%) was prepared by melting-quench and subsequent long-term crystallization to obtain the fully crystallized specimen, which was confirmed by X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The self-healing behavior of such crystalline was investigated using an in situ optical microscopy to provide direct evidence for the design of novel sealing materials, in which the self-healing property can only be attributed to the presence of crystalline phases.

2. Experimental

A 50-g sample of glass was prepared from a batch mixture of reagent grade calcium carbonate and boric acid to form a nominate composition of 33%CaO–67%B_2O_3 (in mole%). The batch was melted in a fused silica crucible in air for 2 h at 1000 °C and the melt was then quenched on a steel plate. Glass powders were crushed and sieved to 45–90 μm. Some glass powers were pressed into pellets (Ø = 10 mm). The sintering and crystallization of glass pellets

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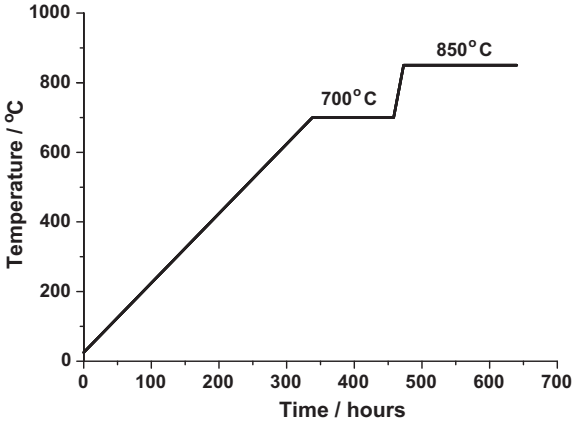

Fig. 1. Schematic diagram of the two-steps heat-treatment for the sintering and crystallization of glass pellets.

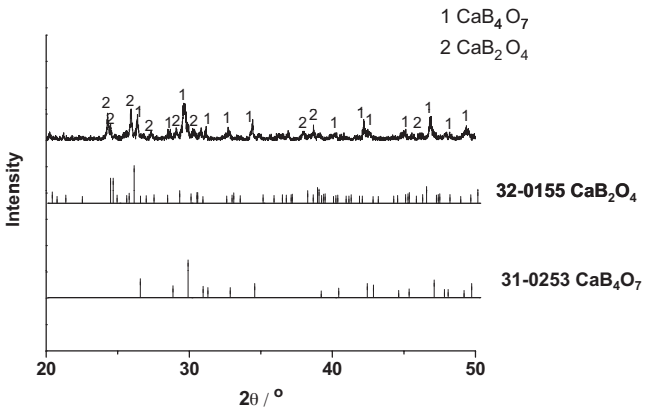

Fig. 3. XRD pattern of the calcium borate specimen with particle size of 45–90 μm, after heat-treatment at 850 °C in air for 1 week.

were performed by a two-steps heat-treatment, as shown in Fig. 1. Some of the crystallized pellets were also crushed and sieved to 45–90 μm. The crystalline phases in the crystallized powders were identified using X-ray diffraction (XDS 2000, Scintag, Inc.) analysis.

The glass transition temperature (T_g), crystallization temperature (T_c) of the glass powders were studied using differential scanning calorimetry (SDTQ600, TA, Inc.). In addition, the melting point (T_m) of crystalline formed during the heating procedure in the DSC instrument was determine using DSC and compared with that of crystallized powders. The measurements were conducted in nitrogen, using an alumina crucible and a sample weight of 10–15 mg. A typical experiment included heating the glass powder in the DSC instrument from room temperature to 1100 °C at a heating rate of 10 °C min^{-1}.

Some micro-indentions were created on the surface of the crystallized pellets using the micro-hardness tester (DHV-1000, Shanghai Jinxiang Group) at a load of 9.8 N. The in situ self-healing behavior was investigated by monitoring the change of the micro-indentations upon heating using a high temperature optical microscopy (EM-4, Uhlon, Inc.). The measurement was conducted from room temperature to 840 °C at a heating rate of 40 °C min^{-1}.

3. Results and discussion

Shown in Fig. 2, are the DSC curves of the calcium borate species with particle size of 45–90 μm. The glass transition temperature (655 ± 5 °C) and the peak temperature of crystallization (790 ± 5 °C) in the DSC curve of the quenched glass (Fig. 2a) indicate

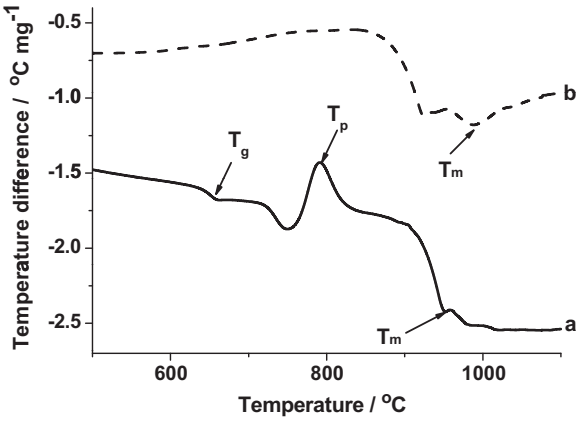

Fig. 2. DSC curves of the calcium borate species with particle size of 45–90 μm, for (a) quenched glass and (b) after heat-treatment at 850 °C in air for 1 week.

its amorphous state; whereas, the absence of the glass transition temperature and crystallization endothermic peak in the DSC curve of specimen after the heat-treatment at 850 °C in air for 1 week (Fig. 2b) confirms that the specimen has been fully crystallized. It is worth noting that the melting point of crystalline phase, after heat-treatment at 850 °C for 1 week, occurs at 986 ± 5 °C, which falls in the range of the reported melting point of CaB_4O_7 in literature (987 ± 10 °C) [12].

Fig. 3 shows the XRD pattern of the calcium borate specimen with particle size of 45–90 μm, after heat-treatment at 850 °C in air for 1 week. The standard diffraction patterns of CaB_4O_7 and CaB_2O_4 are also included for comparison [13]. It is clear that CaB_4O_7 and CaB_2O_4 are the major phases in the calcium borate species. The presence of CaB_4O_7 in the crystalline species is consistent with the result of DSC curves in Fig. 2b. The volatilization of borate in the calcium borate species during the heat-treatment at 850 °C, before the fully crystallization, might generate some borate-deficient zones on the surface of the species and consequently lead to the formation of CaB_2O_4.

To investigate the self-healing behavior of the crystalline specimen, an in situ observation was carried out by monitoring the change of the micro-indentations upon heating using a high temperature optical microscopy, as shown in Fig. 4. It is clear that the micro-indentation, marked by the dash-line circle, becomes obscure when the temperature increases from room temperature (Fig. 4a) to 700 °C (Fig. 4b) and to 800 °C (Fig. 4c). Finally, the micro-indentation disappears completely when the temperature increases from 800 to 840 °C, which indicates that such crystalline specimen can be self-healed at 840 °C immediately, e.g., for a minute in present work. The self-healing behavior of such crystalline specimen can be correlated with the viscoelastic flow of the crystalline phases at temperatures close to their melting points. Considering the much lower melting point of CaB_4O_7 (987 ± 10 °C) compared with that of CaB_2O_4 (1122 ± 10 °C) [12], its viscoelastic flow should be the main reason for the self-healing behavior observed in present work.

It is generally accepted that the addition of B_2O_3 is effective in reducing the glass transition temperature (T_g) as well as the softening temperature (T_d) of sealing glasses, which are desired properties for performing the joining process [5,14]. However, the maximum borate content in sealing glasses should be 10 mole% or less, because of the notorious volatility of boron in glasses at high temperatures, especially with the presence of water vapor [10,15]. For example, the reaction between water vapor and liquid state B_2O_3 leads to the formation of $B_3H_3O_6$ vapor, which causes a weight loss of 0.98 mg cm^{-2} in a glass with 20 mole% B_2O_3 after holding in wet forming gas at 780 °C for 7 days [10]. The finding of self-healing

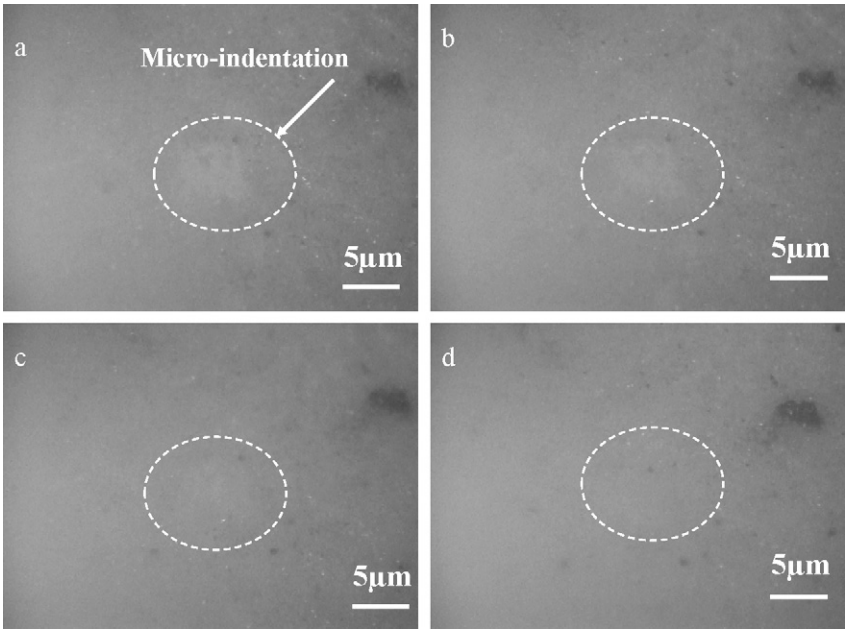

Fig. 4. In situ optical images of the calcium borate specimen after heat-treatment at 850 °C in air for 1 week, (a) room temperature, (b) 700 (c) 800 and (d) 840 °C.

crystalline sealants in present work provides useful information on the design of novel sealants: The glass matrix with high borate content at the beginning provides the desired properties for joining process, e.g., low T_g and T_d; the borate-containing crystalline phases, obtained by controlled crystallization from the glass matrix, fulfill the self-healing as well as thermal stability requirements in routine operation of SOFCs. Combining with the good thermal stability, such crystalline phases with desired self-healing property provides additional solution for the sealing challenge of SOFCs.

4. Conclusions

The self-healing crystalline phases with high borate content (67 mole%) provides additional approach for achieving the self-healing design of SOFCs. The in situ observation gives direct evidence for the excellent self-healing property of such borate-containing crystalline species at the operational temperatures of SOFCs. The self-healing behavior is attributed to the viscoelastic flow of the crystalline phases at temperatures close to their melting points, such as CaB_4O_7 in present work. This finding will also expand the range of candidates for developing reliable sealants with desired self-healing property.

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