Journal of Non-Crystalline Solids 357 (2011) 3074–3079

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Bi-doped borosilicate glass as sealant for sodium sulfur battery

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ARTICLE INFO

Article history:
Received 11 January 2011
Received in revised form 25 April 2011
Available online 2 June 2011

Keywords:
Sodium sulfur battery;
Joining;
Bi_2O_3;
Glass

ABSTRACT

Bi-doped borosilicate glasses as sealants for sodium sulfur battery are developed. The joining properties involving hermeticity, wetting behavior, bonding strength, thermal shock resistance and corrosion resistance have been systematically investigated. As found, the joints achieve good hermeticity by bulk joining. The wetting behavior and bonding strength are governed by the joining temperature and Bi_2O_3 content. The higher temperature and higher Bi_2O_3 content induce better wetting behavior due to the low viscosity. The thermal shock resistance of the alpha-alumina/glass/beta-alumina joint is dependent of the thermal expansion match between the glasses and alpha-, beta-alumina. No microcracks are found in the glasses containing 12–42 wt.% Bi_2O_3 after 200-times thermal shock. The glass/alumina joints show good anti-corrosion behavior against sulfur, especially containing 42 wt.% Bi_2O_3.

1. Introduction

A number of organizations are actively pursuing the research and development of advanced, high-energy secondary battery systems. In particular, sodium sulfur battery has been studied extensively because of its low material cost, long cycle-life and high specific energy [1–3]. Great achievements have been made during the last two decades, especially under the collaboration of Tokyo Electric Power Company and NGK Insulator, Ltd. Sodium sulfur battery is one of the most promising candidates for energy storage applications [4]. Now, the applications of sodium sulfur battery have been extended to emergency power, combined emergency power and load leveling, and electric transmission and distribution system support. The markets covered industrial, commercial owners and wind power generating systems, etc. [5]. The most vital component of sodium sulfur battery is the thin walled beta-alumina electrolyte, and the hostile reactions between liquid sodium and sulfur are in compartments of either side of the beta-alumina electrolyte. Generally, the beta-alumina is sealed to an alpha-alumina insulator ring. The alpha-alumina also serves the purpose of strengthening the beta-alumina at the point of attachment to the remainder of the battery. For both safety and performance reasons, a high-integrity seal between beta-alumina and alpha-alumina is essential. However, seal between ceramics is not an easy task. Due to chemical inertness, low diffusion rate, and high-melting temperatures of ceramics, joining methods prevailing in metals are usually not applicable in ceramics [6,7]. It has been realized that glasses have potential to join ceramic components [8]. The most important advantage is its chemical compatibility with the parent ceramics. Moreover, the thermal expansion, viscosity, flowability and melting characteristics of glasses can be controlled over wide ranges, and adherence of the glasses to the ceramics is usually quite good. Another desirable feature of glasses is that many compositions can be crystallized to improve their mechanical and corrosive properties. However, till date, few works about glass sealants for sodium sulfur battery have been reported except some patents [9–12]. However, the data in these patents are not systematically and completely opened. Therefore, the present work about glass sealants for sodium sulfur battery is significant and worthwhile.

In our previous paper, a Bi-doped borosilicate glass as sealant for sodium sulfur battery has been developed by doping of Bi_2O_3 to borosilicate glass. The effect of Bi_2O_3 on some thermophysical characteristics like thermal expansion coefficient, glass transition and softening temperature, viscosity and density of the glass was systematically studied [13]. It was found that the thermal expansion match between the Bi-doped glasses and alpha-alumina/beta-alumina is satisfactory. The objective of this work is to further study the joining properties involving hermeticity, wetting behavior, bonding strength, thermal shock resistance and corrosion resistance of the Bi-doped borosilicate glass.

2. Experimental

Details of the chemical composition and glass making were given in part 1 of the work published [13]. Table 1 also lists the glass composition. Beta-alumina sheet (Shanghai Institute of Ceramics, Chinese Academy of Sciences) and alpha-alumina sheet (96% of Al_2O_3, CeramTec, Germany) about 1 mm in thickness, respectively, were

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doi:10.1016/j.jnoncrysol.2011.04.014

Table 1
Composition of the Bi-doped borosilicate glasses.

Glass name	Composition (wt.%)						
	SiO_2	Al_2O_3	B_2O_3	Na_2O	K_2O	Li_2O	Bi_2O_3
GA2	50	3	18	3	3	1	22
GA3	40	3	18	3	3	1	32
GA4	30	3	18	3	3	1	42
GA5	20	3	18	3	3	1	52

used as the materials to be joined. The glass plate about 1 mm in thickness was placed between beta-alumina and alpha-alumina sheets and heated to the joining temperature at 3 °C/min and held for 7 min. Ceramic bars were fabricated, which had the function of accurately positioning and clamping the alumina to be joined.

After joining, cross-section of the joints was polished. Hermeticity of the joints was observed with scanning electron microscope (SEM, JSM-6700F, Japan).

The bulk glass was placed on beta-alumina and alpha-alumina sheets, respectively, and was heated to different temperature. The contact angle of glass on alumina as functions of temperature and Bi_2O_3 content was measured to examine the wetting behavior of the glass to the parts to be joined.

The bonding strength of the joints was evaluated on a tensile-testing machine (Instron, 5566, America) at a constant strain ratio of 0.5 mm/min. To make the test feasible, besides clamping the alumina using ceramic bars when joining, each side of the joint was adhesively bonded with a bolt (Fig. 1), and the bolt was perpendicular to the alumina sheet. The bonding strength of each joint was derived from the rupture force and corresponding outline spreading area of the glass.

To test the thermal shock resistance of the joints, the joined parts were put into a furnace at 350 °C and held for 30 min, then taken out of the furnace and cooled down to room temperature quickly. The heating and cooling cycles were repeated for 200 times. After thermal shock, the cross-section of the joints was polished and examined with SEM.

For the investigation of the corrosion resistance, the polished joints were immersed in sulfur and vacuumized inside a glass tube. The sealed glass tube was kept at 350 °C for 100 h. The sulfur on the surface of the joints was wiped by CCl_4. The cleaned joints were examined by SEM and energy dispersive spectroscopy (EDS).

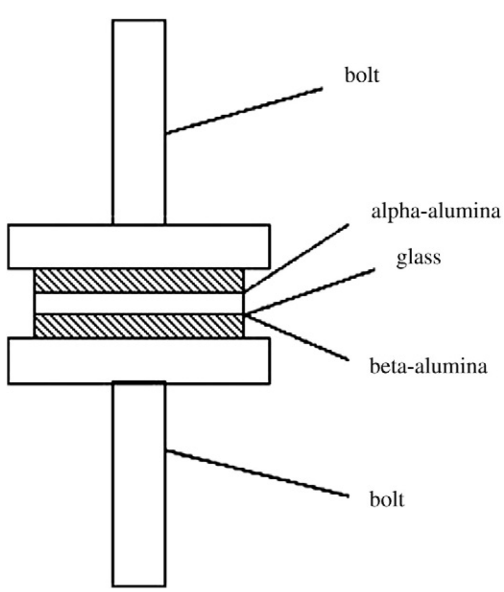

Fig. 1. Schematic illustration of the design for tensile testing sample.

3. Results

3.1. Hermeticity analysis

Fig. 2 shows the SEM cross-section morphologies of the beta-alumina/glass GA3/alpha-alumina interfaces heated at 800 °C for 7 min. As seen in Fig. 2 (a), the joint was pore free and indicated perfect hermeticity. As seen in Fig. 2 (b) and (c), the beta-alumina/glass GA3/alpha-alumina interfaces were joined well. No microcracks and reaction products appeared, indicating the satisfactory thermal expansion match and chemical compatibility between glasses and alpha-, beta-alumina. Other investigated glasses were similar to glass GA3 (not shown).

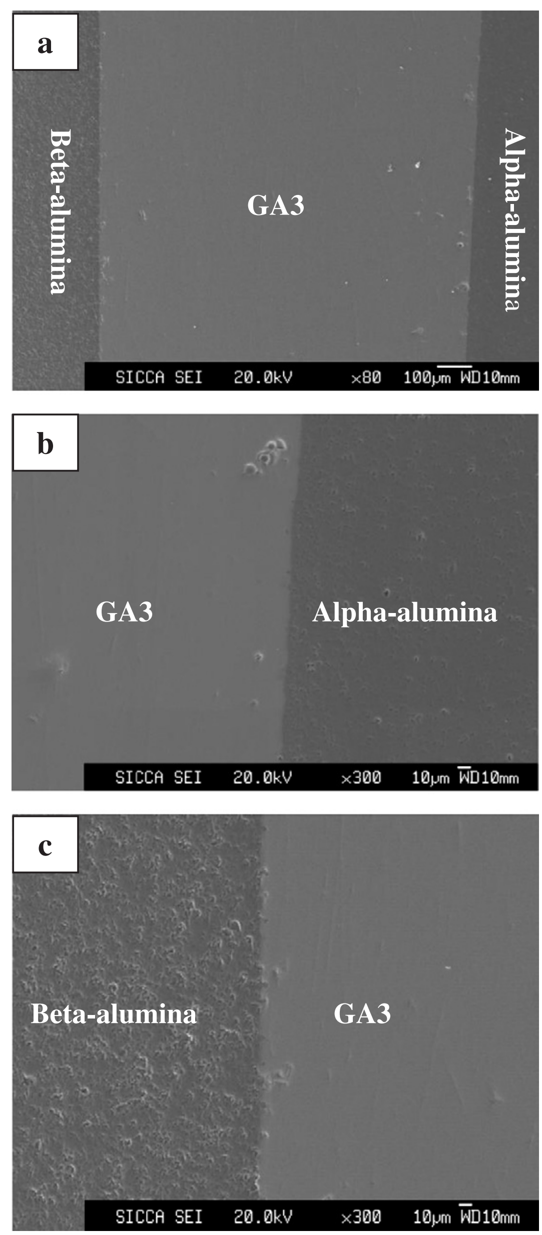

Fig. 2. SEM cross-sectional morphology of beta-alumina/glass GA3/alpha-alumina interfaces heat-treated at 800 °C for 7 min.