Advanced Ceramics Progress

Synthesis and Characterization of Barium Aluminosilicate Glass as the Sealant for Solid Oxide Fuel Cell Application

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ABSTRACT

In this study, barium aluminosilicate glass sealant was synthesizedand characterized for Solid Oxide Fuel Cell (SOFC) applications. First, the stoichiometric amounts of powder were mixed and melted at 1330℃ for 2h, followed by quenching in water. They were then pressed into cylindrical specimens under load of 200 MPa, followed by sintering at different temperatures. The phase content and microstructure of the samples were analyzed by X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM) methods, respectively. Microhardness and toughness of the sintered samples were investigated by means of Vickers micro-hardness test. Young's modulus and nano-hardness of the glass sealant were measured by nano-indentation method. The thermal expansion coefficient of the specimens was estimated by a dilatometer. The results showed that after sintering at 750℃, sealants with homogeneous microstructure and high density were obtained. The sealants were characterized by mechanical and thermal properties appropriate for SOFC applications with a very low leak rate.

1. INTRODUCTION

High-temperature sealants are among the most important components of the planar Solid Oxide Fuel Cells (p-SOFCs) [1]. The p-SOFS are composed of at least three thin layers including cathode, electrolyte, and anode. The fuel is fed into the anode side while the cathode is in contact with the oxidant gas (oxygen) [1]. Different fuels, with their own advantages and disadvantages, are used in SOFCs, among which pure hydrogen, ethanol, methane, etc. can be considered [2]. Usually, in a commercial SOFC, 8mol% Yttria Stabilized Zirconia (8YSZ), Ni/YSZ, and Lanthanum Strontium Manganite (LSM) are used for electrolyte, anode, and cathode, respectively [2]. The fuels and oxidant in a p-SOFC must be kept separate since mixing these gasses deteriorates cell performance. Indeed, sealants that prevent the intermixing of fuel and oxidant plays a crucial role in the development of SOFCs with high output power [3]. The sealants in the SOFCs must be kept stable during the service life and be compatible with other cell components. Therefore, the sealing materials must be thermodynamically, chemically, and mechanically stable in harsh working conditions of SOFC, including reducing and oxidizing conditions, at high temperatures (T~800°C) [4].

The sealants should be compatible with other components and remain chemically inert during their service life. In addition, any mismatch in the thermal expansion coefficients (α) of sealants and other components creates thermal stress in the cell structure, resulting in premature degradation of the SOFC [4].

There are a number of different sealing materials developed for the SOFCs which are categorized into three types including compressive sealants, compliant sealants, and rigidly bonded sealants [5]. The compressive sealants which are based on materials with layered structure, such as mica, can mitigate the mismatch of "α" among different components through the slippage of the structural layers [6]. This kind of sealant behaves like a gasket and does not provide enough sealing performance unless an external pressure is applied on the sealant which complicates the SOFC cell design [7]. The compliant and rigid sealants are mainly based on glass and glass ceramics which soften at high temperatures and provide hermetic joints [8-11]. The glass-based rigid sealants that are rigid materials at low temperatures and are transformed into highly viscous glass at higher temperatures glue the components together through chemical bonding. These kinds of sealants are vulnerable to cracking due to their brittleness and thermal stresses rising during the

heating/cooling cycles in the SOFCs. However, the magnitude of "α" of these sealants can be adjusted by controlling the composition. Various rigid glass sealants were developed for SOFC sealing including alkali silicates, alkaline earth silicates, borosilicates, aluminoborosilicate, etc. [8].

Barium/Calcium Aluminosilicate (BCAS) glasses which are originally developed by Pacific Northwest National Laboratory Institute are among the most significant sealing material used for high-temperature SOFCs and have been the subject of numerous studies [11–14]. It has been reported that adding oxides such as La_2O_3, Nd_2O_3, TiO_2, ZnO, and Y_2O_3 affects different properties of BCAS glass materials [15]. Yang et al. studied the chemical stability of BCAS glass sealant under fuel cell working conditions [16]. Milhans et al. investigated the creep properties of BCAS glass at high temperatures [11]. Batfalsky et al. reported the chemical interaction between BCAS sealants and SOFC interconnect [17].

BCAS glass ceramics are used to join and seal different metallic and non-metallic materials [14,18]. These glass materials are electrically insulating and create gas-tight joints [19]. In this type of glasses, BaO and SiO_2 are network formers, CaO is network modifier, and Al_2O_3 is an intermediate oxide which can be either network former or modifier. The glass composition directly affects the thermal properties of the BCAS glass [18,20].

According to recent reports, adding second phases such as alumina [21], SiC fiber [22], and zirconia particles [19] improved the mechanical properties of BCAS glass ceramics. However, there is not enough comprehensive report on different properties of BCAS glass sealants.

This study aims to synthesize and characterize the BCAS glass for SOFC applications. First, the glass powder is synthesized by solid oxide mixing followed by melt quenching process. An organic vehicle with a basic function of mixing terpineol with ethyl cellulose is developed to render the required flowability to the sealant. Young's modulus, hardness, compressive strength, and toughness of the sintered samples are also investigated. The Coefficient of Thermal Expansion (CTE) and leak rate are also measured at high temperatures.

2. EXPERIMENTAL PROCEDURE

The BCAS glass was synthesized by solid mixing followed by melt quenching method. All powders with more than 99.9 wt% purity were purchased from Merck Company. First, powders were washed in acetone and dried overnight. The composition of the glass is presented in Table 1. The weighted amounts of the powders were mixed with acetone and sonicated for 15 min followed by magnetic stirring until the solvent evaporates. The mixed powders were pressed into cylindrical pellets under load of 200 MPa in order to reduce their volume occupied by the raw materials during melting process.

TABLE 1. The composition of the constituents of the glass powder

Component	B_2O_3	SiO_2	CaO	BaO	Al_2O_3
Amount (wt%)	7.3	22.1	8.8	56.4	5.4

The pellets were then heated to 1330°C with a heating rate of 10 K/min and held at that temperature for 30 min in a platinum crucible.

The melted material was then quenched in water in a stainless steel cylinder and the prepared powders were crushed using planetary ball mill for 2h at 300 rpm. In order to prepare the sample for further analysis, the prepared glass powder was mixed with 5 wt% Polyvinyl Alcohol (PVA). The prepared mixture was formed into a disk with a diameter of 10 mm and height of 5 mm by uniaxial pressing under pressure of 200 MPa. The specimens were sintered at different temperatures from 600°C to 800°C for 2h. The heating rate in all sintering processes was 20K/min.

The density of the sintered samples was measured using Archimedes method (Precisa,Switzerland) with accuracy of ±0.1 g/cm^3.

The phase content of the samples was studied by X-Ray Diffraction method (XRD, PW1730, Philips, Netherland) using CuK_α radiation. The microstructure of the sintered samples was investigated by SEM (Mira3, TESCAN, Czech Republic).

The Vickers micro-hardness of the sintered glass was measured under load of 50g applied on the polished surfaces. The toughness of the samples was measured using the Anstis formula [23] by means of the Vickers micro-hardness test under different applied loads. Young's modulus and nano-hardness of the prepared sealants were evaluated by the nanoindentation method (NHT3-Anton paar, Austria). The compressive strength of the sintered specimens was measured by the uniaxial testing machine with a loading rate of 0.15 MPa/s on the samples with diameter and height of 10 mm.

The thermal expansion coefficient of the sample was measured by dilatometer (DIL 402, Netch, Germany) with a heating rate of 10 K/min.

The sealing performance was studied by homemade setup, as depicted in Fig.1.

To prepare flowable sealant paste, the glass powder was mixed with different amounts of the ethyl cellulose/terpineol with different proportions, and the resulting mixture ball was milled for 2h using zirconia grinding media. A button single cell SOFC was placed at the end of the alumina tube and the paste was applied around the sample. The sealed sample was placed inside

a programmable furnace, heated to 250°C to dry the paste, and kept at that temperature for 1 h. Argon gas was used inthe leak test at pressure of 0.3 KPa and the pressure drops were recorded at different times by a pressure gauge at a temperature of 750°C.
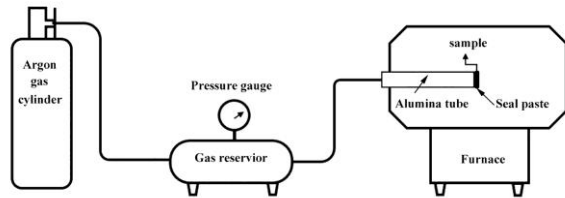

Figure 1. The schematic picture of leak rate test setup

3. RESULTS AND DISCUSSION

The result of the XRD analysis of the prepared glass powders is presented in Fig.2. As observed, the glass was fully amorphous and no crystallization occurred during the sample preparation.
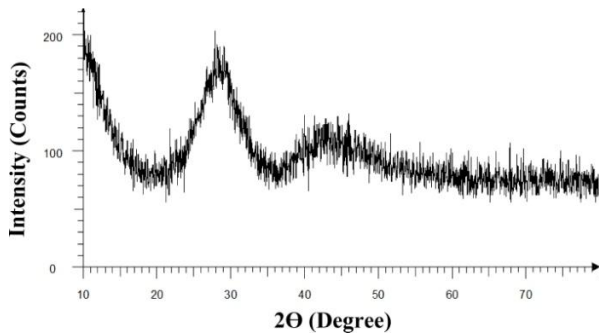

Figure 2. XRD pattern of prepared glass powder

The density variations of the samples as a function of the sintering temperature arepresented in Fig. 3. Given that the theoretical density of the pure glass is $3.93\,g/cm^3$, it is observed that the relative density (measured density/theoretical density) of the sample sintered at 750°C is around 98% and does not increase at higher temperatures. Therefore, it can be concluded that the sintering temperature of the BCAS glass is ~750°C. The properties of the specimens sintered at 750°C are presented in the following.
The SEM image of the sintered sample at 750°C is presented in Fig.4 and it confirms the homogeneity of the microstructure with high density.
The mechanical properties of the sintered pellets are presented in Table 2. The hardness of the sintered glass is consistent with previously reported data on other similar glasses [20].
Nano-hardness was calculated by Eq. 1 [24]:
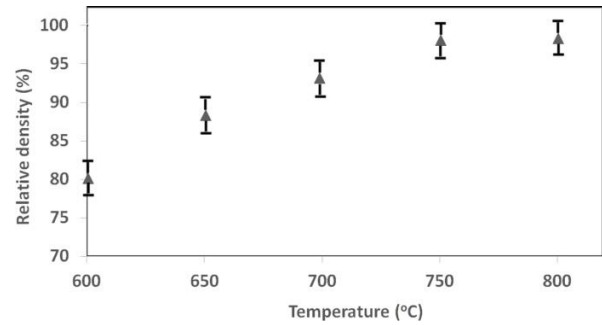
$$H_c = \frac{P_{max}}{A(h_c)} \tag{1}$$

Figure 3. The density variationsof the sample as a function of temperature

where P_{max} is the peak load and A(hc) is the projected area of the Berkovich tip. The value of A(hc) for non-ideal Berkovich indenter is determined through Eq. 2 [24]:

$$A(h_c) = h_{max} - 0.75\frac{P_{max}}{S} \tag{2}$$

Where h_{max} is the maximum penetration depth and S is the contact stiffness which is the slope of the upper portion of the unloading curve.Young's modulus was calculated using Eq. 3 [20]

$$\frac{1}{E_r} = \frac{1-\upsilon^2}{E} + \frac{1-\upsilon_i^2}{E_i} \tag{3}$$

where E_r is the reduced elastic modulus, considering the fact that elastic displacement occurs in both the specimen and indenter. Here, E and υ represent the elastic modulus and Poisson's ratio of the sample, respectively. The elastic constants of the diamond indenter were assumed to be $E_i = 1140\,GPa$ and $\upsilon_i = 0.07$.
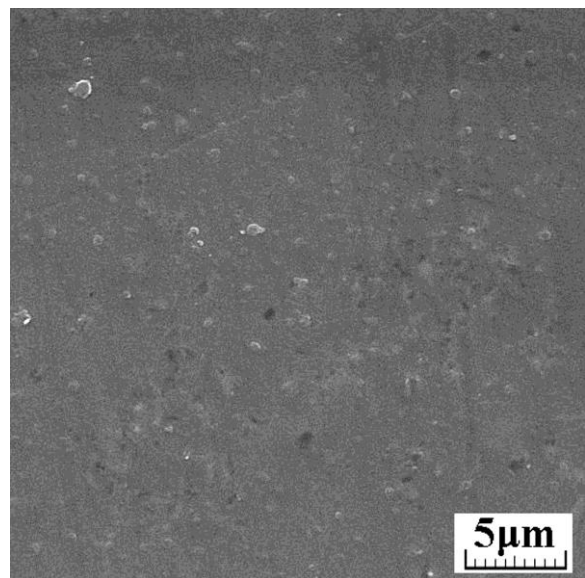

Figure 4. The SEM image of the sintered glass

TABLE 2. The mechanical properties of the sintered sample

Sample	Micro-Hardness (GPa)	Nano-Hardness	Young's modulus (GPa)	Toughness (MPa.m$^{1/2}$)	Compression strength (MPa)
BCAS	6.1 ± 0.1	6.4 ± 0.5	72.74 ± 8.1	0.15 ± 0.2	191.26 ± 23.5

The nanoindentation load-displacement curve is presented in Fig.5. No pop-in behavior is observed in the loading/unloading curve; therefore, it can be concluded that the microstructure is homogeneous with high density. The presence of porosity and/or any microstructural inhomogeneity results in discontinuity in the load-displacement curve in nano-indentation test [21]. Young's modulus is a significant parameter in managing thermal stress of the solid oxide fuel cell seal materials. Young's modulus of different parts of SOFC must be consistent to prevent the rise of thermal stress. In addition, the toughness of the ceramic materials is proportional to the magnitude of Young's modulus. The reported Young's modulus in this study is comparable with the previously reported data[14]. The magnitudes of nano-hardness and microhardness in Table 2 are in complete agreement, thus confirming the homogeneity of the microstructure.

The measured compression strength is 191.2 MPa which is in the common range of the reported values for pure sintered glass seal materials [25]. The glass ceramic sealants in SOFCs are usually under compressive applied pressure of 0.16 MPa. Indeed, the sealants manufactured in this study attained the required level of compressive strength [21].
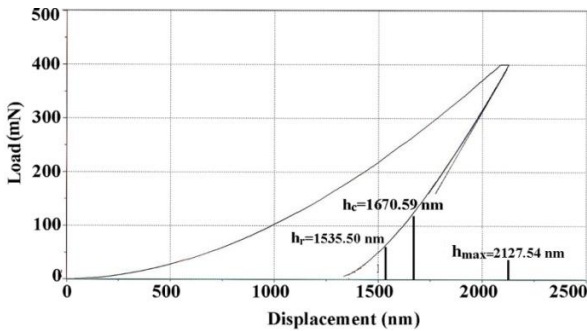

Figure 5. The nanoindentation load-displacement curve for the pure sintered glass

Fig.6 presents the result of dilatometry analysis; in addition, the estimated value of the average thermal expansion coefficient is $12.2 \times 10^{-6} K^{-1}$ which is comparable to the ones reported for other components of the commercial SOFCs. The crystallization temperature (T_g) and softening temperature (T_s) of the sealant are 630°C and 680°C respectively. The softening temperature is a crucial factor regarding the performance of the sealants because at temperatures higher than T_s, the glass softens and flows among the components and makes hermetic joint. The working temperature of the SOFCs must be higher than the softening point of the sealant.
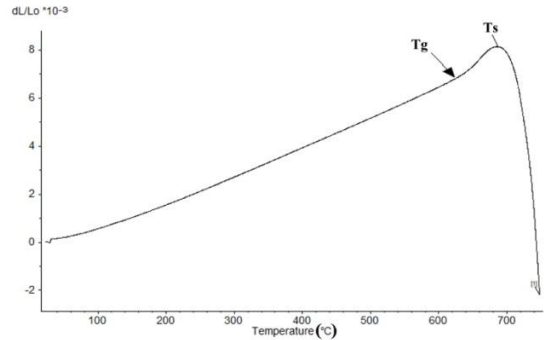

Figure 6. The result of dilatometry analysis of the sintered glass

The result of leak test is presented in Fig. 7 in which the leak rate (LR) was calculated as follows [6]:

$$LR = \frac{(P_f - P_i)V}{RT(t_f - t_i)} \qquad (4)$$

where "P" represents pressure, "R" the gas constant, V the reservoir volume, "T" the temperature, and "t" the time.
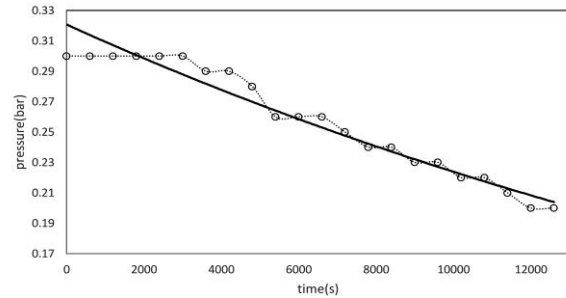

Figure 7. The result of leak test

The proper composition of the sealant paste was 90 wt% glass powder mixed with 10 wt% organic vehicles. The terpineol-to-ethyl cellulose ratio in the organic vehicle was 3 to 1 wt%. These proper compositions were obtained through trial and error, using the leak test as an acceptable condition for the proper performance. The leak rate of the sealant with proper composition at 750°C was 1.408×10^{-4} $sccm/cm$, which was quite low and acceptable for SOFC applications. The prolonged performance of the synthesized sealant under fuel cell working conditions requires more investigations.

4. CONCLUSION

The BCAS glass sealant was successfully synthesized through the melt quenching method. The sintering process at a temperature of 750°C conferred a relative density of 98% to the glass. The micro-hardness and compressive strength of the sealant were 6.1 GPa and 191.2 MPa, respectively. The Young's modulus and nano-hardness measured by nano-indentation test method were 6.4 GPa and 72.7 GPa, respectively. The sealant had a thermal expansion coefficient of $12.2 \times 10^{-6} \mathrm{K}^{-1}$, and the magnitude of T_s was estimated at 680°C. The measured leak rate was 1.408×10^{-4} sccm/cm at 750°C, which is acceptable for SOFC.

5. ACKNOWLEDGMENT

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