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Short communication

Electrical behavior of aluminosilicate glass-ceramic sealants and their interaction with metallic solid oxide fuel cell interconnects

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ABSTRACT

A series of alkaline-earth aluminosilicate glass-ceramics (GCs) were appraised with respect to their suitability as sealants for solid oxide fuel cells (SOFCs). The parent composition with general formula $Ca_{0.9}MgAl_{0.1}La_{0.1}Si_{1.9}O_6$ was modified with Cr_2O_3 and BaO. The addition of BaO led to a substantial decrease in the total electrical conductivity of the GCs, thus improving their insulating properties. BaO-containing GCs exhibited higher coefficient of thermal expansion (CTE) in comparison to BaO-free GCs. An extensive segregation of oxides of Ti and Mn, components of the Crofer22 APU interconnect alloy, along with negligible formation of $BaCrO_4$ was observed at the interface between GC/interconnects diffusion couples. Thermal shock resistance and gas-tightness of GC sealants in contact with yttria-stabilized zirconia electrolyte (8YSZ) was evaluated in air and water. Good matching of CTE and strong, but not reactive, adhesion to the solid electrolyte and interconnect, in conjunction with a high level of electrical resistivity, are all advantageous for potential SOFC applications.

1. Introduction

The most arduous task in the commercialization of planar SOFC is the hermetic sealing provided to its ceramic and metallic components such that the resulting joints remain rugged and stable over the lifetime of the stack. The seals must have CTE similar to those of other cell components $(9–12) \times 10^{-6}\,K^{-1}$; be stable in a wide range of oxygen partial pressure (air and fuel) and be chemically compatible with other fuel cell (FC) components, while minimizing thermal stresses during high-temperature operation which creates a major challenge in the development of planar SOFCs. Substantial work is in progress in this area, aimed at improving the performance of sealants under extreme operating conditions of current fuel cell designs, which involve both high temperatures and highly corrosive environments. Also, a compliant sealant is expected to behave as an electrical insulator, with total conductivity lower than $10^{-4}\,S\,cm^{-1}$, in order to avoid parasitic currents decreasing the system's efficiency [1,2]. Among the various concepts of sealing proposed so far [2,3], GCs have emerged to be the most promising candidates [4]. However, most of the GC based sealants proposed so far have some advantages which are coupled along with some drawbacks. Therefore, still there is a need to fill in this lacuna by developing a suitable sealing material for SOFC technology.

Recently, La_2O_3-containing alkaline-earth aluminosilicate diopside based GC sealants with very low amounts of BaO and B_2O_3 have been proposed [5,6]. However, some adverse reactions were observed at the interface between GC sealant and metallic interconnect leading to the formation of barium–chromium rich oxides. Also, still there is need to increase and stabilize the CTE of the diopside based GC sealants during long term heat treatment and to improve the flow behavior of the resultant GCs in order to qualify those for the applications in SOFC stack. Thus, in the light of above mentioned perspective, the present study is an attempt to design new GC sealants in order to tailor their CTE and reduce adverse chemical reactivity with metallic interconnect without compromising with their electrical and joining properties, so as to fulfill the criteria of a compliant sealing material required for SOFCs.

A new series of alkaline-earth aluminosilicate glasses were prepared by modifying the parent composition with general formula $Ca_{0.9}MgAl_{0.1}La_{0.1}Si_{1.9}O_6$. Table 1 lists the glass compositions. The first glass (labeled as 10) was derived by adding 2 wt.% B_2O_3 to the glass composition $Ca_{0.9}MgAl_{0.1}La_{0.1}Si_{1.9}O_6$. The second glass (10A) was followed by addition of 0.5 wt.% Cr_2O_3 to composition 10. It is well documented that addition of Cr_2O_3 decreases the crystallization temperature [6] and reduces surface tension [7] of the glasses. Also, the presence of Cr_2O_3 in the glasses may help in suppressing the diffusion of Cr from metallic interconnects into the bulk of GC sealant, thus, preventing massive formation of $BaCrO_4$ and other barium–chromium oxide compounds having detrimental impact in air. The remaining three glasses, i.e. 10B, 10C and 10D were derived

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Table 1
Batch compositions of the glasses (wt.%).

Glass	MgO	CaO	BaO	SiO_2	Al_2O_3	La_2O_3	B_2O_3	Cr_2O_3	NiO
10	17.27	21.63	–	48.93	2.18	6.98	2	–	1
10A	17.19	21.52	–	48.67	2.17	6.95	2	0.5	1
10B	16.48	18.34	6.27	46.67	2.08	6.66	2	0.5	1
10C	16.14	16.85	9.21	45.73	2.04	6.53	2	0.5	1
10D	15.83	15.41	12.04	44.82	2.00	6.40	2	0.5	1
7-2B [5]	16.56	18.44	6.30	46.91	2.09	6.70	2	–	1

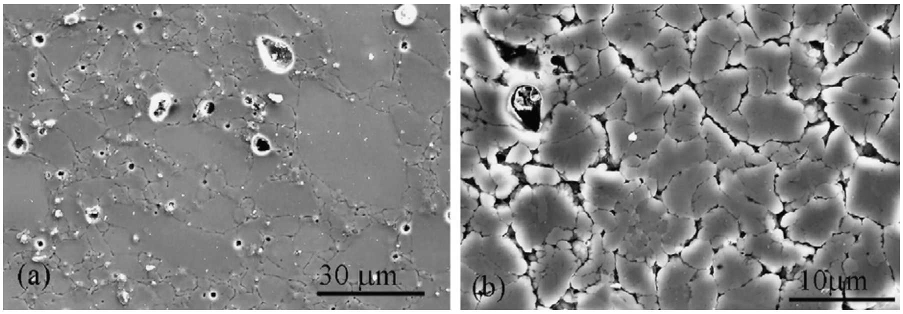

Fig. 1. SEM image of glass-powder compacts from composition (a) 10B heat treated at 800 °C and (b) 10C heat treated at 850 °C for 1 h.

by partial substitution of CaO by BaO in the glass composition 10A. The composition for glass 7-2B is listed in Table 1 for comparison purposes [5]. It is noteworthy that the amount of BaO and B_2O_3 in the investigated glasses is significantly lower in comparison to other sealants proposed in literature [2]. Therefore; negligible seal degradation can be expected.

2. Experimental

All the investigated glasses were prepared in bulk and frit form by melt-quenching technique. A detailed description of the experimental section pertaining to preparation of glasses and GCs has been described in our previous studies [6]. The glass-powder compacts were sintered under non-isothermal conditions for 1 h at 800 °C and 850 °C. A slow heating rate of $2\,K\,min^{-1}$ was maintained in order to prevent deformation of the samples. Further, rectangular bars already sintered at 850 °C, were heat treated under isothermal conditions at 800 °C for 300 h. The amorphous nature of the glasses and crystalline phase evolution in GCs was followed by X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis while dilatometer was employed in order to measure the CTE of the GCs, as depicted in Ref. [5]. The measurement of total conductivity of GCs by AC impedance spectroscopy is detailed in Ref. [5]. The ion transference numbers were assessed by the modified electromotive-force (e.m.f.) technique, as described in Ref. [8].

The experimental description for investigating adhesion and chemical interaction of GCs with 8 mol.% yttria-stabilized zirconia (8YSZ, Tosoh, Japan) and Crofer22 APU (Thyssen Krupp, VDM, Werdohl, Germany) after 300 h of heat treatment at SOFC operating temperature along with thermal shock resistance of GC sealants when in contact with 8YSZ has been described in our previous study [5]. In order to evaluate thermal shock resistance of the GC sealants in contact with stabilized zirconia electrolyte, a series of model cells were made by sealing dense 8YSZ tubes onto 8YSZ disks. Hermetic sealing was performed using powdered GCs, with final annealing at 1275 °C for 0.5 h. Then each pseudo-cell was heated in the furnace up to 800 °C, kept at this temperature for 0.5 h, and quenched in air or in water. After subsequent checking of the gas-tightness, each cell was rapidly heated again, and the quenching cycle was repeated. The 8YSZ pseudo-cells were successfully tested in 15 air-quenching cycles.

3. Results and discussion

For all the investigated compositions (Table 1), melting at 1550 °C for 1 h was adequate to obtain bubble-free, amorphous transparent glasses. The structural, physical and thermal properties of the parent glasses are out of the scope of this paper and will be published in forthcoming article.

The heat treatment of glass-powder compacts at 800 °C for 1 h resulted in well-sintered but amorphous bodies as was confirmed by XRD and SEM studies (Fig. 1a). Augite ($Ca(Mg_{0.85}Al_{0.15})((Si_{1.70}Al_{0.30})O_6$; ICDD card: 01-078-1391) crystallized in all the GCs after heat treatment at 850 °C (Fig. 1b and 2a). The CTE (200–600 °C) values of the GCs sintered at 850 °C for 1 h are presented in Table 2. Since, the amorphous phase in the GCs plays a crucial role in deciding the reaction kinetics between GC sealant and SOFC components; therefore, it is essential to quantify the amount of crystalline and amorphous phase in the GC sealants. This point shall be focused upon it in our further publication. The CTE values decreased with addition of Cr_2O_3 while increased with an increase in BaO content in the glasses until composition 10C. However, with further replacement of CaO by BaO in composition 10D, the CTE decreased considerably. The highest CTE value for the GCs was observed for composition 10C ($9.5 \times 10^{-6}\,K^{-1}$) while the lowest was observed for composition 10D ($8.8 \times 10^{-6}\,K^{-1}$).

The crystalline phase evolution after prolonged heat treatment of GCs (already sintered at 850 °C for 1 h) at 800 °C for 300 h is presented in Fig. 2b. Augite crystallized as the only phase in GC 10 and 10A while hexacelsian (HC; $BaAl_2Si_2O_8$; ICDD: 01-088-1048) appeared as secondary phase along with augite in GC 10B and 10C. The intensity of XRD peaks was lower for all the investigated GCs after 300 h of heat treatment in comparison to GC sintered at 850 °C for 1 h. After heat treatment of 300 h, the

Table 2
CTE × $10^6\,K^{-1}$ (200–600 °C) of the GCs produced at different conditions.

Composition	850 °C, 1 h	800 °C, 300 h
10	9.2	8.8
10A	9.1	9.0
10B	9.4	9.2
10C	9.5	9.2
10D	8.8	9.0