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The glass-ceramic sealant materials obtained from basalt for SOFC

Ediz Ercenk, A. Elif Cicekli and Senol Yilmaz*

Sakarya University, Engineering Faculty, Department of Metallurgical and Materials Engineering, Esentepe Campus, 54187 Sakarya, Turkey

In the current study, utilization possibilities of the basalt based glass-ceramic as a sealant material for solid oxide fuel cell (SOFC) were investigated. Crushed, milled and sieved basalt powders were modified by some additives. The basalt powder and modified mixture were separately melted in alumina crucible and cast into water to obtain glass granules. These granules were milled, and exposed to heating microscopy and differential thermal analysis (DTA). Some parameters such as glass transition and softening temperature were determined by these analyses. The powders were applied on the Crofer 22 APU interconnector material, and heat treatment was carried out. The interface characteristics between the glass-ceramic layer and interconnector were characterized using X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM). The results showed that the basalt base glass-ceramic sealant material exhibited promising properties to use for SOFC.

Key words: Basalt, Glass-ceramic, SOFC, Sealant material.

Introduction

Solid oxide fuel cells (SOFCs), which are electrochemical devices having green technology, produce electricity with a reaction of a fuel and air [1]. Utilization of conventional fuels such as coal can play an important role on air pollution and global warming for future, and SOFC has less harmful emission compared with conventional fuel combustion [2]. Because of this, utilization and spreading of SOFC are significant step to provide clean environment. There are a lot of studies about improvement of SOFC in the literature [3-4]. But, there are some problems about utilization of SOFC as a commercial energy source; one of these is sealant problem of SOFC systems. SOFC component interconnect materials, which connect to other cells for multiple cells, generally are produced from stainless steel. It provides electrical connection between anodes of one individual cell to cathode of another one, multiple SOFC are combined into high-performance cell stacks for power generation on a large scale. A sealant material should have some thermal, mechanical properties to resist against harsh environmental effects and high operating temperatures of SOFC. In recent years, glass-ceramic systems have been investigated to provide required sealing performance for these [5]. Thermal compatibility between glass-ceramic sealant and interconnector is very important parameter; some phases forming in interface at high temperature can cause thermal mismatch effect. Especially, glass-ceramic systems including BaO and SrO oxides seem to be suitable in term of thermal expansion, but $BaCrO_4$ and $SrCrO_4$ phases forming with Cr in stainless steel interconnector cause thermal mismatch [6]. Because of this reason, CaO-Al_2O_3-SiO_2 (CAS) type glass-ceramic systems not including Ba and Sr elements become popular in the literature [7-10].

Basalt, which is dark-coloured, fine-grained rock, is the most common type of extrusive igneous natural rock at the Earth's surface. Basalts have volcanic origin and are formed by the rapid cooling and hardening of lava flows [11]. In generally, crushed and milled basalts are used as fillers and additives for structural materials in construction industry. Furthermore, basalt base glass-ceramics are preferred as pipe systems in terms of their high wear resistance. Basalt can be vitrified by means of melting and sudden cooling, and then glass-ceramic materials can be produced from these glasses. The major oxides making up basalt are SiO_2 and Al_2O_3; other important oxides in basalt composition are CaO, MgO and Fe_2O_3 or FeO. In terms of composition, basalt tends to form CAS type glass-ceramic thanks to high CaO (8-10%), Al_2O_3 (15-20%) and SiO_2 (45-52%).

In the current study, the information about utilization and production for basalt base glass-ceramic as a sealant material in SOFC was reported. The aim of the study is that using possibility of basalt as sealant material for SOFC is investigated. The study was performed with two compositions, (i) the basalt rock obtained from Konya region, Turkey (KB), and (ii) basalt modified with SiO_2, Na_2O, CaO, MgO and B_2O_3 additions. Preliminary works of the study showed that only basalt was not sufficient due to thermal properties

*Corresponding author:
Tel : +90-264-295-57-68
E-mail: symaz@sakarya.edu.tr

such as high softening temperature. It means poor wettability at heat treatment temperatures. Because of this, basalt was modified with alkaline oxides and boron oxide, thus, thermal behaviours such as softening and sphere temperatures decreased compared with basalt not including additives. The other purpose of the study was whether or not chromate phase formation at the interface between interconnector (Crofer 22 APU) and basalt/modified basalt base glass-ceramic layers was examined.

Experimental Procedure

The natural basalt volcanic rocks were obtained from central Anatolia region called Konya. The basalts were crushed and milled by ring mill. The modified mixture was prepared using SiO_2, Na_2O, CaO, MgO and B_2O_3 addition; the chemical composition of basalt (KB) and the calculated composition of modified basalt (MB) were given in Table 1. The basalts and additives were mixed in an alumina ball mill for 2 hrs in dry condition at a 200-rpm rotational speed. The powder mixture was melted at 1450 ºC for 2 hrs in an electrical heating furnace; the melted composition was poured into water to obtain glass granules. These glass granules were milled by ring, ball and jet mills, respectively. The aim of using jet mill was to obtain particles as possible as fine. The glass powders were subjected to sieving process, the particle size of glass was produced less than 25 μm. Shrinkage behaviours of the glass powders were characterized by using cylindrical pellets which were pressed in a one axial press at 100 MPa load for 1 min. The pellets were heated in an electrical heating furnace at different temperature (650 ºC-900 ºC) for 2 h to determine the shrinkage behaviour given in Table 2. To provide good bonding between the interconnect material Crofer APU 22 and the glass powder, the interconnector material was subjected to Al_2O_3 sand blasting for 30 sec. The Crofer 22 APU substrate was pre-oxidized at 900 ºC for 2 hrs in the furnace, oxidised surfaces has a better bonding performance according to the literature [12]. The paste was made with acetone, and then dipping technique was used for the coating procedure. After the coating process, heat treatment was carried out at 1000 ºC for glass-ceramic transformation and sintering, and wetting for the powder on stainless steel surface. Softening temperature for heat treatment is important for this type studies. If it is very high, stainless steel interconnector can damage. If it is very low, excessive softening or melting can occur at operating temperature of SOFC. Softening of glass is significant for good bonding and wetting on interconnector surface. Heating microscopy Misura HSM-ODHT was applied from room temperature to 1200 ºC for thermal characteristics such as softening, melting temperatures. The result of the modified glass-ceramic mixture showed

Table 1. The calculated chemical compositions and codes of the basalt and modified basalt glasses.

Oxides (wt.%)	SiO_2	B_2O_3	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5
Basalt (KB)	47.12	–	18.69	10.22	9.53	6.80	1.68	4.89	1.07
Modified Basalt (MB)	50.21	1.02	11.85	6.48	9.09	7.36	1.07	12.25	0.68

Table 2. Hot stage microscopy test results.

Codes	Sintering Temp. (ºC)	Softening Temp. (ºC)	Sphere Temp. (ºC)	Half Sphere Temp. (ºC)	Melting Temp. (ºC)
KB	852	1184	–	–	–
					
MB	740	956	1136	1160	1168
					

that its softening temperature is 956 °C. Because of this, 1000 °C as above softening temperature was selected for this process performed by using a Protherm electrical heating furnace. A JEOL 6060 scanning electron microscopy (SEM) system and X-ray diffraction (XRD) analysis using a Rigaku-type diffractometer with Cu-Kα radiation, which has a wavelength of 1.54056 A to analyse phases present in the coatings over a 2θ range of 10 °- 90°, were used to characterise the coated samples. Differential thermal analysis (DTA); TA instrument SDT Q-600 was used to detect the glass transition and crystallisation temperature of the coatings, it is noted that the heating rate in DTA was 10 °C min^{-1}.

Results and Discussion

The DTA results of the study can be seen in Fig. 1, it showed that both of glass transition (Tg) and crystallization (Tp) temperatures decrease due to the additives in MB composition. For KB composition, the glass transition and the crystallization temperatures were determined 760 °C and 860 °C, respectively, these temperatures were measured 710 °C and 806 °C for MB composition. The important parameter for glass-ceramic sealant materials of SOFC; glass transition temperature (Tg), it together with glass softening (Ts) are used for determining of flow properties of glass. In glass coating and covering applications, to reach suitable viscosity is necessary for good bonding and wettability. Average viscosity of glass is 10^{13} poise at Tg temperature, and it is $10^{7.65}$ poise at Ts temperature. For without any damage at interface at operating temperature, high Tg temperature and low Ts are needed. If Tg is low (550-650 °C), viscous flow more easily begins at operating temperature of SOFC. The glass softening temperature of KB was measured 1184 °C by HSM, and it was determined 956 °C for MB composition. Alkaline oxides such as Na_2O cause a decrease in Tg due to non-bridging oxygen formation in glass structure. The addition of Na_2O has been proved to weaken the network structure of the silicate glasses, thus promoting the precipitation of crystalline phases from the glass matrix at relatively low temperatures.

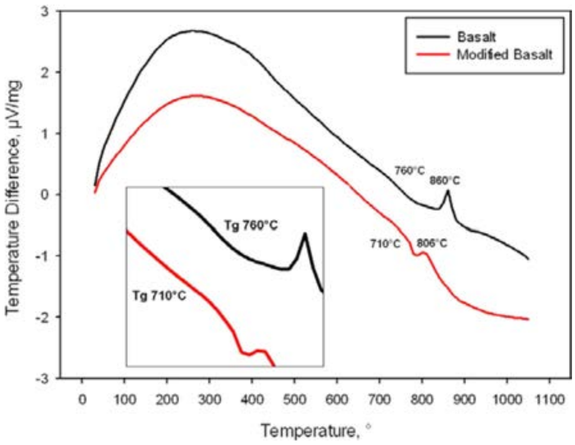

Fig. 1. DTA curves of the basalt and modified basalt.

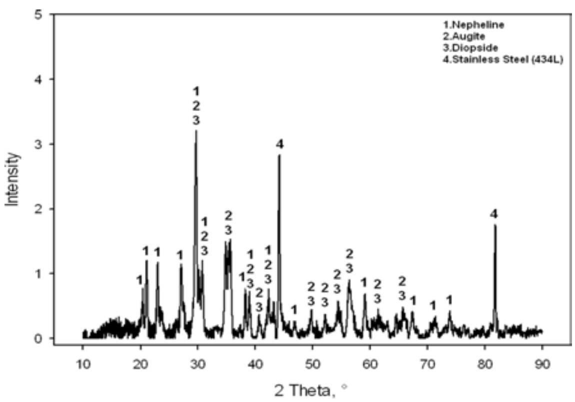

Fig. 2. XRD result of the modified basalt and Crofer 22 APU interface.

The XRD results obtained from the glass-ceramic and Crofer 22 APU interface were given in Fig. 2, Nepheline [$Na_{6.8}(Al_{6.3}Si_{9.7}O_{32})$], Augite [$Ca(Mg_{0.7}Al_{0.3})((Si_{1.7}Al_{0.3})O_6)$], Diopside [$Mg_{0.964}Fe_{0.036})(Ca_{0.94}Na_{0.06})(Si_2O_6)$], and stainless steel [Fe-Cr 434-L] phases were detected. Fe_3O_4 is first crystalline structure in glass obtained from basalts having high iron content during glass-ceramic transformation, other phases crystallize and growth on these crystals in the literature [13, 14]. In initial stage of magnetite nucleation at 600-650 °C, Fe^{3+} ions in glass structure remove and they consist of magnetite crystals. After 700 °C, magnetite structure is decomposed by other cations such as Ca^{2+}, Mg^{2+}, and then other crystalline phases such as augite and diopside occur [15]. An important problem about transforming to commercial products of SOFC is insufficient sealing between interconnectors after long thermal cycles. In concerning with this, glass-ceramic materials as sealant are preferred due to good wetting performance both solid electrolyte and interconnector, it can soften at high temperature and provide good sealing. Considering these issues, many different parameters such as thermal compatibility between glass-ceramic sealant and interconnector are significant. Another issue about sealing is phase formation at interface between glass-ceramic sealant and interconnector. In general, chromate phases causing thermal mismatch are reported in the literature, the glass-ceramic systems including BaO and SrO exhibit good performance in terms of thermal coefficients. When chromium in stainless steel interconnector diffuses at high temperature, the reaction between alkaline oxides BaO/SrO in glass-ceramic system and chromium (III) oxide causes chromate phase formation. In the current study, there was a risk about these type chromate phase formation because of earth alkaline elements; magnesium and calcium in the basalt content. The vital point of the XRD results is that any chromate phase causing thermal mismatch effect was not determined. Augite and diopside are characteristic phases for basalt base glass-ceramics [16, 17]. Mg and Ca oxides in the basalt, major amount of

Table 3. Variation of the volume shrinkage with temperature.

Glass code	Volume shrinkage (%)					
	650 ºC	700 ºC	750 ºC	800 ºC	850 ºC	900 ºC
KB	0.41 ± 0.08	1.23 ± 0.15	2.48 ± 0.17	5.24 ± 0.42	7.12 ± 0.46	8.47 ± 0.44
MB	0.55 ± 0.14	7.79 ± 0.68	27.9 ± 0.82	44.1 ± 1.22	60.84 ± 1.54	68.1 ± 1.96

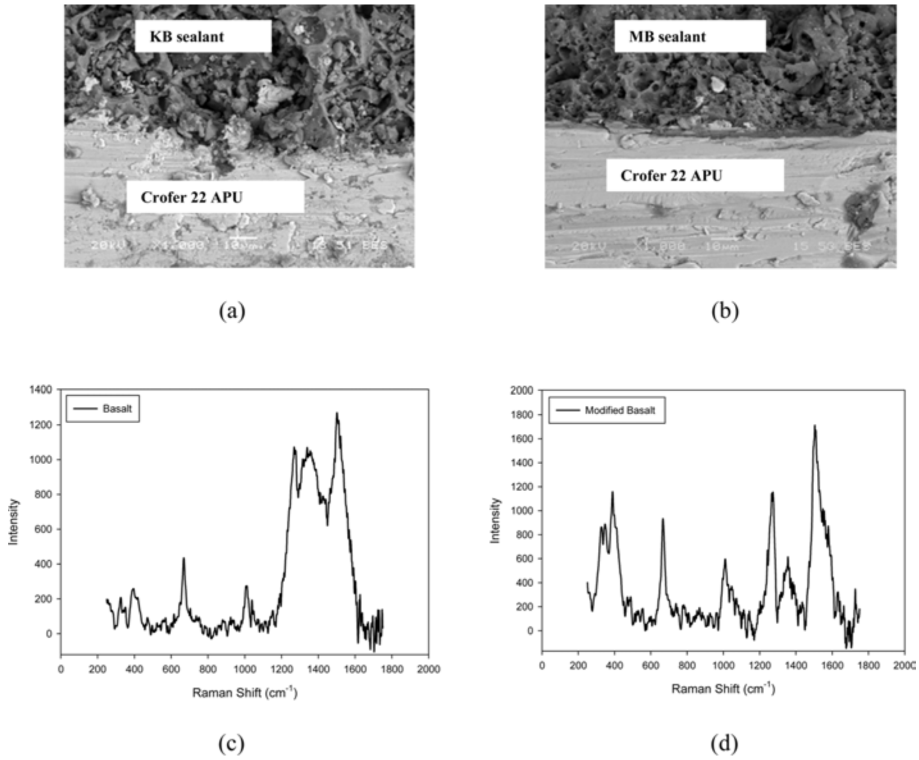

Fig. 3. SEM images and Raman spectra of the samples; (a) KB sample (b) MB sample (c) Raman spectra of KB sample (d) Raman spectra of MB sample.

these probably joined to Augite and Diopside crystals. In general, these phases effectively crystallize above 800 ºC [18, 19]. These crystals are common structures for CAS and CMAS glass-ceramic systems [20].

Sintering, softening, sphere, half sphere and melting temperatures for the modified basalt powder were determined and given in Table 2. These points could be determined for modified basalt powder, the other points except for sintering and softening temperatures could not be determined for basalt powder because the temperatures performed in HSM was realized up to 1200 ºC. The thermal characters of the basalt in terms of sphere, half sphere and melting point are high to provide good bonding and wetting for SOFC applications, the purpose of the study is to obtain lesser thermal points compared with that of KB. In accordance with this, HSM measurement for KB composition above 1200°C was not necessary for the study. Softening temperature is very important parameter for these type studies. For good bonding, wettability of glass layer on metallic surface is a significant requirement. Softening temperature for KB is 1184 ºC; and 956 ºC for MB. Decreasing in softening temperature means lower heat treatment temperature, thus, the risk about high temperature damage for stainless steel interconnector decreases. Viscosity of glass is an important parameter in terms of wettability between interconnector and glass-ceramic sealant at high temperature. Alkali oxides and alkaline earth oxides are added to silica glass to lower its viscosity so that it can be worked at points joining glass tetrahedron structure and break up the network [20, 21]. In the current study, Na_2O, CaO and MgO oxides as additives provide this effect. But, the softening temperature 956 ºC in MB composition is still high compared with operating temperature of SOFC.

The volume shrinkage results of the KB and MB glass sealants were shown in Table 3. Test was performed by using the glass powder compacts heated at 650 ºC- 900 ºC. It can be clearly seen from the results that the shrinkages of MB samples are higher than KB samples for all temperatures. Sintering temperature of MB composition is lower than KB sample, it is mentioned that sintering effects are stronger in MB at low temperature compared with KB. While sintering temperature of KB sample is

852°C, it is determined as 740 °C for MB composition. The strong shrinkage starts above 700 °C for MB, the values at 750 °C-900 °C are observed within the range of 27-68%. Na_2O and B_2O_3 additions provide decrease in softening temperature of basalt base glass and better sintering conditions were provided due to these additives at lower temperatures.

Fig. 3. shows the SEM analysis and their Raman spectra obtained from the interfaces. They showed the homogeneous microstructures over entire cross-sections of the joint. It can be observed that the interface is free of cracks and some pores were formed in the glass-ceramic zone. When the interface between interconnector and glass-ceramic layer was observed, any incompatibility and mismatch effect were not detected both KB and MB samples. In MB sample, more smooth and regular interface was detected compared with KB sample. It was possible that a small quantity of KB glass-ceramic particles plastered on interconnector surface during cutting of the sample. The basalt base seal material adheres well to the interconnector, which demonstrates its good sealing performance. Sharp cornered and angular particles can be observed in KB and MB samples; it is shown that exact vitrification and wetting can't be provided, sufficiently. HSM results show that sphere temperatures are above 1100°C for MB sample. Raman data of diopside phase determined by XRD are good agreement with modified basalt's Raman datas. Raman shift points 350 cm^{-1}, 580 cm^{-1} and 680 cm^{-1} have accordance with diopside phase's Raman data. On the other hand, there is no accordance about chromate phase's Raman data.

Conclusions

Basalt base glass-ceramic sealant material production for SOFC was investigated in this study. Basalt is natural and cheap raw material, in this case, utilization for application such as SOFC sealant material is significant step for developing of these tools. The basalt rocks were modified by some additives, and then these were coated on Crofer 22 APU surface. Coated basalt base glass layer was subjected to heat treatment and a glass-ceramic transformation was occurred. Nepheline [$Na_{6.8}(Al_{6.3}Si_{9.7}O_{32})$], Augite [$Ca(Mg_{0.7}Al_{0.3})((Si_{1.7}Al_{0.3})O_6)$], Diopside [$Mg_{0.964}Fe_{0.036})(Ca_{0.94}Na_{0.06})(Si_2O_6)$], and stainless steel [Fe-Cr 434-L] phases were detected by XRD analysis. Augite and diopside phases are characteristic structures for CAS glass-ceramic systems. Softening for glass is necessary for good bonding and wetting for this type sealant systems. Softening temperature of the basalt decreased from 1184 °C to 956 °C thanks to the additives. However, it is not enough for sufficient bonding and wetting, probably. In micro and macro structural analysis of the samples, any crack and mismatch effect were not observed at the interface between the glass-ceramic layer and interconnector material. Despite of these, better bonding can be necessary for thermal cycles of SOFC. An important problem about sealing of SOFC presented in the literature is that glass-ceramic systems include alkali oxides such as BaO and SrO are suitable in terms of thermal coefficient, but these element compose chromate structures combined with Cr element diffusing from stainless steel interconnector to interface. The basalt composition does not include Ba and Sr elements, but it has CaO and MgO. Potential chromate phases $MgCr_2O_4$ or $CaCr_2O_4$ were not detected by Raman spectra.

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