

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids



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

The effect of CaO/MgO content on properties of barium aluminosilicate sealants for solid oxide fuel cells

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ARTICLE INFO

Keywords: Adhesion CTE Glass-ceramic sealant SOFC Softening point

ABSTRACT

Design of an appropriate sealant is crucial for reliable sealing and stable long-term operation of solid oxide fuel cells. We have investigated sealants based on barium aluminosilicate glass-ceramic modified with CaO and MgO. Focus of the research was on the $0.33BaO-0.20XO-0.33SiO_2-0.05Al_2O_3-0.09B_2O_3$ system, where XO is CaO, MgO, or a mixture of the two. Key properties of the system were studied, and its applicability of different compositions to sealing of high-temperature solid oxide fuel cells was investigated. Thermal properties, such as softening point and a half-ball point of the glass, coefficients of thermal expansion and adhesion to Crofer 22APU steel were of primary concern. CaO-containing sealants of this system showed much lower softening point compared to that of MgO-containing sealants. The substitution of CaO with MgO had no detectable effect on the coefficients of thermal expansion of the sealants. The coefficients of all the studied compositions were in $11.2-11.6 \cdot 10^{-6}$ 1/K range. All the compositions have good adhesion to both Crofer 22 APU steel and ZrO₂-based electrolyte. CaO-containing sealant was tested under operation conditions of a fuel cell stack for ten days; the seal remained hermetic for that period with no visible signs of degradation or oncoming failure of the seal.

1. Introduction

Fuel cells are electrochemical devices that convert chemical energy of a fuel and an oxidant directly into electrical energy bypassing fuelburning and transformation to mechanical energy stages. The direct conversion leads to superior energy efficiency of the fuel cells [1–3]. For stationary generation of electrical power and of useful heat high-temperature fuel cells with oxygen-conducting ceramic membranes (SOFCs – solid oxide fuel cells) are the most promising [4]. They are especially well suited for large scale distributed power generation systems due to their compatibility with both hydrocarbon and hydrogen fuels and due to high tolerance to impurities in the fuel [5–7].

Four different SOFCs stacking designs were developed and fabricated so far: monolithic design, tubular design, segmented-cell-in series design, and flat-plate design [8,9]. Tubular and flat-plate designs are among the most extensively studied and widely implemented. The flat-plate SOFCs offer improved performance and higher power density as compared to the tubular design SOFCs [1]. This is due to the longer current path through the electrodes in the tubular design SOFCs and the associated power loss. The flat-plate SOFCs have their own shortcomings; mainly, they include greater susceptibility to thermomechanical stresses and more complicated sealing in comparison to that of the tubular SOFCs [10–12].

Sealing is a crucial procedure for the fabrication of high performance SOFCs. Since the electrolyte-supported SOFCs operate at temperatures of 800–1000 °C only inorganic seals are suitable for the purpose; usually glass or glass-ceramic seals are used [13–16]. The seals prevent the fuel and the oxidant from direct mixing, thus protecting from burning of the fuel, local overheating of the cell and from overall loss of the SOFC efficiency or even failure. The seals also provide mechanical joining of the cells and provide mechanical support taking part of the mechanical load from fragile membrane electrode assembly.

A potential sealant for the SOFCs should satisfy a number of requirements. It should be thermomechanically compatible with the interconnect and with the electrolyte materials (for the electrolyte supported cells). It means that the coefficient of thermal expansion (CTE) of the sealant should be preferably in the $10-13 \cdot 10^{-6}$ 1/K range to avoid thermomechanical failure of seals upon the start-up of the

https://doi.org/10.1016/j.jnoncrysol.2024.122842

Received 26 October 2023; Received in revised form 17 January 2024; Accepted 18 January 2024 0022-3093/© 2024 Elsevier B.V. All rights reserved.

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SOFC. A potential seal should have a suitable behavior at the elevated temperatures:

- 1) Its softening point should be well below the sealing temperature and be comparable with the operating temperature of the cells;
- 2) The glass-transition temperature should be below operating temperature of SOFC;
- 3) The sealant flow temperature should be significantly above the SOFC sealing temperature to avoid the sealant leakage and loss of gastightness as a result.

Choice of a suitable sealant depends on the desired sealing temperature of the SOFC stack, its operation temperature and on the expected long-term performance. Higher sealing and operation temperatures require sealants with high content of SiO₂ and Al₂O₃, while for lower temperature operations sealants with higher contents of network modifiers such as MeO or Me₂O or fluxing agents such as B₂O₃ is preferable. A potential sealant for SOFC should form strong interface with the electrolyte material such as doped zirconia and with the metal interconnect (chromium-rich steel such as Crofer 22 APU or chromium-based alloys). Adhesion to the electrolyte and the interconnect ensures that no pathways for the fuel or the oxidant are formed along the interface. In addition, properties of the sealants for SOFCs should be stable under exposition to high temperature and high humidity, the latter is particularly important for SOFCs working on reformed hydrocarbon fuels. Finally, the sealant should be electrically insulating to prevent shorting of the cells.

A number of glass and glass-ceramic sealant systems were studied as candidates for application in the SOFCs [16]. The investigated systems include alkali-containing silicate glasses [17,18], barium alumina-silicate (BAS) glasses [19–22], calcium alumina-silicate glasses [23], magnesium alumina-silicate glasses [24], and various low-silica borate glasses [25–27]. Numerous oxide additives, such as ZnO, TiO₂, ZrO₂, Y₂O₃, and La₂O₃ are used to finely tune their behavior and properties [16].

In this study, barium aluminosilicate glass-system modified with CaO/MgO and small amounts of B₂O₃ was investigated. The system was chosen because barium aluminosilicate sealants (BAS) show excellent thermomechanically compatibility with the metal interconnect and the electrolyte materials due to formation of BaAl₂Si₂O₈ hexacelsian phase. BAS sealants also have potential for quick crystallization, which makes it attractive for preparation of the rigid-bonded seals. These sealants are frequently modified with MeO or Me₂O to adjust CTE, crystallization rate and softening temperature of the sealants. Alkaline-earth oxides such as CaO or MgO are frequently considered options for BAS modification because of the formation of phases desirable for the sealing purposes such as Ba3CaSi2O8 and Mg2SiO4. However, the effect of network modifiers such as CaO and MgO on properties of modified BAS glasses is not yet fully studied: some reported compositions are MgO-rich [28,29], while the others are CaO-based [30,31]. 0.33BaO-0.20-CaO/MgO-0.33SiO₂-0.05Al₂O₃-0.09B₂O₃ system was studied in the present work. The purpose of the study was to investigate the effect of modification of the glass system with CaO and MgO and to evaluate the effect of CaO/MgO choice in the studied system on suitability of the glasses for the sealing of SOFC.

2. Materials and methods

Three glass compositions were investigated in the present work. Nominal compositions and designations used for these compositions further in the paper are given in the Table 1. Moderate amounts of the network formers (SiO₂ and B₂O₃) were used to achieve the sealant softening point in the desired range. Minor amount of alumina was introduced to improve flow of the glass and to prevent rapid crystallization before the end of the sealing procedure [16]. BaO, CaO, and MgO were used as network modifiers. Moderate quantities of B_2O_3 were used

Table 1

Nominal	compositions	of the studied	sealants.

Designation	Component content, mol. fraction					
	BaO	CaO	MgO	SiO ₂	Al_2O_3	B ₂ O ₃
C20_M0	0.33	0.20	0.00	0.33	0.05	0.09
C10_M10	0.33	0.10	0.10	0.33	0.05	0.09
C0_M20	0.33	0.00	0.20	0.33	0.05	0.09

as both network former and a flow improving component.

The following substances were used as starting materials for the preparation of the sealant: $B(OH)_3$, $BaCO_3$, $CaCO_3$, $MgC_2O_4 \bullet 2H_2O$, SiO_2 , and Al_2O_3 . All the materials were supplied by Chemcraft (Russia), and had purity over 99.9 %. The starting materials were weighed and mixed with small amount of distilled water. After thorough mixing and air drying at 80 °C for 16 h the resulted mixture were additionally ground by hand and uniaxially pressed into pellets with 50 mm diameter. Precursor powders were pressed into pellets to improve contact between the particles, promoting formation of low-melting phases and facilitating formation of homogeneous melt.

The compositions were melted in platinum crucible at 1500 °C in LHT 02/17 LB (Nabertherm, Germany) furnace with heating rate of 300 °C/h and 1 h dwell at the maximum temperature. The melt was cast into the room-temperature distilled water. Platinum crucible was used for melting to minimize chemical interaction of the melt with the crucible. The resulting glass frit was crushed in electrically-driven zirconia mortar grinder Pulverisette 2 (Fritsch, Germany) to particle size d50 \approx 5–10 µm as measured with Analysette 22 NeXT (Fritsch, Germany).

X-ray diffraction (XRD) analysis was employed to assess phase composition of the sealants after the casting and after the thermal treatment (sealing procedure). Smartlab (Rigaku, Japan) X-ray diffractometer with copper X-ray tube in Bragg-Brentano reflective geometry was used. The X-ray reflections were identified with the use of PDF database. For the purpose of XRD analysis after heat treatment the studied sealants were thermally treated on a dense zirconia substrate, thus minimizing chemical interaction of the studied sealant compositions with the substrate.

Thermal treatment consisted in heating to 500 °C at 120 °C/h rate, soaking at 500 °C for 2 h, heating to 950–1000 °C at 90 °C/h rate, dwell for 1.5 h and cooling to room temperature at < 90 °C/h rate. The thermal treatment used in the test repeats the sealing routine for the electrolyte-supported SOFC used by our team.

Time of flight secondary ion mass spectrometry was used to evaluate amount of boron oxide in the resulting glass. Only boron oxide content was investigated because it was the most volatile component in the studied sealants. TOF.SIMS 5 (ION-TOF, Germany) mass-spectrometer was used for the purpose. For the evaluation ratio of Si/B peaks intensity were calculated and then were compared to the ratio obtained on a SiO₂/B₂O₃ mixture with the known components ratio.

CTEs of the prepared sealants were investigated only for the sealants after the heat treatment, because the CTEs of the initial untreated glass does not necessarily accurately predicts CTE of the rigid seal after the heat treatment. For the study rectangular samples approximately 7 mm long were cut from the heat-treated sealant and were tested in vertical dilatometer L75Vertical (LINSEIS, Germany). Dilatometric testing routine included heating of the sample to 850 °C at 2 °C/min rate and cooling to room temperature at the same rate.

Misura 3 HSML (ESS, Italy) hot-stage microscope was used to study high temperature behavior of the sealant. For this purpose we have pressed sealant into rectangular samples with 3 mm side. The samples were placed on a zirconia plate in the microscope and were heated at 2 °C/min rate to 1050 °C. Images of the samples at different temperatures were analyzed to calculate characteristic temperatures of the sealants.

In order to investigate microstructure of the sealants and their

adhesion of the sealants to Crofer 22 APU (conventional heat-resistant steel for the interconnects) steel interconnect-sealant-electrolyte sandwich structures were prepared for all the studied sealants. 150 μ m thick 10Sc1YSZ membrane was used as electrolyte in the experiment. Sealant-containing paste was deposited on the steel surface, then it was covered with the electrolyte membrane and loaded to compressive load of 2.5 kPa to facilitate the sealant flow. The paste was used to homogeneously distribute the sealant along the steel surface. The sealed "sandwiches" were then placed into epoxy resin and polished to prepare cross-sections for SEM study. Supra 50 VP (Carl Zeiss, Germany) microscope was used for the purpose. Built-in energy-dispersive X-ray spectroscope (EDX) INCA (Oxford Instruments, Great Britain) was used to evaluate atomic compositions in different areas of the sandwich structures.

The most promising sealant composition was tested in the SOFCs stack consisting of two unit cells. Membrane electrode assembly consisted of LSM (cathode), doped zirconia (membrane), and Ni-CeO₂ (anode); Crofer 22 APU steel was used as interconnect. Dimensions of the electrodes were 90 \times 90 mm. The SOFC was tested in both fuel cell and electrolysis cell modes with hydrogen used as a fuel, and air used as an oxidant. Various parameters of the SOFC were monitored to assess behavior of the sealant during operation of the cell. The stack was disassembled after the operation in order to assess the state of the sealant material and locate possible fractures.

3. Results

All the sealants after casting into distilled water were transparent and visually homogeneous, i.e. no opaque inclusions were observed in the pieces of the sealants. It indicates that complete melting and homogeneous mixing was achieved. According to XRD analysis of the sealants after casting, all the studied compositions were amorphous. XRD pattern of as-cast C10_M10 sealant is shown as example in Fig. 1. Full width of the peaks at half maximum according to the Scherrer's equation corresponds to a crystallite size of only 0.28 Å. It indicates that the observed reflections are not diffraction peaks of crystalline phases but are results of scattering of the X-ray in an amorphous material.

Hot-stage microscopy images of the pressed sealants were used to determine end of sintering point, softening point, ball and half ball points as well as flow temperature of the studied sealants. Fig. 2 shows images of C20_M0 sealant at the specific temperatures. Table 2 summarizes the key temperatures of the studied sealants. Sintering temperatures of all the sealants were similar and close to 710 °C. Significant



Fig. 2. Hot-stage microscopy image of pressed sealant at specific temperatures.

Table 2High-temperature behavior of the studied sealants.

Sealant	Sintering temperature, °C	Softening temperature, °C	Ball temperature, °C	Half ball Temperature, °C
C20_M0	710	800	820	980
C10_M10	710	950	_	990
C0_M20	710	980	>1050	>1050

difference in softening temperatures was observed with C20_M0 having the lowest value of the three – 800 °C. C10_M10 and C0_M20 had much higher softening point at about 950 °C and 980 °C respectively. Predictably, ball and half ball temperatures of C20_M0 were lower than that of C10_M10 and C0_M20. Ball temperature of C20_M0 is about 820 °C, and that of C0_M20 exceeded the temperature limit of our experiments, that is, it was higher than 1050 °C. Ball temperature of C10_M10 was not reliably determined from hot-stage microscopy image analysis. C10_M10 samples upon heating quickly transformed to half ball



Fig. 1. XRD pattern of as-cast C10_M10 sealant.

geometry with no clear temperature range where sealant had a ball shape. Half ball temperature of C20_M0 and C10_M10 were reliably determined to be 980 °C and 990 °C respectively.

The highest softening point among the studied sealants is 980 °C, so the sealing experiments were conducted at 980 °C to ensure that all the sealants were sufficiently soft at the sealing temperature for adequate comparison of their sealing ability. Consequently, for study of the phase composition of the sealants after the sealing procedure test temperature of 980 °C was also used. Fig. 3 shows XRD patterns of the studied sealants after the dwell at 980 °C for 1.5 h imitating the sealing routine. Crystalline phases corresponding to the diffraction peaks are marked in the figure. It should be noted however that high sealing temperature of 980 °C is detrimental for some SOFCs infiltrated electrodes and for metal interconnects resistivity. Thus, C20_M0 sealant composition is better suited for sealing of SOFCs as compared to C10_M10 and C0_M20 because of its lower softening temperature.

The sealants after the thermal treatment contain a number of crystalline phases as can be seen from the Fig. 3. The simplest pattern is observed for C20_M0 sealant, only barium-calcium silicates with Ba_xCa_{2-x}SiO₄ (PDF 017–0930, 036–1449) composition and CaAl₂B₂O₇ (PDF 019–0205) were identified. More complex phase composition was observed on C10_M10 diffraction pattern: MgSiO₃ (PDF 011–0273) and Ba₂MgSi₂O₇ (PDF 010–0049) peaks were detected in addition to Ba_xCa_{2-x}SiO₄ and CaAl₂B₂O₇. XRD pattern of C0_M20 contained peaks of MgSiO₃, Ba₂MgSi₂O₇, and Al₂SiO₅ (PDF 011–0046).

Time of flight secondary ion mass spectrometry measurements of Si/ B atomic ratio in all sealants after casting and thermal treatment at 980 °C yielded value of 1.77–1.85 with nominal ratio calculated from the sealant's composition being 1.83. Thus, no significant boron oxide loss was detected after melting, casting, and heat treatment at 980 °C.

Fig. 4 shows dilatometric curves of all the sealants after thermal treatment imitating sealing procedure. All the sealants are showing similar nearly linear expansion from room temperature to about 650 °C. CTEs were calculated in this range by linear fitting. CTEs of the sealants slightly decrease with lowering CaO content. The values were 12.1 \pm 0.2•10⁻⁶ 1/K for C20_M0, 11.95 \pm 0.15•10⁻⁶ 1/K for C10_M10, and 11.55 \pm 0.2•10⁻⁶ 1/K for C0_M20. The errors were calculated over measurements on three samples for each sealant composition. Behavior of the sealants at higher temperatures differs as all sealants show different degrees of contraction in 750–900 °C. C20_M0 shows the slightest decrease in length, while C10_M10 shows the most pronounced one. Contraction of C0_M20 is intermediate between the two other

sealants. All the samples showed no notable deviation from rectangular shape such as rounding of the corners or bulging of the sides.

It is crucial for the potential rigid sealants for SOFCs to have strong adhesion to surface of metal interconnect. Strong interface prevents delamination of the sealant from the interconnect due to inevitable thermal stresses that could not be mitigated by rigid seals. Fig. 5 shows SEM images of the steel interconnect -sealant-electrolyte assemblies after sealing at 980 °C for 1.5 h. On all the presented images steel interconnect is located at the bottom. From the presented images it is clear that all the sealants form continuous interface at both steel and ZrO2 interface. No delamination was observed on the obtained images, and although occasional pores few tens µm in diameter can be seen, they do not form continuous channels that could lead to fuel or oxidant leakage, thus they should have no effect on tightness of the seal. From microstructural standpoint all the sealants demonstrate presence of needle-shaped crystals light-colored in SEM-contrast image. Microstructure of C0 M20 seal exhibits quite dense packing of these crystals nearly fully hiding darker colored background. A notable microstructural feature of C10 M10 seal is presence of nearly rectangular lightcolored regions with typical size of 15-40 µm. Interfaces of all the sealants with the interconnect show thin reaction layer seen as darker layer at the interface. The thickness of the reaction layer does not exceed 1-2 µm. The reaction layer is slightly more pronounced in assembly with the C0_M20 sealant. The reaction site can be observed in the center of interface presented on high-magnification image for C0_M20 in Fig. 5. The pores observed on the SEM images of all the studied sealants are closed; they do not form a continuous network that could compromise gas-tightness of the seal. The pores are large and almost spherical. It may be assumed that these pores appeared as a result of organic solvent evaporation from the sealant-containing pastes at the initial stages of heating of the studied steel interconnect -sealant-electrolyte assemblies.

In order to obtain additional information on microstructure and possible interactions of the sealants at the interface with steel EDX analysis of the cross sections was performed. Fig. 6 shows points at which the spectra were taken; Table 3 presents atomic composition in the investigated areas. It must be noted that the Table 3 does not include data on boron, because it cannot be detected with EDX. On the CO_M20 sample the spectra were taken in three points: spectrum #1 was taken in proximity to the steel interconnect -sealant interface, spectrum #2 was taken at some from the interface at a large light-colored crystal, spectrum #3 was registered in the dark-colored area of sealant. On C10_M10 various areas of the sealant were investigated, spectrum #1 was



Diffraction angle, °

Fig. 3. XRD patterns of the studied sealants.



Fig. 4. Dilatometric curves of the studied sealants after thermal treatment.



Fig. 5. SEM images of cross-sections of the steel interconnect-sealant-electrolyte assemblies after sealing at 980 °C.

registered in the dark area, spectrum #2 - in one of the large rectangular formations, spectrum #3 - in the area of needle-shaped crystals. On CO_M20 due to dense packing of the needle-shaped crystals and following difficulties of collecting data selectively from certain microstructural features, the spectra were registered in wide rectangular areas near the interface and at some distance from it. The aim was to assess diffusion of steel-composing elements into the bulk of the sealant with sealant-related deviations ruled out by averaging over large area.

EDX shows notable differences in composition in different areas of the sealants. For C20_M0 we registered significant increase in calcium content from 5 mol. % to 12 mol. % near the interface with steel interconnect. Furthermore, aluminum content was significantly lower in the near-interface region. It would be even more informative to take data from 1-2 μ m distance from the steel; however such measurements could produce distorted reading because of a few μ m size of the spectra collection spot. Comparison of spectra #2 and #3 shows slightly higher aluminum and lower silicon content in the former. Another noteworthy difference is detection of minor quantities of Cr and Fe in these regions, somewhat higher in needle-shaped crystals, although the difference is bordering instrumental error. It should be noted that composition of needle-shaped crystals is likely to differ more significantly from that of dark area, but the difference is somewhat obscured by the finite area of spectra collection.

For C10_M10 sealant a notable difference in composition of large rectangular formations and the rest of the sealant can be seen: composition in point #2 is magnesium-rich, while points #1 and #3 have higher calcium content and are nearly magnesium free. Point #2 is also characterized with higher silicon, aluminum and barium content. At the same time difference between spectra #1 and #3 is insignificant, all the variations fall within the instrumental error. Composition of large bright particles in C10_M10 sealants together with the results of XRD analysis suggests that these particles are composed of Ba₂MgSi₂O₇ crystalline phase. Needle-shaped crystals (spectra #3) show minor content of Mg. Taking into account that the spectra were collected not only on the needles themselves but also on the surrounding sealant, it may be assumed that the needle-shaped crystals are MgSiO₃ crystals. It is indirectly supported by higher content of these crystals in C0_M20 composition, more rich in magnesia.

No reliable signal was registered from either iron or chromium in the studied points of C10_M10 sealant. For C0_M20 sealant the spectra averaged on a few tens of μ m wide regions close to the steel-sealant interface and some distance from it are nearly identical. Content of all the discovered elements lies reliably within the instrumental error. Minor quantities of iron were discovered in both regions, but no



Fig. 6. Areas of EDX spectra taken on assembly cross-sections.

difference in its content was found between the regions. Spectra were not registered at the interface itself for the reasons given above.

Fig. 7 demonstrates electrochemical performance of the two-element assembly sealed with the C20_M0 sealant. We have performed electrochemical tests on only one sealant because of the limited availability of the equipment on operational experiments with the fuel cells. The C20 M0 sealant was chosen because of its relatively low softening temperature and its expected ability to form homogeneous sealing layer at temperatures below 1000 °C, namely at 980 °C. The assembly was sealed according to the routine described earlier and then was held at operating temperature of 850 $^\circ$ C for 10 days. The assembly was tested in both fuel and electrolysis modes to evaluate stability of the sealant in low- and high-humidity environments. At the start of the experiment open circuit voltage of each of the fuel cells in the assembly was 1.04 V in full accordance with Nernst voltage calculated for the measurement condition (humidity, temperature). Compliance with the Nernst equation indicates absence of fuel or oxidant leaks at the start of the experiment and, consequently, tight sealing of the assembly.

In order to observe possible breaches of the seal during operation of the SOFC stack voltage as a function of time was monitored in galvanostatic mode in both fuel (on day 1) and in electrolysis (days 7–10) modes. Fig. 7a shows data obtained in fuel cell mode. No abrupt voltage falls, that could serve as breach indicators, are observed. Steplike increase in voltage observed towards the end of the experiment are caused by sudden humidity change in the water vapor generation system. Gradual decrease in voltage is associated with electrode degradation. Fig. 7b shows voltage vs. time curve in galvanostatic electrolysis mode. Again, no abrupt voltage changes were observed. Open current voltage of the assembly after the 10-day test did not change. After disassembly of the SOFC stack it was discovered that breakage of the seals (upon disassembly) took place inside glass seals, not on the sealant-interconnect interface. It may serve as indication of strong sealant-interconnect adhesion. Furthermore, no traces of oxidant or fuel leakage were detected neither visually nor through a gas leaking test.

Disassembly of the stack confirmed structural integrity of the sealant layer during the operation. Fig. 8 shows image of one of the elements in the stack after the disassembly. The sealant form continuous uninterrupted layer isolating both fuel and oxidant channels and sealing the external perimeter of the stack. No traces of fuel or oxidant leakage were

Table 3

Elemental composition of the studied sealants in the areas shown in Fig. 6.

	Element content, mol. %							
	Si	Ва	Ca	Mg	Al	Fe	Cr	0
C20_M0								
Spectrum	7 ± 2	8 ± 2	$12 \pm$	—	$3 \pm$	_	_	70 \pm
1			2		1			2
Spectrum	9 ± 2	7 ± 2	5 ± 1	—	$7 \pm$	$3 \pm$	~ 1	$68~\pm$
2					2	1		2
Spectrum	$11 \pm$	7 ± 2	6 ± 1	—	$5 \pm$	~ 1	_	70 \pm
3	2				1			2
C10_M10								
Spectrum	8 ± 2	9 ± 2	8 ± 2		$3 \pm$	—	_	$71 \pm$
1					1			2
Spectrum	$13 \pm$	$13 \pm$	—	4 ±	$7 \pm$	—	_	$63 \pm$
2	2	2		1	2			2
Spectrum	$10 \pm$	7 ± 2	6 ± 1	~ 1	$3 \pm$	—	_	$73 \pm$
3	2				1			2
C0_M20								
Spectrum	$13 \pm$	$11 \pm$	—	4 ±	$5 \pm$	~ 1	_	$66 \pm$
1	2	2		1	1			2
Spectrum	$13 \pm$	11 \pm	—	$5 \pm$	$5 \pm$	~ 1	_	$65 \pm$
2	2	2		1	1			2

discovered during the post mortem analysis of the stack. Fracture of the seal upon the disassembly took place predominantly inside the sealant layer, and not on the sealant-steel or sealant-electrolyte interface. It should be noted that the sealant after ten days of the stack operation became green-colored, which indicates diffusion of Cr^{3+} into the sealant. It was confirmed by EDX measurements of the sealant after the operation.

4. Discussion

The obtained data on high-temperature behavior (Table 1), showing increase in softening, ball and half ball temperatures when replacing calcia with magnesia is in a qualitative agreement with the results previously reported by Lara et al. [32]. The paper by Lara et al. [32] covers the effect CaO/MgO/ZnO in CaO/MgO/ZnO-Al₂O₃-BaO-SiO₂ glass on sintering and softening temperatures of the sealants. Since the authors studied another glass-composition absolute values of the temperatures are different from the ones observed in our work, but the observed trends agree. Similar situation was reported in detailed work by Lahl et al. [33]. They showed in particular that replacement of CaO with MgO leads to dramatic increase in glass-transition temperature, from which similar difference in softening temperatures can be



Fig. 7. Seal hermeticity test in fuel cell (a) and in electrolysis cell (b) modes.



Fig. 8. The disassembled stack after the ten days operation.

expected. The observed tendency can be explained by the effect of the field strength of a modifier cation, increasing from Ca^{2+} to Mg^{2+} . The effect of the field strength on specific temperatures was conclusively shown by a number of authors. One can mention paper by Shelby et al. [34], where they reported increase in glass-transition proportional with ionic strength temperature in rare-earth oxide aluminosilicate glasses.

Among the studied sealants C20_M0 has the most promising for practical purposes softening temperature allowing to seal SOFCs in entire 950-1000 °C range or even at slightly lower temperatures. C10_M10 with softening temperature of 950 °C can only be used for sealing at temperatures closer to 1000 °C, for example at 980 °C as was done in the present study. Softening temperature of C0 M20 makes it difficult to use it for sealing of SOFCs with Crofer 22 APU interconnect because temperatures about 1000 °C are required for effective sealing, at the same time such high temperatures may cause increase in interconnect resistivity and degradation of some infiltrated electrode materials. For compositions C10 M10 and C0 M20 to be attractive for sealing of SOFCs with Crofer 22 APU interconnect it may be necessary to lower softening point without compromising other properties of the glass. Viable option is slight change in B₂O₂/SiO₂ increase; however, its effect on CTE, adhesion and long-term chemical stability of these glasses is not yet conclusively studied.

A composition similar to the C20_M0 sealant (BaO-CaO-SiO₂-Al₂O₃-B₂O₃) was studied in particular by Luo *et al* [35]., where a single composition was investigated for the purposes of planar SOFCs sealing. The sealant studied in the work showed similar promising CTE and reliable sealing of the SOFCs. Similarly to the present study, the authors have detected mixed barium-calcium silicate. In addition, due to the difference in the compositions, they have also observed presence of BaSiO₃ and BaAl₂Si₂O₈ phases. High long-term stability of the sealant reported by Luo [35] suggests that similar stability may be expected from the C20_M0 sealant.

The effect of CaO/MgO choice on properties of BaO-XO-SiO₂-Al₂O₃-B₂O₃ was experimentally studied in details by Puig et al. [36]. Their research covered a number of compositions with varying CaO/MgO ratio. The BaO and SiO₂ content was slightly higher than the ones reported in the present study, and somewhat lower CaO and MgO contents were used. Puig et al. [36] reported much higher CTE values of the prepared glasses: $14.5 \cdot 10^{-6}$ 1/K for calcia-rich, and $13.6 \cdot 10^{-6}$ 1/K for magnesia-rich compositions. In agreement with the present study, they have discovered that magnesia-rich sealant had higher half-ball temperature, although absolute values differ significantly from the ones reported presently. It is noteworthy that they found no difference in softening point of these sealants. The authors also investigated mixed compositions, containing both calcia and magnesia, finding somewhat decreased half-ball temperature in the mixed-composition sealant.

Comparison of XRD patterns (Fig. 3) with SEM images of crosssections (Fig. 5) allowed us to make some assumptions about composition of certain microstructural features. Spectra #1 registered on C20_M0 shows increased calcium content and decreased aluminum content. Judging from the phases determined by XRD, it may be assumed that $Ba_{2-x}Ca_xSiO_4$ mixed silicates are present in the area. Presence of calcium aluminoborate is unlikely due to low aluminum content in the area. Presence of some quantities of calcium-rich amorphous phase, that was not detected by XRD due to dominance of crystalline peaks, is also possible. Spectra #2 with area center on needleshaped formations show increased alumina content, which may be associated with $CaAl_2B_2O_7$ crystals.

On C10_M10 only on spectra #2 solid assumptions on composition may be made due to large area of the crystalline formations and consequent low distortion of estimated elemental composition. Large crystalline formations are rich in Mg and Si with also increased Ba content. From the phases determined by XRD, MgSiO₃ and Ba₂MgSi₂O₇ may be expected to be present in the area. On CO_M20 sample no significant difference can be seen between the studied area, so we could not derive any information about phase compositions of certain microstructural features.

An important information we procured from SEM imaging and from EDX analysis is that no visible chromium- or iron-rich microstructural formations appear after sealing. Furthermore, we detected no gradient of Cr and Fe in the material, which indicates that chemical interaction between sealant and interconnect takes place primarily on the interface with no significant effect on "deep" layers of the sealant.

Dilatometric study of high temperature behavior of the sealants after thermal treatment shows interesting results. It should be kept in mind that we studied the partially crystallized sealants after the sealing thermal treatment. All the studied sealants showed similar thermal expansion when heated from room temperature to about 650 °C. Their CTE being in 11.55–12.1·10⁻⁶ 1/K makes them thermomechanically compatible with conventional steel interconnect material Crofer 22 APU with CTE 10.3–12.3·10⁻⁶ 1/K in 200–900 °C. Difference in CTEs of the studied sealants is not significant, although falling outside instrumental error. Lower CTE was observed in magnesia-rich sealant C0_M20, making it slightly more attractive for forming thermomechnical compatibility connection with zirconia-based electrolytes.

At the temperatures exceeding 650 °C behavior of the sealants varies. They all show some contraction, most likely due to softening of the sealant that can be explained by presence of amorphous phase. It can be assumed thus that C20_M0, showing the least pronounced contraction, has the lowest content of amorphous phase. Higher softening temperature and correspondingly crystallization temperatures of C10_M10 and C0_M20 allowed them to retain greater amount of amorphous phase. It

may be expected that the most contraction would appear on C0_M20 test, however, it is not the case. The reason behind it is higher softening temperature of C0_M20 that partially counteracts high amorphous phase content, making the sealant relatively solid at maximum dilatometric test temperature of 950 °C. Among the studied sealants C0_M20 offers the highest stability of CTE: low amorphous phase content means that upon its crystallization no significant change in CTE may be expected. Furthermore, C20_M0 offers the highest dimensional stability: it shows the lowest plastic deformation during thermal cycle. C10_M10 and C0_M20 do not have these advantages, but higher content of amorphous phase in them gives an additional mechanism to relieve thermomechanical stresses in an assembly.

Hermeticity tests conducted on the SOFC stack has shown that at least C20_M0 sealant provides reliably sealing, capable of withstanding exposure to operation conditions of SOFC. C20_M0 has the most attractive sealing temperature, allowing to seal assemblies in 950–1000 °C range, while C10_M10 and C0_M20 need temperatures about 1000 °C; higher sealing temperatures in turn cause increase in ohmic resistance due to chromium diffusion in steel interconnects.

5. Conclusions

Three sealant compositions of $0.33BaO-0.20CaO/MgO-0.33SiO_2$ - $0.05Al_2O_3$ - $0.09B_2O_3$ system with varying CaO and MgO ratio were investigated. All the studied sealants after thermal treatment show presence of significant content of crystalline phases, although presence of residual amorphous phase is indirectly evidenced by dilatometric study, showing some high-temperature contraction of the sealants after thermal treatment. High degree of crystallinity and thermomechanical compatibility with steel interconnects and zirconia electrolytes makes these sealants a promising material for preparation of rigid seals, but with minor ability to compensate thermomechanical stresses due to residual amorphous phase. Applicability of the studied materials for sealing of SOFCs is also supported by SEM images of sealantinterconnect interfaces showing good adhesion with no delamination or cracking, and with visible, although thin, reaction layer.

Among the studied sealants C20 M0 has the most attractive softening temperature, allowing sealing of SOFC assemblies in a comfortable temperature range. Hermeticity of sealing with C20 M0 and its resistance to degradation was proved by tests on SOFC stack conducted for 10 days of continuous operation. C10_M10 and C0_M20 sealants, although showing higher residual amount of amorphous phase and thus better buffering of thermomechanical stresses, have notably higher sealing temperature, which limits their possible application. C10_M10 and C0_M20 compositions may be modified to address this problem. One of the possible routes for this is to increase amount of flow-improving oxides, such as B₂O₃. However, introduction of these additional oxides would affect CTE and adhesion to interconnect. So, additional research is needed for C10_M10 and C0_M20 sealants. At the same time C20_M0 sealant can be recommended as a sealant for SOFC sealant because of good combination of softening temperature, adhesion to steel interconnect and suitable CTE.

Funding

This research was funded by the Grant of the President of Russian Federation, project number MK-3060.2022.1.2.

CRediT authorship contribution statement

Andrey O. Zhigachev: Methodology, Validation. Anastasia R. Iskanderova: Methodology. Darya V. Zhigacheva: Methodology. Ekaterina A. Agarkova: Validation, Visualization. Natalia V. Demeneva: Investigation. Sergey I. Bredikhin: Conceptualization, Formal analysis, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

Authors would like to express their gratitude to Solovyeva E.A. for mass-spectrometry analysis of the sealants, and to Matveev D.V. for his help in SOFC stack tests.

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A.O. Zhigachev et al.

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