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Non-Crystallising Glass Sealants for SOFC: Effect of Y₂O₃ Addition

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Abstract.

The joining of ceramic and metal (interconnect) parts is one of the main challenges in the development of solid oxide fuel cells (SOFC). A promising approach to solving this problem is the use of glassy sealants. In this work, we investigated the effect of yttria additions on the properties of SiO_2 -Al₂O₃-CaO-Na₂O-ZrO₂-Y₂O₃ glass sealants. An increase in the concentration of yttria is shown to reduce the tendency of the glasses under study to crystallisation. A glass containing 4 wt.% of Y₂O₃ is found to be amorphous, even after exposure at 850°C for 100 h. Moreover, the defectiveness of the glass microstructure, after sealing, is found to decrease along with a growth in the Y₂O₃ concentration. The developed non-crystallising sealant was successfully applied for joining a YSZ ceramic and an Fe-Ni-Co alloy having the phase transition of around 500°C. The use of the non-crystallising sealant allows us to join materials with very different thermal expansion coefficients and to avoid cracking under cooling, which might occur due to a large difference in thermal expansion coefficients.

Keywords: glass sealant; SOFC; sealing microstructure; non-crystallising sealant; crystallisation.

1 Introduction.

Due to their high efficiency, environmental safety and low noise level, solid oxide fuel cells (SOFC) are seen as promising candidates for substituting ineffective thermal power plants [1,2]. However, the issue associated with joining ceramic components is still hampering SOFC development. Elevated SOFC operating temperatures (~ 900°C) impose strict requirements on sealant materials, which are expected to exhibit a high chemical stability in both oxidising and

reducing atmospheres as well as in contact with the materials to be joined, a low electrical conductivity, a good adhesion and mechanical strength, and a thermal expansion coefficient (CTE) comparable to that of the materials to be joined [3-5].

Considering the above-mentioned requirements, high-temperature glasses based on aluminosilicate systems can be considered promising in terms of the creation of a tight contact between the SOFC functional components. Under the influence of elevated temperatures (600-900°C), glass sealants become viscous, thus reducing the mechanical stresses between the parts to be joined and eventually optimising the cell design. Another advantage of glasses is their extended homogeneity region, which allows the glass composition to be varied over a wide range of component concentrations. The required CTE value can be reached by selecting a composition of a glass sealant [6] such that an SOFC could maintain its integrity during heating to operational temperatures.

However, the viscous state is known to be metastable and glasses tend towards a more thermodynamically stable crystalline state when heated above the glass transition temperature. The formation of crystalline phases results in mechanical stresses due to a difference in molar volumes and a change in the CTE of a glass sealant, thus leading to cracking of the cell. In most cases, crystallisation during sealing or exposure at operating temperatures cannot be avoided, a fact which explains the popularity of glass-ceramic sealants among researchers [7-11]. At the same time, non-crystallising sealants have received little attention. The glass of 30BaO-40SiO₂-20B₂O₃-10Y₂O₃ composition was shown to be stable after exposure at 800°C for 100 h. The sample studied remained predominantly amorphous and the change of CTE value was only 3% which indicates the high stability of the amorphous state [12]. A similar result was observed for the glass of the same composition in which BaO was replaced by CaO [13]. The authors explained the effect of Y₂O₃ on the crystallisation ability by its intermediate nature (the possibility of being both a glass former and modifier). However, in this case, a La₂O₃-containing glass sealant was found to be more promising due to its higher long-term stability. In the study Kim [14], a glass sealant of the 18BaO-45B₂O₃-24SiO₂-6Al₂O₃-3.5CaO-3.5SrO bv composition remained amorphous after exposure at 850°C for 2000 h. However, all the mentioned glass sealants are shown to contain a great amount of boron oxide, which is undesirable for long-term SOFC operation due to the high volatility of B_2O_3 [15].

Glasses containing rare earth metal oxides are the most interesting among boron-free aluminosilicate glasses due to their positive effect on both the stability of the CTE value of a sealant at long-term use [16,17] and on restraining the crystallising ability of glasses. Thus, glasses with the compositions of 11.69MgO-14.24CaO-11.28SrO-39.22SiO₂-1.85Al₂O₃-2.0B₂O₃-19.72Gd₂O₃ and 11.49MgO-13.99CaO-11.08SrO-38.55SiO₂-1.82Al₂O₃-2.0B₂O₃-

21.07Yb₂O₃ (wt.%) were produced in the work by Goel [18]. In these glasses, the amorphous phase amounts to 95% after exposure at 850°C for 1 h, which makes them promising candidates for application as self-healing sealants. However, the rather low CTE values of these glasses hampers their application for joining ceramics with Cr-containing steels and alloys. It was shown in our previous work [19] that a small addition of cerium oxide reduces the difference between the CTEs of the as-cast glass and glass–ceramics (heat-treated glass).

Most of the published work has been devoted to the study of the effects of yttrium [20-27] and lanthanum [28-30] oxides on the properties of glass sealants. As was mentioned above, yttria has a dual nature and can act simultaneously as both a glass former and a modifier [12] which, in the case of glass sealants, has a positive effect on the glass properties. According to Singh [25], the introduction of small (up to 6 mol.%) additives of Y_2O_3 suppresses the crystallisation process and increases the characteristic temperatures. Similar results were obtained by Mahdy et. al. [21], and the authors attribute the change in material properties to the position of yttrium ions in the glass network. The growth of the activation energy of crystallisation in ZnO–B₂O₃–SiO₂ glasses with over stoichiometric additions of Y₂O₃ (up to 6 mol. %) was noticed by Wang in [27]. It was also found that even a small addition (up to 1 wt.%) of yttria allows the inhibition of the formation of crystalline phases with high CTE values [23] and an introduction of 1.5 mol.% Y₂O₃ leads to an increase in the microhardness of the glasses [20]. The effect of La₂O₃ and Y₂O₃ additives on the properties of aluminosilicate glass-ceramic sealants has been studied elsewhere [24-29] The activation energy of the crystallisation process for Y₂O₃-containing glasses was found to be higher than that for La₂O₃-containing ones, which indicates a low crystallisation ability of yttrium oxide. A number of studies devoted to the effect of Y_2O_3 on the crystallisation kinetics of aluminosilicate glasses also showed that a Y_2O_3 addition improves the stability of their vitreous state [31,32]. Based on the literature review given above, it can be concluded that Y₂O₃-containing glasses are interesting for study in terms of their high long-term stability and low crystallisation ability.

Previously, we have studied the properties of a $59.6SiO_2-11.0Al_2O_3-10.6ZrO_2-3.4CaO_15.4Na_2O$ glass sealant and found that its CTE value fits that of YSZ ceramics. This material was shown to exhibit a rather high chemical stability when in contact with the materials to be joined (YSZ and a Crofer22APU alloy) [**33**]. However, we observed bulk crystallisation which could reduce the stability of the CTE during long-term operation. According to numerous studies, the introduction of small additives of Y_2O_3 can suppress the undesired crystallisation. Therefore, the present work investigates the effect of ZrO_2 substitution by Y_2O_3 on the physical and chemical stability in contact with an Fe-Ni-Co alloy.

2 Experimental Section.

2.1 Glass preparation and characterisation

Zirconia (99.9%), yttria (99.9%), alumina (99.9%), silica (aqueous) and sodium and potassium carbonates (99.9%) were used as starting materials. All components were taken in a stoichiometric ratio and mixed thoroughly in a porcelain mortar. The obtained mixture was pressed into pellets with a diameter of ~ 20 mm to improve the reaction between the batch components and to obtain a homogeneous glass. The glasses were prepared by melting the batch **in corundum crucibles** at a temperature of 1500°C followed by casting the melt into a glassy-carbon mould. Subsequently, the glasses were annealed at a temperature of 600°C for 30 min to remove thermal stress. The compositions of the 59.6SiO₂–11.0Al₂O₃–(10.6-*x*)ZrO₂–3.4CaO–15.4Na₂O–*x*Y₂O₃ (*x* = 0; 2; 4 wt.%) glasses are given in Table 1.

		-		,			
#	Concentration, wt.%						
	SiO ₂	CaO	ZrO ₂	Al ₂ O ₃	Na ₂ O	Y ₂ O ₃	
1 nominal	59.6	3.4	10.6	11.0	15.4	—	
1 AES	57.8	3.5	8.3	13.9	16.5	_	
2 nominal	59.6	3.4	8.6	11.0	15.4	2.0	
2 AES	59.0	3.1	6.9	13.0	16.3	1.8	
3 nominal	59.6	3.4	6.6	11.0	15.4	4.0	
3 AES	59.7	3.5	6.3	11.1	15.4	3.9	

Table 1. Nominal composition values and those determined by AES for $59.6SiO_2-11.0Al_2O_3-(10.6-x)ZrO_2-3.4CaO-15.4Na_2O-xY_2O_3$ glasses (x = 0; 2; 4 wt. %).

The chemical composition of the as-obtained glasses was determined by atomic emission spectroscopy (AES) with inductively coupled plasma using an Optima 4300 DV (Perkin Elmer, USA) spectrometer; accuracy was 2-3%.

The phase composition of the glass samples was determined by X-ray powder diffraction using a D/MAX-2200V (Rigaku, Japan) diffractometer with $Cu_{K\alpha}$ ($\lambda = 1.5418$ Å) radiation in a 20 range of 10-75° and an angle scanning step of 2°/min.

2.2 Alloy treatment

As a rule, the surface of alloys used for SOFC applications is pre-treated by coating [34] or oxidation [35] to avoid the alloy degradation due to increased temperatures and oxidative atmospheres. In addition, an inhomogeneous natural coating formed on the untreated surface,

after high-temperature annealing, features the presence of unevenly-distributed segregation centres of oxide phases, which can affect the mechanical strength under long-term tests.

In order to minimise the aforementioned effects, the surface of the 30.29Fe–12.62Co– 1.11Ni alloy (33-NC alloy in Russian classification) was initially modified by a novel electrocrystallisation method consisting of a subsequent deposition of Ni and Mn from solution. An aqueous acid solution of NiCl₂·6H₂O (99.9%) and a solution of MnCl₂·4H₂O (99.9%) in dimethyl sulfoxide (DMSO, 99.9%) were prepared for the deposition of a coating. Since the potential of the manganese reduction from aqueous solutions is rather high (–1.18 V), the use of an organic solvent is required. DMSO was chosen due to its wide range of working temperatures, rather high permittivity (ϵ = 48.9) and resistance to decomposition during metallic reduction.

After modifying, all the alloy products were annealed following two stages. Firstly, the products were annealed at a temperature of 850°C for 2 h in a high-vacuum (with a residual pressure of 10^{-5} atm) experimental set up with a furnace to remove organic compounds from the surface. Afterwards, to form an oxide coating, the samples were annealed at 1000°C for 10 min in an oxygen atmosphere. The heating rate was 100°/h in both regimes. The obtained products with a protective coating were used as interconnects.

2.3 Thermal analysis

Differential scanning calorimetry (DSC) was used to determine the characteristic temperatures of glasses using an STA 449 F1 Jupiter (Netzsch, Germany) calorimeter. The measurements were carried out in a platinum crucible across a temperature range of 35-1100°C in an argon atmosphere with a heating rate of 10°/min. The obtained data were treated using the Netzsch Proteus software.

In order to determine the sealing temperature, films made of a glass powder mixed with a polymeric binder were prepared. The samples, with dimensions of $10 \times 10 \times 0.4$ mm, were cut and applied onto a YSZ ceramic substrate followed by heating to various temperatures. Exposure at each temperature was 10 min. The temperature, at which a glass drop with a good adhesion to the substrate had formed (contact angle < 90°) [36], was taken to be the sealing temperature, the accuracy of temperature set was \pm 5°C. The sealing temperature was determined by the shape of a drop: a detailed description is given elsewhere [11].

2.4 Dilatometry

Thermal expansion of the obtained glasses, YSZ ceramics, and an Fe-Ni-Co alloy was determined by a dilatometric method using a Tesatronic TT-80 (TESA, Switzerland) dilatometer with a measuring probe TESAGT 21HP (measurement range of \pm 200 µm, sensitivity of 0.01

 μ m). The measurements were carried out in air across a temperature range of 50-750°C with a heating rate of 2°/min. A ruby single-crystal rod standard was used to test the dilatometer. Experimental results were treated by the method described in detail elsewhere [11].

2.5 Scanning electron microscopy

The microstructure of the YSZ|glass|YSZ and the Fe-Ni-Co alloy|glass junctions was studied by scanning electron microscopy (SEM) using a MIRA 3 LMU microscope (TESCAN, Czech Republic) equipped with an INCA Energy 350 X-max 80 (Oxford Instruments, Great Britain) system of X-ray energy dispersive microanalysis (EDX). A glass film with a polymeric binder was placed between the alloy and YSZ plates, which "sandwich" was subsequently heated to the sealing temperature and held for 10 min. In order to study cross-sections of the junction, samples were pre-treated by an epoxy impregnation technique under vacuum followed by the preparation of cross-sections using a MetPrep 4/PH-4 (Allied, USA) polishing-grinding machine with a diamond suspension.

3 Results and Discussion.

3.1 Characterisation

According to XRD analysis (Fig. 1), all as-cast glasses exhibited an amorphous structure and showed no reflexes of crystalline phases in the XRD patterns.



Fig. 1. XRD patterns of SiO₂-Al₂O₃-ZrO₂-CaO-Na₂O-Y₂O₃ glasses

The chemical composition, determined by AES, is close to the nominal one (Table 1). An increased Al₂O₃ content, in comparison with the nominal composition, is likely to be connected

with an interaction between the glass melt and the crucible material (corundum), which contributes an additional error to the result.

3.2 Characteristic temperatures

The glasses used as sealing materials should withstand high temperatures for a long time due to the specifics of the SOFC operation. Therefore, it is necessary to determine a safe temperature range, across which the glass sealants maintain their features. This range depends on the characteristic temperatures of the glasses. In order to avoid glass spreading, the operating temperature should be higher than that of the glass transition (to transform into a viscous-flow state) and lower than the melting temperature. Glass transition (T_g) and crystallisation (T_c) temperatures were found from DSC curves shown in Fig. 2.



Fig. 2. DSC curves of SiO₂-Al₂O₃-ZrO₂-CaO-Na₂O-Y₂O₃ glasses

The bends corresponding to the glass transition are observed over a temperature range of 600-700°C (Fig. 2), while exothermal peaks, indicating the crystallisation process, are seen over a temperature range of 900-1000°C. It is difficult to determine the glass transition temperature from the DSC data, since the corresponding bends tend to smooth out along with a growth in the yttria concentration. Therefore, Table 2 presents only glass transition intervals. When the yttrium oxide content increases, the intensity of the crystallisation peaks significantly declines, thus indicating a decrease in the crystallisation rate. It is important that the operating temperatures of electrochemical devices, for which the developed glasses are intended, cover the range of 700-850°C, i.e., be lower than the crystallisation temperature. In this case, the glass sealants will be amorphous under the operating conditions of the electrochemical devices.

Table 2. Temperatures of glass transition (T_g), crystallization (T_c), and sealing (T_s) for SiO₂–Al₂O₃–ZrO₂–CaO–Na₂O–Y₂O₃ glasses

#	T_g , °C	T_c ,	T. ℃	
		onset	peak	<i>Is</i> , <i>C</i>
1	615	922	1020	950
2	630–700	<mark>930</mark>	1050	950
3	610–690	932	1073	940

In order to assess the feasibility of the developed glasses, their sealing temperatures (T_s) should be determined. This involves the estimation of the shape of a glass drop and the contact angle (< 90°). Fig. 3 presents the SEM images of the cross-section of glass drops obtained at various temperatures.



Fig. 3. SEM images of the contact angle of a glass #1 drop onto an YSZ substrate

It can be seen that, although the contact angle is lower than 90° at the temperature of 925°C, the temperature of 950°C was chosen as the sealing one. The reason lies in the fact that the best contact between the materials to be joined is achieved at the lowest contact angles. Therefore, the temperature at which the contact angle is smallest should be considered as preferable [18]. Table 2 displays the values of glass transition, crystallisation, and sealing temperatures for the developed glasses. It can be seen that the substitution of zirconia by yttria slightly affects the value of crystallisation temperatures and has almost no effect on the sealing temperature.

3.3 Thermal expansion

The glass sealants studied in this work are developed for the commutation of tubular elements, i.e., an YSZ electrolyte (CTE of ~ $9.5 \cdot 10^{-6}$ K⁻¹) and a Cr-free alloy (Fe-Ni-Co alloy

with a CTE of ~ $8 \cdot 10^{-6}$ K⁻¹). SOFC devices are assumed to be safely working at elevated temperatures across a range of 700-850°C. The tightness of all the junctions should be maintained while heating the device to working temperatures. Therefore, the sealant material should meet strong requirements so that the compatibility between of all the elements to be joined could be achieved in terms of their thermal expansion behaviour. The CTE of the investigated glasses was measured for the as-cast bulk glasses, and for the pressed powder samples sintered at 850°C for 10 min. According to XRD analysis, zirconia was formed in glass #1 during the heat treatment, while silicon oxide was found in glasses #2 and #3. In general, the structure of all the samples remained amorphous without a noticeable amount of crystalline impurities.

Fig. 4 presents dilatometric curves for the as-cast (bulk) and heat-treated (powdered) glasses.



Fig. 4. Dilatometric curves of bulk and pressed (*) samples of SiO₂-Al₂O₃-ZrO₂-CaO-Na₂O-Y₂O₃ glasses

It can be seen that the bulk and pressed samples demonstrated almost identical thermal expansion behaviour at temperatures of up to 550°C. A further increase in temperature made the bulk glass transform to a viscous-flow state, while the behaviour of the pressed samples remained unchanged up to the softening temperature. The CTE values were calculated from the slope of dilatometric curves assuming their linear character [11]. The concurrence of the CTE of samples with different thermal histories confirms the absence of a significant amount of

crystalline phases in the sealant. In addition, the CTE values were calculated by Appen's method [37] (Table 3); a good agreement is observed between the calculated and experimental results.

Table 3. Coefficients of thermal expansion calculated by Appen's method (α_A) and determined from dilatometric curves ($\alpha_{bulk} \ \varkappa \ \alpha_{pressed}$) across a temperature range of 50-500°C, and the temperatures of glass transition (T_g) and softening (T_d), determined from dilatometry data.

#	$\alpha_{\rm A} \cdot 10^6, {\rm K}^{-1}$	$\alpha_{\text{bulk}} \cdot 10^6, \text{ K}^{-1}$	$\alpha_{\text{pressed}} \cdot 10^6$, K ⁻¹	$T_g,^{\circ}\mathrm{C}$	T_d , °C
YSZ		~9.5		_	—
Alloy (33NC)		~8.0		_	—
1	9.1	9.8	9.4	635	670
2	9.2	9.8	9.5	630	690
3	9.4	9.8	<mark>9.1</mark>	—	—

The CTE values of the pressed samples were found to be slightly lower than those for the as-cast glass. This can be explained by the difference in properties of compacted glass powder and the as-cast glass. Pressed samples can be considered as a huge amount of fine particles, each of which has its own grains, and during sintering not all these grains form close contact. This can lead to the appearance of some anisotropic properties. At the same time, the samples cut from the as-cast glasses can be considered as a huge single grain with isotropic properties. Thus, the morphology of the sintered sample differs from the morphology of the ascast glass, which can cause a slight CTE difference, as observed. According to the obtained data (Table 3), all the glasses under investigation have a good thermal compatibility with YSZ ceramics and Fe-Ni-Co alloys, thus making them suitable for the commutation of tubular single cells.

3.4 Microstructure

In order to investigate the morphology of the glasses under investigation by SEM, the YSZ|glass sealing couples were prepared by heat treatment at T_s (950°C, 10 min). According to XRD data, the glass structure remained amorphous (Fig. 5), with only reflexes corresponding to the YSZ ceramics being observed in the XRD patterns.



Fig. 5. XRD patterns of SiO₂-Al₂O₃-ZrO₂-CaO-Na₂O-Y₂O₃ glasses on an YSZ substrate (heat-treatment at 950°C for 10 min).

Two YSZ ceramic substrates (produced by the Eastern Institute of Refractory Materials) were joined using the glasses (Fig. 6a). The investigated glasses demonstrated a good adhesion and chemical stability to the YSZ ceramics, as confirmed by both XRD and SEM results (Figs. 5 and Fig. 6). An amorphous structure with a small amount of the crystalline phase was characteristic of glasses #1 and #2. It should be noted that some pores were indeed observed in glass #1, however, their amount and size sharply decreased with the addition of yttria (Fig. 6). The same behaviour was observed on the glass/alloy sealing couples (Fig. 6b). The precursor alloy was pre-treated by the technique described in 2.2. According to XRD analysis, the obtained protective layer comprised iron in the following phases: Fe₃O₄, CoFe₂O₄, NiFe₂O₄, NiMn₂O₄ and Fe₂O₃ (Fig. 6b).



Fig. 6. SEM images and EDX maps of cross-sections of an YSZ|glass|YSZ sealing (a) and alloy|glass (b)

For a more detailed study of the interface, SEM images of the glass #3|YSZ and glass #3|coating interface were obtained with higher magnification (Fig. 7).



Fig. 7. SEM image of a cross-section and EDX maps of YSZ|glass #3 (a) and coating|glass #3 joining (b)

As can be seen, no interaction products are observed at either grain boundary which indicates a rather high chemical stability of the sealant to the joined materials. However, the diffusion of cobalt ions is observed on the glass #3|coating boundary (Fig. 7b). This process is undesirable because it can potentially lead to the formation of Co-containing phases in the volume of glass sealant which, in turn, causes changes in the CTE value and can be critical over long-term use. Therefore, the study of the glass|Ni-Co alloy interface during long-term exposure at the SOFC operating temperature will be carried out.

3.5 Glass stability

In order to test whether the glass crystallisation occurs under long-term exposure at the operating temperatures, glasses containing minimum and maximum amounts of Y_2O_3 (#1 and #3, respectively) were heat-treated by the sealing regime (950°C, 10 min) followed by exposure at 850°C for 100 h (Fig. 8). The exposure time was chosen based on literature data: the crystallisation of glass sealants has been shown to be more intensive during the first 100-150 h of

exposure, or during the sealing process [38-40] Samples for this experiment were prepared in two different ways. Thus, cubic samples (~ $3 \times 3 \times 3$ mm) were cut from the as-cast glass (bulk samples), while tablets (thickness ~ 1mm, diameter ~15 mm) were prepared from the powder glass by pressing (powdered samples).



Fig. 8. XRD patterns of bulk and pressed samples of SiO₂-Al₂O₃-ZrO₂-CaO-Na₂O-Y₂O₃ glasses after exposure at 850°C for 100 h

Fig. 8b presents the XRD patterns of bulk and powdered sample #1 after heat treatment for 100 h. Reflexes corresponding to zirconium oxide are observed on the XRD pattern of powdered sample #1, while the bulk sample remains amorphous (Fig. 8b). This fact can be explained by a correlation between particle size and crystallisation kinetics: the smaller the particles, the lower the crystallisation activation energy [41,42]. Since glasses are isotropic with no grain boundaries, the bulk sample can be considered as a single grain with the above mentioned dimensions. On the contrary, pressed and sintered samples do have boundaries between powder particles; therefore, each of them can be considered as a single grain with a size of about ~ 45μ m. The presence of such boundaries and a smaller particle size promotes crystallisation processes. In addition, glass #1 contains the highest amount of ZrO₂, which can act as a nucleating agent accelerating the crystallisation of the SiO₂ phase [43,44]. As a result, a significant amount of ZrO₂ and SiO₂ crystalline phases is observed in powdered sample #1.

Glass #3 remained amorphous in both powdered and bulk samples with only a slightly pronounced peak, corresponding to SiO_2 , being observed in the XRD patterns (Fig. 8). In the case of this sample, the effect of Y_2O_3 addition on the glass crystallisation kinetics is clearly seen: the retained amorphous state of powdered sample #1 indicates that the particle size factor reduces its influence and that ZrO_2 behaves as a nucleating agent.

It should be noted that powdered glass samples are conventionally used for the development of various sealants. Therefore, crystallisation processes in pressed samples become determining factors in selecting a glass as a sealant. It can be seen that glass #3, having the highest amount of Y_2O_3 in its composition, contains a significantly lower content of the crystalline phase after exposure than glass #1. According to the obtained results, the introduction of yttria hampers glass crystallisation in the SiO₂–Al₂O₃–ZrO₂–CaO–Na₂O–Y₂O₃ system.

3.6 Unit cell sealing

In this work, we aimed to develop sealing materials for SOFCs of a tubular construction, the details of which can be found in [11]. The unit element was designed after the investigation of the sealing and interaction processes of the glasses with a ceramic electrolyte and an interconnect material. Since $SiO_2-Al_2O_3-ZrO_2-CaO-Na_2O$ glasses have low CTE values, they cannot be used for joining ceramics with Cr-containing alloys (CTE of $11-12\cdot10^{-6}$ K⁻¹)⁵; however, they can be joined with Cr-free alloys, e.g., Fe-Ni-Co ones (CTE ~8-10·10⁻⁶ K⁻¹). In addition, the use of chromium steels is undesirable due to the tendency of calcium and sodium oxides to form chromates on the alloy|sealant boundary, as was shown based on thermodynamic calculations [11].

Fig. 9a presents typical dilatometric curves for glasses, an Fe-Co-Ni alloy, and a YSZ ceramics. It can be seen that the character of the alloy thermal expansion behaviour is non-linear, which is likely to be connected with the phase transition characteristics of Fe-Ni-Co alloys [45].



Fig. 9. Dilatometric curves of electrolyte ceramics, interconnect and glass (a) and the SEM image of an YSZ|glass #1|Ne-Fe-Co alloy unit tubular cell (b).

Across a temperature range of $50-500^{\circ}$ C, the CTE of these alloys is close to that of the materials being joined. At temperatures above 500° C, the dilatometric curve slope of the alloys changes sharply, which indicates an increase in CTE. The CTE of the alloys over a temperature range of $500-800^{\circ}$ C equals $16.5 \cdot 10^{-6}$ K⁻¹. It is obvious that such changes are undesirable due to a possible damage of the construction when cooling the cell after sealing, or when subsequently heating the cell to the operating temperature. However, our experimental results demonstrate no cracks on the YSZ| glass| alloy single cell after sealing followed by cooling to room temperature (**Fig. 9b**). In our opinion, this can be explained by the use of a non-crystallising sealant, since glass in the viscous-flow state is capable of withstanding increased mechanical stresses arising under cooling due to a large difference in the CTE of various materials. As mentioned above, glass crystallisation is accompanied by a sharp increase in the CTE value, which negatively affects the integrity of the sealing. Non-crystallising sealants are free from these disadvantages, which make them suitable for joining materials with unstable CTEs.

Further detailed studies should be conducted to investigate the behaviour of noncrystallising glass sealants in contact with Fe-Ni-Co alloys under the conditions of prolonged high-temperature exposure and thermal cycling.

Conclusions.

A number of glasses of the 59.6SiO₂-11.0Al₂O₃-(10.6-*x*)ZrO₂-3.4CaO-15.4Na₂O*x*Y₂O₃ composition (x = 0; 2; 4 wt.%) have been obtained and thoroughly studied. Using differential scanning calorimetry and X-ray diffraction, it was established that a partial substitution of zirconia by yttria restrains the crystallisation ability of these glasses. Dilatometric measurements demonstrated that a change in the ZrO₂/Y₂O₃ ratio has a negligible effect on the glass CTE value: the CTE value is shown to be ~ 9.5·10⁻⁶ K⁻¹ over the temperature range from 50 to 500°C.

It was found that yttrium oxide is capable of suppressing the crystallisation ability of the glasses, even under exposure at 850°C for 100 h. Therefore, the CTE value of this glass sealant is expected to be stable during prolonged SOFC operation. According to the SEM results, the glasses formed a tight contact of YSZ|glass|Fe-Ni-Co alloy tubular single elements. No interaction was observed on the boundaries of YSZ|glass and glass|alloy. Moreover, the use of this non-crystallising sealant allows the tightness of the junction to be maintained despite a sharp increase in the CTE of a Ni-Fe-Co alloy.

The development of non-crystallising sealants that are capable of retaining their properties at SOFC operating temperatures is extremely important in terms of designing SOFCs with enhanced durability.

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