

Characterization and performance of glass-ceramic sealant to join metallic interconnects to YSZ and anode-supported-electrolyte in planar SOFCs

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Abstract

This work describes the design, development and performance of a glass-ceramic sealant used to join the ceramic electrolyte (YSZ wafer and anode-supported-electrolyte (ASE)) to the metallic interconnects (Crofer22 APU and AISI 430) in planar SOFC stacks. The designed glass-ceramic sealant is a barium-free silica-based glass, which crystallizes by means of the heat treatment after being deposited on substrates by the slurry technique. The sealing process of the glass-ceramic was optimized and joined ceramic/seal/metal samples were morphologically characterized and tested for 400 hrs in air atmosphere followed by 200 hours in H₂-3H₂O atmosphere at the fuel cell operating temperature of

800°C. The study showed that the use of the glass-ceramic was successful in joining the ceramic electrolyte to the metallic interconnect and in preventing adverse corrosion effects at the interface.

1. Introduction

Solid Oxide Fuel Cells (SOFCs) are highly efficient energy conversion devices which produce electricity by the electrochemical reaction between fuel and an oxidant [1-3].

Among the different types of SOFCs, the planar type is expected to be cost-effective and mechanically robust and offers an attractive potential for increased power densities compared to other concepts [4]. A fuel-cell device is composed of an anode electrode (exposed to the fuel), an electrolyte and a cathode electrode (exposed to the oxidant) [5].

Several individual cells are connected in series in order to form a “stack” to obtain usable cell voltage and power. In a conventional SOFC, a dense yttria-stabilized zirconia oxygen-ion conducting electrolyte membrane separates a porous nickel-zirconia cermet anode and a doped lanthanum-manganite-perovskite cathode. The repeating unit of a planar configuration is formed by the combination of joint anode-electrolyte-cathode structures and interconnect which provides electrical connection between the anode of one individual cell (repeating unit) to the cathode of the neighbouring one [6, 7].

A key problem in the fabrication of planar SOFCs is the sealing of the electrolyte (yttria-stabilized zirconia wafer or anode-supported, depending on the cell configuration) with the metallic interconnect, in order to obtain a hermetic (gas tight) joint.

The materials selected as sealants must be thermo-mechanically and thermo-chemically stable in both oxidizing and wet-reducing environments at 800°C for long-term exposures (500-1000 hours) [38].

Currently, five main approaches are being studied for sealing SOFCs [8, 9]: brazing [10], compressive seals [11,12], glass [13-16], glass-ceramic [17] and glass-composite seals [18-21]. Glasses and glass-ceramics show better resistance to the severe service environment (both oxidizing and reducing) than brazing alloys, and by carefully choosing the glass composition, they can meet most of the requirements that need to be exhibited by the ideal sealant material [22-30].

Glass-ceramics can be prepared by controlled sintering and crystallization of glasses and have superior mechanical properties and higher viscosity at the SOFC operating temperature than glasses. Furthermore, glass-ceramics can have thermal expansion coefficients very different from the parent glass, due to the different crystalline phases and their relative concentration. In order to develop a suitable glass-ceramic sealant, it is therefore necessary to understand the crystallization kinetics, the sealing properties and the chemical interactions when in contact with other components of the cell [31, 32]. For example, barium aluminosilicate sealants have shown high reactivity with the metallic interconnect at 800-900°C forming a porous and weak interface composed of barium chromate ($BaCrO_4$) and monocelsian ($BaAl_2Si_2O_8$) [33] [34] , while phosphate and borate glasses are not sufficiently stable in a humidified fuel gas environment [35].

In a previous study, a barium- and boron-free glass-ceramic (labeled as SACN) was chosen to join Crofer 22 APU alloy to an yttria stabilized zirconia (YSZ) wafer. In the work that is reported here, the same glass-ceramic has been used to seal AISI 430 to YSZ

and Crofer 22 APU to the anode-supported-electrolyte (ASE) in order to examine the compatibility of the SACN composition with the metallic interconnect and the electrolyte. In addition, the joined samples were submitted to thermal ageing tests for 400 hours in air atmosphere and, successively, for 200 hours in H₂-3H₂O atmosphere at the fuel cell operating temperature of 800°C. This paper describes the interaction of the sealant (SACN) with Crofer22APU, AISI 430, YSZ and the anode-supported-electrolyte (ASE) at 800°C, at both reducing and oxidizing conditions.

[36] - [38]

2. Experimental

The heat resistant metal alloys used for this study were Crofer22 APU (manufactured by Thyssen Krupp, Germany and supplied by HT Ceramix, Switzerland) and AISI 430 which are ferritic stainless steels containing 22 wt% and 16 wt% chromium respectively and exhibiting a thermal expansion coefficient of $11.2\text{-}11.5 \times 10^{-6}$ K⁻¹. The Crofer 22APU was pre-oxidized as described in ref [1]. The yttria 8 mol% zirconia wafer (with a thermal expansion coefficient of 10.5×10^{-6} K⁻¹) had a thickness of 200 μm. The anode-supported-electrolyte (ASE) and the YSZ were supplied by HT Ceramix (Switzerland). The Crofer22 APU, AISI430, YSZ, and ASE samples to be joined were cut to dimensions: 8 × 6 × 2 mm³.

The sealant composition ranged between 50-55 wt% SiO₂, 10-12 wt% Al₂O₃, 20-23 wt% CaO and 10-12 wt% Na₂O. The melting procedure, thermal and thermo-mechanical characterization of the sealant are described elsewhere [1].

Studies of the wettability of the SACN glass on the AISI 430 alloy (as-received and preoxidised at 900°C in air for 2 hours) and on the ASE wafer were carried out by heating microscopy (LEITZ WETZLAR, Germany) or in a tubular oven under air or Ar atmosphere. The SACN glass powders (38-75 μ m) were deposited on AISI 430 and ASE samples by slurry coating and heated to obtain the joint and subsequently examined by optical microscopy and scanning electron microscopy (SEM).

The joined samples were obtained by placing the Crofer 22APU or AISI 430 plates on YSZ or YSZ surface of the anode-supported-electrolyte with the SACN slurry sandwiched in between. Heat treatments were performed in a tubular oven (Ar atmosphere) at a temperature above the glass softening point, without applying any load. Reproducible results, in terms of joint thickness and homogeneity were obtained. The joining thermal treatment was carried out from room temperature to 900°C with a dwelling time of 30 minutes at 900 °C and a heating rate of 5 °C/min.

In order to evaluate the bonding strength of the glass-ceramic sealant, SACN and Crofer 22 APU (about 6X6 mm²) square samples were joined by the glass-ceramic to obtain a sandwich-like structure. A modification of ASTM C633-01 [39] was designed and performed according to the apparatus reported in figure 1, where the specimen is joined to the upper and lower grips by an epoxy resin (araldite AV 119). The Crofer 22APU/SACN/ Crofer 22APU and AISI430/SACN/AISI430 joints were tested in uniaxial tension at room temperature, by using a loading rate of 0.5 mm/min.

Joined AISI430/SACN/YSZ and Crofer22APU/SACN/YSZ samples were submitted to thermal ageing in air atmosphere at 800 °C up to 400 hours in a tubular furnace and, successively, exposed to H₂-3H₂O atmosphere (800°C for 200 hours). The experimental

apparatus built for the tests consisted of an alumina cylinder (80X80X30 mm³) containing the joined samples; this housing was connected to an alumina tube (diameter 10 mm) (scheme?) and filled with H₂-3%H₂O gas (500 Nml/min). The reducing mixture (H₂-3% H₂O) was obtained by using H₂ gas, which was humidified by passing over a water bath kept at a constant temperature of 22.8 °C.

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The whole system was placed inside a furnace and a thermocouple was positioned near the samples in order to monitor the sample temperature. The heating rate was 30°C/hour and the dwelling time at 800°C was 200 hours.

Cross-sections of joined samples were characterized by SEM (FEI Inspect and Philips 525 M) after polishing. EDS (SW9100 EDAX) analysis was carried out in order to detect any elemental diffusion into the seal before and after H₂-3%H₂O atmosphere exposure (800°C for 200 hours) and to study the chemical interactions of Crofer22APU, AISI 430, and ASE with SACN at the three-phase-boundary at 800°C under reducing and oxidizing conditions.

3. Results and discussion

3.1 Crofer22APU/SACN/ASE joined samples: morphological analysis.

Figure 2 shows a SEM micrograph of a Crofer22APU/SACN/ASE cross-section. The joint region has an average thickness of 150/200 µm. Examination around the seal shows that a very low amount porosity (which is closed) is present indicating that this sealant

will provide high gas tightness and a hermetic structure. A very good adhesion between the glass-ceramic and both Crofer 22 APU and YSZ can be observed. The choice of the glass-ceramic composition is partly based on the value of its thermal expansion coefficient of $10.7 \times 10^{-6} \text{ K}^{-1}$ [1] which matches very well those of Crofer 22 ($11.2-11.5 \times 10^{-6} \text{ K}^{-1}$) and YSZ ($10.5 \times 10^{-6} \text{ K}^{-1}$). The absence of cracks near the interface of the glass ceramic with both Crofer 22 APU and YSZ demonstrates their good physical compatibility with the SACN glass-ceramic. Figure 3 is a magnification (rectangular area in Figure 2) of the interface zone between the glass-ceramic and the YSZ. The interface is continuous and without pores or cracks. Two distinct zones can be observed in the anode supported electrolyte; the upper zone in the figure represents the porous anode, while the lower region shows the dense YSZ electrolyte. The thickness of the YSZ electrolyte, supported on the anode, is about 5 microns. This feature ensures the capability of the SOFC to operate at a temperature of 800°C.

3.2. AISI 430/SACN/YSZ joined samples: morphological analysis.

A SEM cross-section image of the AISI430/SACN/YSZ joined sample is shown in figure 4a. Both interfaces are continuous and defect-free. The SACN adhered well to both the preoxidised AISI430 and YSZ substrates. Concerning the AISI430/SACN interface, it must be highlighted that in order to obtain a good adhesion between AISI 430 and the glass-ceramic sealant, the preoxidation heat-treatment (900°C, 2 hrs, air) was essential, since in the case of the as-received AISI 430, the glass-ceramic layer was detached from the metallic interconnect. The pre-oxidation treatment gave rise to the formation of a 1-2 μm thick chromium–manganese–iron oxide layer, as detected by means of XRD.

Figure 4b shows the SEM micrograph of the AISI 430/SACN interface. The coherent pre-oxidation layer is clearly visible. The SACN glass-ceramic adhered well to the preoxidised AISI 430 and a defect free structure, without voids and micro cracks, can be observed.

3.3. Crofer22APU/SACN/YSZ joined sample exposure to H₂-3%H₂O atmosphere

The Crofer22APU/SACN/YSZ joined samples were previously tested in air at 800°C up

to 400 hrs. The results of the thermal ageing are reported in detail in a previous paper [1].

After a mid-term exposure (200 hours) at 800°C in a reducing atmosphere (H₂-3%H₂O),

it was observed that the seal remained intact. Figure 5 shows a SEM cross-section of the

of Crofer22APU/SACN/YSZ sample after 200 hours exposure to H₂-3%H₂O atmosphere.

The SEM micrograph is focused on the central part of the joined sample. It is evident that no interfacial delamination at the glass-ceramic/steel interface took place. It can be also observed that the joint region does not exhibit substantial modifications from the morphological point of view. No cracks or pores are present, and the interfaces between the SACN glass-ceramic and both Crofer 22 APU alloy and YSZ ceramic are still continuous and free of cracks.

As described before, the Crofer 22APU was preoxidised (900°C, 2h) before the joining process. It has previously been reported [15] that the oxidation of Crofer22 APU in air resulted in a chromium-manganese oxide layer at the alloy surface. The oxide layer is thermodynamically very stable. Figure 5a shows a details of the interface between the SACN glass-ceramic and the pre-oxidized Crofer 22 APU, where the chromium-manganese oxide layer is clearly visible. EDS spot-analysis conducted at point 1 revealed

the presence of chromium, manganese and oxygen, while at point 2 only O, Na, Al, Si and Ca were detected (as before exposure to H₂-3%H₂O atmosphere). This observation confirmed that no undesired reactions took place and no corrosion products were formed at the Crofer 22 APU-glass-ceramic sealant interface during exposure to the H₂-3%H₂O atmosphere. As discussed by Ogasawara et al. [41], the enrichment of sodium in the pre-oxidation layer is potentially dangerous and can lead to the formation of Na₂CrO₄. The high vapour pressure of this alkali chromate can result in its vaporization which can be accompanied by the decomposition and removal of the (Mn,Cr)₃O₄ spinel oxide, and chromium depletion in the surface vicinity. In addition, depletion of sodium from the SACN at the interface with Crofer 22APU is likely to reduce the quality of the joint due to the formation of cracks. Interfacial delamination cracks between the sealant and the metallic interconnect must be avoided, because they can act as a preferential path for fuel transport.

In contrast to the study by Ogasawara et al. [41], the results of the present study showed that there was no transport of sodium away from the SACN sealant which maintained good adhesion to the two substrates. The reason for this was probably due to the higher thermodynamic stability of the SACN glass-ceramic that was used in the present study compared to the glass sealant used by Ogasawara et al. [41]. The main composition difference between the two studies was that the glass ceramic that was used in the present study contained 20-23% CaO, while the glass sealant used in reference 41 had no CaO at all. Unfortunately Ogasawara et al. [41] provided only the composition of the glass sealant that they used, but gave no information on the phases that were present. As a result a thermodynamic comparison between the two sealants is not possible. However,

the high amount of CaO in the glass ceramic used in the present study is very likely to lead to the formation of a more stable oxide at the interface.

Figure 5b shows a magnification of the interface between the SACN glass-ceramic and YSZ indicating that the interface is free of pores and cracks.. An EDS line scan analysis (from YSZ to 15 microns into the glass-ceramic; Figure 5c) revealed no diffusion of yttrium from YSZ into the glass-ceramic. This result confirmed the thermo-chemical compatibility of the SACN and YSZ at 800°C under a dual atmosphere. This is in contrast with what was previously observed by Lahl et al.[40], where the presence of CaO in glasses in contact with YSZ lead to the formation of monoclinic ZrO₂, because of yttrium diffusion into glass. This result could be detrimental to SOFCs, because of the formation of monoclinic ZrO₂ could lead to the formation of cracks at the interface.

Since corrosion products and undesired reactions between the glass-ceramic and Crofer 22APU could be found at the three-boundary zone (metal-sealant-gas) after exposure to reducing conditions for 200 hours, SEM was conducted at the edges of the joined samples.

Figure 6 shows a magnification of the three-phase-boundary zone, between Crofer 22APU, the glass-ceramic and the H₂-3%H₂O atmosphere at 800°C after 200 hours at 800°C. A grain boundary-dominated internal oxidation in Crofer 22 APU (corrosion zone) can be observed only in the area that is not protected by the SACN glass-ceramic sealant. In our system (SACN/Crofer 22 APU), there was no internal oxidation of the ferritic steel beneath the SACN glass-ceramic sealant and the quality of the bond between the SACN and Crofer 22 APU was still outstanding. The crystalline phases of the SACN

glass-ceramic did not change after thermal ageing, thus confirming the thermo-chemical stability of the SACN glass-ceramic seal.

3.4 AISI430/SACN/YSZ joined samples exposure to air and H₂-3%H₂O atmospheres

These joined samples were first subjected to heat-treatment in air for up to 400 hours at 800°C. Examination of a cross-section of the joint sample indicated that there were no cracks near the interface. As for the Crofer22APU/SACN/YSZ system, SEM and XRD observations in the AISI430/SACN/YSZ joint confirmed that no undesirable reactions took place and no corrosion products were formed at the AISI 430-glass-ceramic sealant interface.

Concerning the AISI430/SACN/YSZ samples exposed to H₂-3%H₂O atmosphere, as for the Crofer22APU/SACN/YSZ system, there was no formation and vaporization of alkali chromates and consequently there was no chromium depletion at the three-phase-boundary. As a consequence, no swelling of the metal with consequent bulging was observed. Figure 7a shows a SEM cross section of an AISI430/SACN/YSZ sample; it can be observed that no interfacial delaminations at the glass-ceramic steel interface took place. Figure 7b presents a magnification of AISI 430/SACN interface; also in this case no undesired reactions took place and no corrosion products were formed at the interface, as confirmed by EDS analyses. Figure 7c shows the AISI 430/SACN interface at the three-phase-boundary after the tests in H₂-3%H₂O atmospheres. As discussed for the Crofer22APU/SACN samples, there was no internal oxidation within the zones where the SACN covered the metal alloy.

3.5 Bonding strength of Crofer 22 APU to glass-ceramic sealant

The bond strength of the joint between the Crofer 22 APU and the glass-ceramic was investigated by carrying out uni-axial tensile tests at room temperature. The average tensile strength value was 6 MPa. Figure 8 shows the fracture surfaces where 2 layers of SACN are viewable on both Crofer 22APU samples. Examination of these samples revealed that the fracture always occurred through the glass ceramic and never at the metallic interconnect/glass-ceramic interface. This observation suggested that the bonding strength for the joint was high with very good adhesion.

Conclusions

A detailed characterization and performance of a glass-ceramic sealant that was specially developed for use in SOFCs to join the metallic interconnects to the YSZ and anode-supported-electrolyte, the Crofer 22 APU and AISI 430 was carried out. The tests of the joined samples after exposure to air and humidified hydrogen at 800 °C (respectively for 400 and 200 hours) revealed no corrosion products at the interfaces between metallic interconnects and glass-ceramic sealant. There was no chromium depletion at the surface of the Crofer 22 APU close to the three-phase-boundary. As a consequence, no swelling of the metal (both Crofer 22 APU and AISI 430) with subsequent bulging was observed. The overall conclusion of the work that was presented was that the glass-ceramic sealant was effective to joining both Crofer 22 APU and anode-supported-electrolyte.

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Figure Captions

Figure 1 Experimental apparatus to measure the tensile strength of joints (Crofer 22 APU/SACN/ Crofer 22 APU and AISI430 /SACN/AISI430)

Figure 2 Crofer 22 APU/SACN/ASE SEM cross section

Figure 3 SEM cross section of the interface zone between the SACN and the YSZ side of ASE in Crofer 22 APU/SACN/ASE joined sample

- Figure 4a AISI430/SACN/YSZ SEM cross section
- Figure 4b AISI430/SACN interface: SEM cross section
- Figure 5 Crofer 22 APU/SACN/YSZ after exposure to H₂-3%H₂O atmosphere at 800°C up to 200 hours: SEM cross section
- Figure 5a Crofer 22 APU/SACN interface after exposure to H₂-3%H₂O atmosphere at 800°C up to 200 hours
- Figure 5b YSZ/SACN interface after exposure to H₂-3%H₂O atmosphere at 800°C up to 200 hours
- Figure 6 Magnification of the three-phase-boundary zone, between Crofer 22APU, SACN and H₂-3%H₂O atmosphere at 800°C , 200 hours (Crofer22APU/SACN/ YSZ joint)
- Figure 7 SEM cross section of the of pre-oxidized AISI430/SACN/YSZ sample after exposure to H₂-3%H₂O atmosphere at 800°C up to 200 hours
- Figure 7a SEM magnification of pre-oxidized AISI 430/SACN interface after exposure to H₂-3%H₂O atmosphere at 800°C up to 200 hours
- Figure 7b Magnification of the three-phase-boundary zone, between pre-oxidized AISI 430, SACN and H₂-3%H₂O atmosphere at 800°C up to 200 hours
- Figure 8 Fracture surfaces of Crofer22APU/SACN