INTERACTION OF METALLIC SOFC INTERCONNECT AND GLASS-CERAMIC SEALING UNDER VARIOUS ATMOSPHERIC CONDITIONS AT 800°C

Norbert H. Menzler¹, Doris Sebold¹, Sonja M. Gross², Vladimir Shemet¹ and Mohsine Zahid¹

¹Institute for Materials and Processes in Energy Systems
²Central Department of Technology
Forschungszentrum Jülich, 52425 Jülich, Germany

ABSTRACT

The interaction of the metallic parts of a solid oxide fuel cell (SOFC) and the glass-ceramic sealant was characterized under various atmospheric conditions by a quick and simple test method. The metallic material used was a high-chromium steel specially developed for SOFC applications (two different compositions) designated Crofer22APU ¹st and JS-3 while the glass-ceramic composed of BaO-CaO-Al₂O₃-SiO₂ (BCAS, known as glass A) was also designed for SOFC use. Air, humidified air and humidified hydrogen were used as atmospheres. The tests were carried out at an SOFC operating temperature of 800°C for times varying from 1 to 500 hrs. The results show that air or humidified air does not lead to enhanced negative interaction effects, either in the metallic or in the glass-ceramic material. In contrast, the interaction under humidified hydrogen causes internal oxidation in the steel. However, the corrosion intensity is much higher in the steel material where some special minor constituents were added, especially aluminum and silicon, than in the nearly Al- and Si-free steel material. Thus the final purity of the metallic material is of crucial importance for long-term use in SOFCs. Additionally, the presence of either humid hydrogen or humid hydrogen and a low oxygen partial pressure in the surrounding atmosphere has a detrimental effect on the interaction behavior of the glass-ceramic and metallic parts of the SOFC. The test method presented here can act as an initial fast and simple screening test to characterize the interaction of the metallic and glass-ceramic parts of an SOFC.

INTRODUCTION

To date, SOFC research has mainly focused on the development and optimization of one of the SOFC part, i.e. the development of novel cell materials for the electrodes and the electrolyte, or the type and composition of sealant materials, or the implementation of steel alloys as interconnect material. In recent years, greater work has been done on characterizing the interactions between the different SOFC parts either under artificial atmospheres or under realistic SOFC gases. Especially, the scaling material was investigated, for example by Horita et al. (1) who characterized the reaction of pyrex glass used as sealant with either YSZ (yttria-stabilized zirconia, electrolyte) and calcium-
doped lanthanum chromite (ceramic interconnect). Lahl et al. (2) described the interaction of an aluminosilicate glass sealant with the components on the anodic part of the cell, e.g. YSZ and nickel oxide. Furthermore, Yang et al. studied the interaction between barium-calcium-aluminosilicate glasses and ferritic stainless steel interconnect materials (3,4). They found that at the edges of the sandwich samples (glass sealant between two metallic plates), barium-chromate phases were formed. Both investigations were conducted under air conditions only for short durations. Thus the investigations can be referred to as short-term testing. In a subsequent paper Yang et al. (5) performed similar tests but for time periods up to 168 hrs (1 week) at 750°C. Additionally a steel material named Crofer22APU 1st specifically developed for SOFC applications was characterized (6). The authors found enhanced chemical compatibility with their glass seal material and the Crofer22APU 1st steel. After prolonged reaction times even barium-chromate is formed. These tests may be referred to as mid-term tests. But even these tests were performed only under air conditions. Haanappel et al. (7) created a novel method to investigate the interaction between glass-ceramic sealants and metallic interconnects under simulated SOFC stack conditions by exposing the glass-ceramic / steel samples to an air – hydrogen dual atmosphere and simultaneously addressing the short-circuiting phenomena by measuring the electrical resistance over the glass-ceramic layer between two metal sheets. Test runs varied from a few hours up to long-term exposures. Results of these investigations are reported in a separate contribution (8).

To date, there have been no reports on easy and simple mid-term or long-term test procedures under varying atmospheres at elevated temperatures characterizing the interaction of metallic and glass-ceramic parts within an SOFC at SOFC operating temperatures and atmospheric conditions (oxidizing or reducing).

This paper deals with the description of the interaction of Crofer22APU 1st and JS-3 used as metallic interconnect materials and a sealant glass-ceramic called glass A (9), which is mostly composed of silica, alumina, barium and calcium oxide, by a fast and simple test method. Additions of minor constituents of transition metal oxides complete the composition. The tests were performed under three different atmospheric conditions (air, humidified air and humidified hydrogen) at SOFC operating temperature (800°C) for durations between 1 and 500 hrs.

**MATERIALS AND EXPERIMENTS**

The sealant material is based on a four-component oxide system including barium oxide, calcium oxide, alumina and silica (B-C-A-S). Minor constituents are boron, zinc, lead, and vanadium oxide (9). The manufacturing of the material follows as described in detail in (10), starting with melting, rapid cooling, fritting, remelting and cooling. Subsequently a paste is formulated for applying the glass by a dispenser system. After application and drying, the paste is burned-out so that the glass becomes viscous and is subsequently crystallized at 850°C followed by annealing at 800°C for several hours. After the crystallization step, the glass-ceramic is stable in oxidizing and reducing atmosphere, is gastight and has long-term stability. The material is thus termed a glass-ceramic and designated as glass A. The glass-ceramic used for the tests was either applied in the aforementioned way or in a parallel test regime was pre-crystallized, crushed and a paste...
was formulated. Thus for the tests, the glass phase exists at the beginning either as an amorphous phase or is already crystallized.

As the metallic part, two high-chromium steels especially designed for SOFC applications were used, a pre-pilot material known as JS-3 developed at Research Centre Jülich (6) and a commercial steel designated Crofer22APU 1st (ThyssenKrupp VDM, Werdohl, Germany) (11), which is industrially produced according to the JS-3 formula. The main difference between the two steels is a minor amount of silicon and aluminum in the commercial material. JS-3 is almost free of Si and Al.

To conduct the tests, metal plates of dimensions 10x20 mm² were cut from metal sheets with a thickness of 2 or 2.5 mm. The plates were subsequently polished on one side and then cleaned with deionized water and ethanol. The glass paste was applied on the polished side by dispensing five droplets. Besides these samples, an additional type of specimen was prepared. Here the glass droplets were put on one steel plate and on top of the droplets a second steel plate was applied. Thus a sandwich sample was created. One metal plate was always Crofer22APU 1st while the other one was JS-3.

Three different atmospheres were chosen for the tests. Starting with ambient air, a second test run was carried out under humidified air (50% H₂O abs.) followed by a third under humidified hydrogen (3% H₂O abs.). All tests were run at 800°C which corresponds to the normal operating temperature of the planar Jülich SOFCs. Air simulates the cathode side of the SOFC. The two moist atmospheres are based on stack post-mortem characterizations where it was found that either water vapor or hydrogen may cause different forms of interactions within the metal bipolar plates and the glass-ceramic sealant (not yet published). Humidification of the gases is obtained by bubbling the gas through water.

After applying the glass or glass-ceramic paste, the samples were heated in conditions compared to stack testing. After times of 1, 5, 25, 150 and 500 hrs the samples were retained for characterization. Firstly, the adhesion was characterized (fast cooling from 800°C to room temperature), secondly the samples were photographed and then cut, polished and prepared for SEM (LEO 1530 – Gemini) investigations.

By combining three atmospheres, two steels and the glass in two starting conditions, a matrix of 12 tests with altogether 60 samples (for 5 duration times) was established. Additionally 6 tests (30 samples) were carried out as “sandwich-tests”, which means that the glass droplets were applied within two steel plates composed of both steel materials.

**RESULTS**

**Annealing Under Air**

After retrieving the samples from the furnace, the first result was always the adhesion of the glass-ceramic droplets on the steel. Since the tests for all time periods were carried out within the same furnace, the retrieved samples were quickly cooled down from 800°C to ambient temperature. This procedure results in spalling off of some droplets. Subsequently the adhesion of the droplets on the steel can be described qualitatively. The
pre-crystallized glass-ceramic droplets have less adhesion than the non-pre-crystallized ones. The glass-ceramic and the metal form a strong interaction zone within the sealing of the glass-ceramic material, resulting in enhanced adhesion. Additionally, the adhesion on JS-3 is better than on Crofer22APU 1st. The yellowish color of the samples is from the formation of barium-chromate on the top of the sealant. This finding was earlier reported by Yang et al. (3, 4), by Lahl et al. (2) and by Geasee (12). After 500 h of exposure, no internal oxidation in the steel is visible (Fig. 1). Thus it can be concluded that ambient air has no negative influence on the interaction of the metallic and the glass-ceramic part.

**Annealing Under Humidified Air (50% abs.)**

No negative influence of the humidified air could be observed even after the longest duration of 500 hrs. The adhesion of the glass droplets was comparable and there was also no internal corrosion of the steel. So it could be concluded that the presence of moisture has no significant influence on the interaction of both materials tested.

**Annealing Under Humidified Hydrogen (3% abs.)**

**Mid-term Exposure (25-150 h):** After an exposure of 25 h, first internal oxidation in the steel is visible. Fig. 2 shows optical micrographs of both glass-ceramic-metal combinations. However, the microstructure of the oxidized region and the oxidation scale differs considerably. While the oxidation for the JS-3 / glass A combination is greater on a volumic scale with dimensions of 50 μm width and 15 μm depth, Crofer22APU 1st oxidation is more grain-boundary-oriented with a width of about 120 μm and a depth of approx. 20-25 μm. The starting point for both oxidation reactions is the triple phase boundary metal / glass-ceramic / atmosphere. Oxidation progresses after prolonged exposure times (150 h) for both material combinations. The structure of the oxidation is similar for both combinations after 25 h. After annealing time, of 150 h all glass droplets spall off after being removed from the furnace.
Long-term Exposure (500h): Prolongation of annealing has influence on the internal oxidation of the steel. The oxidation is strongly progressed. Fig. 3 shows a cross section of the sandwich sample after 500 h in humidified hydrogen. It is obvious from Fig. 3 that either the scale of oxidation or the oxidation morphology is different between the two steel materials. While JS-3 oxidizes, as previously stated, in volume with widths of approx. 100 µm and depths of 20 µm, Crofer22APU 1st oxidation is more grain-boundary dominated. The oxidation width reaches 350 µm and the depth is up to 100 µm. In both cases, the resulting oxide is chromia and the composition is nearly identical (with less amounts of manganese and tracer elements; especially alumina and silica are enriched in the oxide formed in Crofer22APU 1st). Due to the enhanced chromium oxidation in the Crofer22APU 1st the steel surface bulges dramatically. Increases of up to 50 µm were observed.

A careful characterization was made of the grain-boundary-dominated oxidation of Crofer22APU 1st. Fig. 4a shows, as an example, the grain boundary oxidation with enhanced oxidation propagation into the steel sample. Fig. 4b shows the obvious grain boundary domination of the oxidation process followed by spreading into the metal grains. In Fig. 5, the result of a line scan of the oxidized grain boundary and the neighboring metal grains is shown. The analytical result shows homogeneous distribution within the grains of iron, chromium, manganese and oxygen with depletion of iron in the oxidation zone and vice versa an enrichment of the chromium, manganese and oxygen. Additionally, in the oxidation zone, aluminum and presumably silicon can be detected. This leads to the conclusion that aluminum and silicon are enriched in the grain boundaries. It remains to be clarified whether the aluminum and silicon enrichment is a result of internal oxidation or whether this is the reason for the oxidation.

In Fig. 6, result of a line scan of an oxidation peak is presented. Aluminum and oxygen are clearly detectable. The detection of silicon is less definite (thus not shown). This result shows that aluminum is present at the grain boundary before the oxidation occurs.

All the above-mentioned statements are similar for the metal samples exposed in combination with the pre-crystallized glass-ceramic.

Table 1 summarizes the depth of internal oxidation, the adhesion properties and the thickness of the oxide layers formed under aforementioned atmospheric conditions.
depending on the steel/glass-ceramic material combinations (only for the samples with non pre-crystallized glass).

![Figure 3. SEM cross section of sandwich sample annealed for 500 hrs under humidified hydrogen.](image)

![Figure 4. SEM cross section of Crofer22APU 1st sample annealed for 500 h in humidified hydrogen; a) overview of the grain-boundary-dominated internal oxidation, and b) higher magnification of the rectangle marked in picture a.](image)

**Table 1. Oxidation depth depending on material combinations and atmospheric conditions.**

| Metal/glass-ceramic combination | Atmosphere and oxidation depth |
|--------------------------------|--------------------------------|
| JS-3/glass-ceramic             | Air none none ~20μm            |
| Crofer22APU 1st/glass-ceramic  | Humidified air none ~100μm; oxidation tips up to 250μm |
Figure 5. SEM cross section and line scan of a sample annealed for 500 h in humidified hydrogen; EDX analysis of Fe, Cr, Mn, O, Al and Si.

Figure 6. SEM cross section and linescan of the oxidation peak.
DISCUSSION

Annealing Under Air and Humidified Air

Exposure times of up to 500 h for specimens containing material combinations of a glass-ceramic sealant in the pre-crystallized or non-pre-crystallized state with Crofer22APU 1st or JS-3 do not lead to corrosion or internal oxidation effects of the metal. Both metals interact with the glass-ceramic sealant to form a bonding layer. The formation of the oxidic double layer on the steel is influenced in the wetting zone of the glass-ceramic on the steel. However, no negative influence with respect to adhesion, cracking or enhanced interdiffusion was observed. Thus it can be concluded that the combination of the high-chromium containing steel Crofer22APU 1st and JS-3 and the barium-calcium-aluminum-silicate glass A could be used within an SOFC stack to seal the air compartment side.

Annealing Under Humidified Hydrogen

Exposure to humidified hydrogen, which can be regarded as the model gas for the anodic side of an SOFC, of both material combinations leads to internal oxidation of the steel. JS-3, which is purer with respect to minor trace elements than Crofer22APU 1st, which is a commercial product, forms chromia beginning at and localized on the triple-phase boundary of the edges of the glass-ceramic sealant (glass-ceramic/steel/atmosphere). This oxidation is three-dimensional and volumic. The oxidation is caused by the interaction of chromia or chromia vapor species with the barium oxide of the glass-ceramic. Barium and chromium react to form barium-chromate on the surface of the sealant. Thus chromium is released from the oxide layer and oxidation subsequently occurs. During the exposure times of this test, no cessation of the oxidation was observed. Normally it should stop after the availability of the barium is reduced due to the incorporation of the barium in the crystalline phases of the glass-ceramic. The chemical stability of crystallites is usually better than the corresponding amorphous phase. There are two sources of oxygen for the formation of chromia; either the oxygen partial pressure due to the water content of the surrounding atmosphere (3% abs. water vapor) or the oxidic amorphous sealant.

For the material combination Crofer22APU 1st and glass A, the internal oxidation is, compared to JS-3 / glass A, dramatically enhanced. Besides this fact, the oxidation morphology is different. While JS-3 oxidizes on a volumic scale, Crofer22APU 1st reacts alongside the grain boundaries of the metal. SEM-EDX characterizations show that the tracer elements such as aluminum and possibly silicon are enriched at the grain boundaries. Due to the enrichment of Al and Si, the grain boundaries behave like a weak point of the metal. The oxidation starts at this weak point and subsequently reacts into the grains. The question, whether both trace elements or possibly only one of the two is necessary to support this oxidation, has not been answered to date. Additionally, the actual reaction mechanism is not yet clear.

There are several reasons which can lead to the observed oxidation:

1. It was found that silica enriches between the steel surface and the double oxidation layer formed on top of the surface as an intermediate zone. Thus it may be speculated that the Si influences the density of the double oxide layer and thus
oxygen may migrate further into the steel; but if this is the case it should take place on the steel surface throughout and not only at those zones where the glass-ceramic sealant is present. Also this reason is less likely.

2. If aluminum and silicon are localized at the grain boundaries and subsequently oxidized, the resulting greater volume may cause internal stresses and thus the grain boundary behaves, as described above, as a weak point of the system and is predominantly oxidized.

3. Due to the fact that the internal oxidation is located mostly on the triple-phase boundary of steel / glass-ceramic / atmosphere and the directly surrounding area, it may be concluded that not only the amount of aluminum and silicon in the steel but additionally the glass-ceramic or elements of the glass-ceramic support the internal oxidation of the steel. This is found to be correct for Pb in the glass-ceramic as described by Haanappel et al (8).

4. Under the chosen atmospheres, only the humidified hydrogen leads to internal metal oxidation; thus either hydrogen or the combination of humid hydrogen with a low oxygen partial pressure is necessary to initiate the oxidation.

5. If hydrogen is necessary for internal metal oxidation, it may be attributed to an interaction of hydrogen with the double oxide layer; possibly the layer is not dense for oxygen migration under the chosen atmospheric conditions.

In fact, the existence of aluminum and silicon, the humidified hydrogen atmosphere (or additionally the low pO2) and elements from the glass-ceramic (e.g. lead) are necessary to lead to enhanced internal metal oxidation in the material combination Crofer22APU 1st / glass A (to a minor degree also for JS-3 / glass A). A result of the oxidation is the swelling of the metal which leads to bulging. This bulging may be, for two reasons, problematic. On one hand, it could lead to cracking of the sealant and thus cause a leak between the two gas compartments and therefore re-oxidation of the anodic nickel to nickel oxide may occur. The re-oxidation can lead to internal stress within the anode and subsequently to cracking of the electrolyte and therefore complete destruction of the cell. On other hand, if the swelling starts from both sides of the interconnect, the gap between the metals may be bridged over and thus lead to short circuiting. Note that the swelling was approx. 30-50 μm after 500 h of exposure and the gap between the interconnects was only about 200 μm. For long-term operation of a stack this may lead to a problem.

Additionally, hydrogen is easily diffused in steel. Thus H2 may migrate from the anode side of the bipolar plate to the cathodic side (if the hydrogen is the initiator of the reaction). If hydrogen reaches the cathode side and the oxide layer on the steel does not behave as a diffusion barrier for H2, the hydrogen can cause internal oxidation even on the air side of the interconnect and thus the existing material combination here is critical for SOFC use.

CONCLUSIONS AND OUTLOOK

The annealing of sealed samples of a barium-calcium-aluminum-silicate glass-ceramic in the pre-crystallized or amorphous state with high-chromium-containing steel materials leads under humidified hydrogen atmosphere to enhanced internal oxidation of the metal part. If a nearly trace element-free steel (JS-3) is compared to a commercial product with
minor elements of Al and Si, the commercial steel Crofer22APU 1st oxidizes more strongly than the JS-3 material. Additionally the oxidation morphology is different. While JS-3 oxidizes on a volumic scale, Crofer22APU 1st forms chromia alongside the grain boundaries. The reaction depth and width for Crofer22APU 1st is approx. five times that of JS-3. The internal oxidation is dramatically promoted by the combination of minor steel constituents such as aluminum and silicon, the surrounding atmosphere and elements from the glass-ceramic. Due to the enhanced internal oxidation, the steel swells. It should be noticed that the aforementioned conclusions relate to the specific metal/glass-ceramic combinations chosen. By varying either the sealant or the interconnect material the results may be different. Thus it is concluded that each SOFC interconnect steel composition needs a specially adapted glass-ceramic material for successful long-term operation.

Future work will focus on the clarification of the reaction mechanism, on the question of which of the trace elements causes the main oxidation reaction in the steel material, Al or Si or both, and on the question of what amount of trace element is acceptable for suppressing the strong interaction.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the assistance of Mr. A. Cramer (ZAT) for preparing the samples and of Mr. H. Wesemeyer (IWV-3) for conducting the tests under humidified conditions.

REFERENCES

1. T. Horita, N. Sakai, T. Kawada, H. Yokokawa, M. Dokiya, Denki Kagaku, 61(7), 760-762 (1993).
2. N. Lahl, D. Bahadur, K. Singh, L. Singheiser, K. Hilpert, J. Electrochem. Soc., 149(5) A607-A614 (2002).
3. Z. Yang, K. D. Meinhardt, J. W. Stevenson, J. Electrochem. Soc., 150(8), A1095-A1101 (2003).
4. Z. Yang, J. W. Stevenson, K. D. Meinhardt, Solid State Ionics, 160, 213-225 (2003).
5. Z. Yang, G. Xia, K. D. Meinhardt, K. S. Weil, J. W. Stevenson, J. Mat. Eng. Perf., 13(3), 327-334 (2004).
6. W. J. Quadakkers, J. Piron-Abellan, V. Shemet, L. Singheiser, Metallic materials for interconnects in SOFC systems, 3rd Int. Workshop on “Life Cycle Issues in Advanced Energy Systems,” Proc. in Materials at High Temperatures, 20(2), Woburn, United Kingdom, 115-127 (2003).
7. V. A. C. Haanappel, V. Shemet, I. C. Vinke, W. J. Quadakkers, A novel method to evaluate the suitability of glass sealant-alloy combinations under SOFC stack conditions, J. Power Sources, accepted for publication.
8. V. A. C. Haanappel, V. Shemet, S. M. Gross, Th. Koppitz, N. H. Menzler, M. Zahid, Interaction phenomena between various glass-ceramic sealants and ferritic steels under simulated SOFC stack conditions, *these proceedings*.

9. S. M. Gross, R. Conradt, P. Geasee, V. Shemet, W. J. Quadakkers, J. Remmel, U. Reisgen, in *Sixth European Solid Oxide Fuel Cell Forum Proceedings*, M. Mogensen, Editor, pp. 800-809, European Fuel Cell Forum, Oberrohrdorf, Switzerland, (2004).

10. T. Schwickert, P. Geasee, A. Janke, U. Diekmann, R. Conradt, Electrically insulating high-temperature joints for ferritic chromium steel, in *Proc. Int. Brazing and Soldering Conf.*, Albuquerque, USA, 116-122 (2000).

11. *Crofer 22 APU Material Data Sheet No. 8005*, June 2004 Edition, ThyssenKrupp VDM, 58778 Werdohl, Germany.

12. P. Geasee, *Development of crystallizing glass sealants for high temperature planar solid oxide fuel cells*, PhD thesis, RWTH Aachen, D 82 (2003), available online at http://www.bth.rwth-aachen.de/job/disslist.pl.