INTERACTION PHENOMENA BETWEEN VARIOUS GLASS-CERAMIC SEALANTS AND FERRITIC STEELS UNDER SIMULATED SOFC STACK CONDITIONS

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ABSTRACT

The suitability of various combinations of glass-ceramic sealants with high-chromium ferritic steels under conditions simulating SOFC stacks has been evaluated. The test method used is based on test samples consisting of two metallic sheets, joined together with a glass-ceramic sealant. The samples were exposed to different gas compositions, i.e. air, hydrogen saturated with 3 vol% water vapor, and hydrogen - air dual atmosphere. Optionally, an external voltage can be applied across the sheets. Experiments revealed that the chemical and electrical behavior of the sandwich samples strongly depends on the experimental conditions. Under oxidative conditions (air) no undesirable interactions take place, which detrimentally affect the electrical properties, indicating satisfactory suitability of the tested sealant – steel combinations. However, under experimental conditions simulating SOFC stacks including a dual atmosphere, it was obvious that excessive internal Cr oxidation inducing deformation of the ferritic steels, sometimes accompanied by external Fe-oxide formation, only occurred in the case of ferritic steels containing Si and glass-ceramics containing minor amounts of PbO.

INTRODUCTION

During the past decade Forschungszentrum Jülich (FZJ) has worked on advanced SOFC stack designs using planar cells with thin electrolyte layers (1). The rigid fixation of the cells in the metallic frame of the stacks and the sealing of the anode and cathode compartments are provided by glass-ceramics based on the BCAS system. The main properties required for these glass-ceramic-based materials are gas tightness, electrical insulation, thermal expansion coefficient similar to that of the material to be joined, and long-term mechanical and chemical stability under oxidizing, reducing, as well as dual environmental conditions at high temperatures.

During a period in the development, various glass-ceramic/ferritic steel combinations used in stacks led to severe degradation limiting the operation time due to short-circuiting. An interdisciplinary working group was established to analyze the failure causes. In several series of experiments, the interactions between glass-ceramics and ferritic steels were investigated to isolate and to identify degradation and corrosion...
processes and their governing mechanisms. Results of the investigations using a simple test method addressing only the direct interaction are reported in a separate contribution (2). This contribution summarizes the results obtained using a test method simulating 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 (3,4).

EXPERIMENTAL

The test samples consisted of two metallic sheets of various ferritic steels. One sheet contains a small hole allowing the desired gas composition to reach the inner part of the sample. Table I shows the chemical compositions of the various steels tested. Both sheets were joined together with various glass-ceramic sealants all based on mixtures of Al₂O₃, SiO₂, CaO, and BaO with minor amounts of transition metal oxides to optimize the SOFC-relevant physical and chemical properties. The chemical compositions of the various glass-ceramic sealants used are given in Table II.

Table I: Chemical composition of the steels used (wt%).

| Alloy:     | Fe | Cr | Mn | Ti  | Si | Al | Re-el. | Ni |
|------------|----|----|----|-----|----|----|--------|----|
| Steel T-1  | Bal.| 22.6| 0.4| 0.06| 0.1| 0.1| La-0.1 | 0.2|
| Steel T-2  | Bal.| 23.3| 0.4| 0.05| -  | -  | La-0.1 | -  |
| Steel T-3  | Bal.| 22.1| 0.5| -   | 0.4| 0.2| Zr-0.1 | 0.3|
| Steel T-4  | Bal.| 17.3| 0.3| 0.01| 0.9| 1.0| -      | 0.2|
| Steel T-5  | Bal.| 22.1| 0.4| 0.05| 0.1| -  | La-0.1 | -  |
| Steel T-6  | Bal.| 22.0| 0.4| 0.05| -  | 0.1| La-0.1 | -  |
| Steel T-7  | Bal.| 22.7| 0.4| 0.04| -  | -  | La-0.05| -  |

Table II: Chemical composition of the various glass-ceramic sealants used (wt%).

| Glass sealant: | SiO₂ | CaO | BaO | Small additives                              |
|----------------|------|-----|-----|---------------------------------------------|
| GS-A           | 34.7 | 8.6 | 41.4| Al₂O₃, B₂O₃, ZnO, PbO, V₂O₅                 |
| GS-B           | 46.8 | 15.8| 36.7|                                            |
| GS-C           | 36.8 | 8.7 | 44.7| Al₂O₃, B₂O₃, ZnO, V₂O₅                     |
| GS-D           | 27.9 | 5.7 | 49.1| Al₂O₃, B₂O₃, ZnO, PbO, V₂O₅                |
| GS-E           | 35.0 | 8.5 | 42.8| Al₂O₃, B₂O₃, PbO, V₂O₅                     |

In order to measure the electrical resistance of the sample, each sheet was connected to two Pt wires, one to apply the external voltage over the glass sealant and the other to measure the current density. The samples were placed on top of a hermetically sealed alumina housing, which contained four gas outlets. More details about the experimental parameters and set-up can be found elsewhere (3,4).

Samples were tested at 800°C in i) air, ii) in hydrogen saturated with 3 vol% H₂O, and iii) in a dual atmosphere with the inner part of the sample exposed to hydrogen saturated with 3 vol% H₂O, and the outer part to air. Microstructural characterization of the samples was performed using electron microscopy equipped with EDX analysis system.
Table III: Schematic overview of phenomena related to various glass-ceramic sealant – steel combinations exposed in various atmospheres for 400 hrs at 800°C (SC: short-circuiting; IO: internal oxidation along grain boundaries; EO: external oxidation by outwardly growing iron-rich oxide nodules).

| Steel: | T1 | T2 | T3 | T4 | T5 | T6 | T7 |
|--------|----|----|----|----|----|----|----|
| Glass-ceramic sealant: | air atmosphere | | | | | | |
| GS-A | SC: no | SC: no | | | | | |
| | IO: - | IO: - | | | | | |
| | EO: - | EO: - | | | | | |
| GS-B | | | | | | | |
| GS-C | | | | | | | |
| GS-D | SC: no | SC: no | | | | | |
| | IO: - | IO: - | | | | | |
| | EO: - | EO: - | | | | | |
| GS-E | | | | | | | |
| | | | | | | |
| hydrogen (3 vol.% H₂O) atmosphere |
| GS-A | SC: no | SC: no | | | | | |
| | IO: +++ | IO: - | | | | | |
| | EO: - | EO: - | | | | | |
| GS-B | | | | | | | |
| GS-C | | | | | | | |
| GS-D | | | | | | | |
| GS-E | | | | | | | |
| | | | | | | |
| air – hydrogen (3 vol.% H₂O) dual atmosphere |
| GS-A | SC: yes | SC: no | SC: yes | SC: no | SC: yes | SC: no | SC: no |
| | IO: +++ | IO: - | IO: +++ | IO: + | IO: +++ | IO: - | IO: - |
| | EO: +++ | EO: - | EO: +++ | EO: + | EO: +++ | EO: - | EO: - |
| GS-B | sc: no | sc: no | | | | | |
| | IO: - | IO: - | | | | | |
| | EO: - | EO: - | | | | | |
| GS-C | SC: no | SC: no | | | | | |
| | IO: - | IO: - | | | | | |
| | EO: - | EO: - | | | | | |
| GS-D | | | | | | | |
| GS-E | SC: yes | | | | | | |
| | IO: +++ | | | | | | |
| | EO: +++ | | | | | | |

- negligible; + small; ++ moderate; +++ severe
RESULTS

Electrical Resistance Measurements

Results from resistance measurements with various combinations of ferritic steel/glass-ceramic sealants and exposed to air at 800°C have shown that the resistance was far above values necessary to cause short-circuiting.

Also measurements were made in only a hydrogen atmosphere (with 3 vol% H₂O) with the ferritic steels T1 and T2 and glass-ceramic sealant type GS-A. Also here, no short-circuiting was detected after 400 hrs of exposure at 800°C.

![Figure 1. Specific resistance as function of the exposure time of three glass-ceramic sealant/ferritic steel combinations, i.e. T5/GS-A, T6/GS-A, and T7/GS-A, exposed in hydrogen – air atmosphere at 800°C.](image)

A third series of experiments concerned the exposure of various glass-ceramic sealants / ferritic steel combinations in a dual atmosphere. During exposure at 800°C some samples showed after a few tens of hours a sudden increase of the resistance, after which it reduced to values around 1 Ω.m., indicative of short-circuiting. Figure 1 shows, as an example, the specific resistance as a function of the exposure time for three various samples, i.e. T5/GS-A, T6/GS-A, and T7/GS-A. From this figure, it is clear that sample T5/GS-A showed finally short-circuiting. The other samples did not show any obvious variation of the specific resistance during the whole exposure period.

A complete overview of short-circuiting effects regarding the tested various glass-ceramic sealant/ferritic steel combinations exposed in the three above-mentioned atmospheres is shown in Table III.

Microstructural Analysis

Figure 2a shows the surface morphology of the inner part of the sample T1/GS-A,
exposed in air for 400 hrs at 800°C (no externally applied voltage). The outer surface of the ferritic steel T1 (bottom) consists mainly of a chromium- and manganese-rich oxide. Near the three-phase boundary between air, glass-ceramic sealant, and the ferritic steel, a relatively bright crystalline phase rich in barium, chromium, and oxygen, was formed. Similar features were found with the other samples exposed in air, see Table III. Furthermore, it was found that an external voltage did not affect the reaction products formed near the three-phase boundary.

Figure 2. SEM micrographs of the surface morphology of two samples after 400 hrs of exposure at 800°C: a) T1/GS-A in air; b) T1/GS-A in hydrogen (3 vol% H₂O).

Figure 3. SEM micrographs of the surface morphology near the three-phase boundary at the hydrogen side (a), and the air side (b) of sample T1/GS-A after 400 hrs of exposure in a dual atmosphere at 800°C with an external applied voltage of 800 mV.

Two sets of samples, i.e. T1/GS-A and T2/GS-A were also tested in hydrogen, saturated with 3 vol% water vapor. Figure 2b shows the region near the three-phase boundary between hydrogen, glass-ceramic sealant and ferritic steel of sample T1/GS-A. It appeared that here no barium-, chromium-, and oxygen-rich reaction products were formed. The outer oxidized surface of the steel shows the presence of small cracks parallel to the three-phase boundary. These cracks were not found in the case of sample T2/GS-A.
Several glass-ceramic sealant/ferritic steel combinations were also tested in a dual atmosphere. Figures 3a and 3b show SEM micrographs of the surface morphology of specimen T1/GS-A. Near the air – glass-ceramic sealant – steel interface, significant amounts of an iron-rich oxide are formed (Figure 3b). Apart from this corrosion product, the outer edge of the glass-ceramic sealant was rich in barium, chromium, and oxygen.

Figure 4. SEM micrographs of the cross section of (a) sample T2/GS-D after 400 hrs of exposure in air, and (b) sample T1/GS-A after 400 hrs of exposure in hydrogen, both at 800°C. No external voltage was applied.

EDX analysis revealed the presence of low concentrations of Pb on the oxidized steel surface in the vicinity of the glass-ceramic sealant. Figure 3a shows the three-phase boundary on the hydrogen side. Here, a rather smooth interface between the glass-ceramic sealant and the steel is observed without the presence of iron-rich oxide products. Furthermore, no substantial barium-, chromium- and oxygen-rich reaction products were observed at the edge of the glass-ceramic sealant. White particles, rich in elemental Pb were locally found near the reaction zone between the sealant and the steel. Similar surface morphological features were found for the investigated specimens T3/GS-A, T4/GS-A, T5/GS-A, and T1/GS-E.

Figure 5. SEM micrographs of the cross section of sample T1/GS-A exposed for 400 hrs at 800°C in hydrogen – air atmosphere: a) air side, b) hydrogen side.
With respect to the other specimens, tested in a dual atmosphere, i.e. T2/GS-A, T6/GS-A, T7 / GS-A, T1/GS-B, T2/GS-B, and T1/GS-C, the surface morphology near the three-phase boundary at the air side was comparable with that of specimens exposed for 400 hrs in air at 800°C: no excessive corrosion products were found.

Figure 4a shows a micrograph of the cross section of sample T2/GS-D. Near the three-phase boundary a bright phase rich in barium, chromium and oxygen was formed. No other oxidation products were found which might finally lead to degradation of the sample. The other samples, also exposed in air, showed similar features.

In the case of exposure in hydrogen, different results were obtained. Cross sectional analysis of the sample T1/GS-A revealed severe internal oxidation (Figure 4b). Internal chromium-rich oxides were found at the steel grain boundaries as well as in the grains. In this internal oxidation zone, the metallic grains were depleted in chromium. This internal oxidation was not found in the case of sample T2/GS-A.

Figures 5a and 5b show SEM cross-sections of sample T1/GS-A after exposure at 800°C in a dual atmosphere. Severe material degradation has taken place at the air side and near the glass-ceramic sealant – steel edge area. EDX analysis revealed the presence of voluminous outwardly growing iron-rich oxide nodules. Internal chromium-rich oxides were found at the steel grain boundaries as well as in the grains. The glass-ceramic sealant left behind formed a bright phase rich in barium, chromium, and oxygen. Severe internal oxidation was also found on the hydrogen side. It is important to note that internal oxidation of the steel was not always only found on local sites beneath the glass-ceramic sealant or at the three-phase boundary, but also on sites at a certain distance from the glass-ceramic sealant – steel interface. However, near this three-phase boundary, neither large iron-rich oxide nodules nor the formation of a barium and chromium rich oxide at the outer zone of the glass-ceramic sealant were found. Similar observations were found for the samples T3/GS-A, T4/GS-A, T5/GS-A, T1/GS-E. Cross-sectional analysis of the other combinations, see also Table III, revealed neither the formation of outward-growing iron-rich oxide products nor internal oxidation of chromium.

**DISCUSSION**

The present study, simulating SOFC stack conditions, has shown that excessive interaction of the glass-ceramic with the interconnect steel can lead to a rapid degradation of stack components due to short-circuiting phenomena. The latter could be shown to be related to voluminous Fe-oxide formation on the steel surface near the boundary between steel, glass-ceramic, and oxidant (air). Due to the high electronic conductivity of Fe-oxides, especially Fe$_3$O$_4$ and FeO, the voluminous oxide growth results in the formation of a "bridge" with extremely small electrical resistance between the adjacent metallic plates and thus in short circuiting.

The systematic parameter variation (3, 4) revealed the following findings with respect to this undesired degradation phenomenon:

- The presence of an externally applied voltage did not change the electrical, physical and chemical behaviour of the test samples exposed in air, hydrogen, or hydrogen –
air atmospheres.

- The voluminous, outward Fe-oxide growth finally resulting in short-circuiting only occurs at the boundary between the oxidant (air), the glass-ceramic, and the steel, and is accompanied by excessive internal oxidation of chromium in the steel.

- Internal oxidation of chromium also occurs at the boundary between the hydrogen-based environment, the glass-ceramic, and the steel. After prolonged exposure times it is also found locally near the interface between the glass-ceramic and the steel. In these cases, however, no voluminous external Fe-oxides are formed.

- Neither the voluminous external Fe-oxide formation nor the excessive internal oxidation of Cr is found if the exposures of the samples are carried out in air instead of a dual atmosphere. See also ref. (2).

- If the exposures are carried out in a hydrogen/water vapour mixture instead of a dual atmosphere, the internal oxidation of Cr at the boundary between the environment, the glass-ceramic, and the steel is similar to that described above. However, no voluminous external Fe-oxide formation is found and no short-circuiting occurs. See also ref. (2).

- The excessive internal oxidation of chromium, sometimes accompanied by voluminous, external Fe-oxide formation, only occurs in case of glass-ceramics GS-A and GS-E, i.e. glass-ceramics containing minor amounts of PbO.

- The rate of corrosion attack strongly depends on the detailed steel composition. Increasing Si content apparently increases the rate of the corrosion attack which, in a dual atmosphere, eventually results in short-circuiting (4).

Based on these findings, the following sequential steps are proposed to explain the occurrence of the short-circuiting phenomenon:

- The transition metal oxides, in this case to improve the adhesion and wetting behavior, reduce to elemental metal. According to the Gibbs free energies of formation of various oxides as a function of temperature, PbO is less stable than chromia. At high temperatures, a reduction - oxidation reaction takes place between chromium (in the bulk material) and PbO. This also explains the presence of small elemental Pb drops along the glass-ceramic/steel interface.

- In the hydrogen/water vapour environment, elemental Pb will not be re-oxidised because the oxygen partial pressure of the environment is lower than the dissociation pressure of PbO. Furthermore, due to its low melting point (328 °C) it is obvious that Pb will be present in liquid rather than in solid form. Additionally, substantial amounts of vapor phase will be present due to the relatively high vapor pressure of Pb.

- The internal grain boundary attack of the steels exhibits a morphology which is very similar to that frequently described in the literature as “liquid metal corrosion” (5-7), here likely initiated by liquid Pb at the steel grain boundaries. It is assumed that a
very small amount of Pb will already be sufficient to induce this internal attack, because EDX analysis did not show the presence of Pb at the grain boundaries of the steel. The attack makes the grain boundaries accessible for gaseous species such as water vapor, resulting in excessive internal oxidation of chromium. Because of the low melting point and high vapor pressure (vapor phase transport), it is likely that the Pb attack may not only occur in the immediate vicinity of the boundary between the hydrogen-based environment and the glass but also at a small distance from the glass-ceramic edge, in agreement with the actual experimental findings.

- The excessive internal oxidation of Cr, initiated on the hydrogen-based side of the sandwich sample used, results in a volume change of the ferritic steel, which leads to a local bulging of the steel. As a consequence, the glass-ceramic is pushed away from the steel surface and crack formation at/near the interface between the glass-ceramic and steel occurs. This explains the increase in resistance before the onset of short-circuiting.

- The hydrogen-based gas can penetrate into the crack leading here to the occurrence of local internal oxidation of Cr in a manner similar to that initially started near the edge of the glass ceramic. Also here, elemental Pb is available along the interface, due to the redox reaction between chromium in the bulk phase and PbO. The crack tip propagates and once the crack reaches the air-side, internal oxidation of Cr also occurs at the boundary between air, glass-ceramic, and steel.

- The excessive internal oxidation leads to a severe Cr depletion in the steel matrix. Once the matrix concentration has decreased below a critical level the steel is no longer able to retain a protective chromia layer and consequently it will start to form external Fe-based oxide products. Due to the strong pO2-dependence of the Fe-oxide growth kinetics (8), near the glass/steel interface on the hydrogen side of the sample this process will result in an only slightly increased growth rate. However, very rapidly growing, external Fe-based oxide products will be formed near the glass/steel interface on the air side. This rapid formation of large Fe-oxide nodules will, after prolonged exposure times lead to “bridge”-formation between the two metallic sheets, and as a result, to short-circuiting.

CONCLUSIONS

The present study emphasises that the evaluation of suitable combinations of glass-ceramic sealants and steels for SOFC applications requires the use of realistic test methods which closely simulate the conditions prevailing in actual SOFC stacks. During high temperature exposure of various glass-ceramic/steel combinations under purely oxidising conditions (air) no severe interactions detrimentally affecting the electrical properties of the sandwich specimens were observed. However, when using experimental parameters which closely simulate SOFC stack conditions, i.e. in the presence of a dual atmosphere, excessive corrosion of the ferritic interconnector steel may occur, which eventually results in a short-circuiting between adjacent interconnector plates.

The “trigger” for this process clearly starts on the side of the sandwich specimen which is in contact with the hydrogen/water vapor environment. Here, the presence of PbO in the
glass-ceramic induces an excessive internal oxidation of chromium. This results in a local volume change of the ferritic steel, which is manifested in bulging of the steel. As a consequence, the glass-ceramic is pushed away from the steel surface and crack formation at/near the glass-ceramic – steel interface occurs. In this way the process “spreads” along this interface to the air side of the sandwich sample where the resulting chromium depletion of the alloy matrix is accompanied by formation of rapidly growing, external Fe-based oxides. The rate of this corrosion attack strongly depends on the detailed steel composition. Increasing Si content apparently increases the rate of the corrosion attack, which eventually results in short-circuiting.

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