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Interaction of metallic SOFC interconnect materials with glass–ceramic sealant in various atmospheres

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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–Al_2O_3–SiO_2 (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 h. The results show that air or humidified air does not lead to enhance negative interaction effects, neither in the metallic nor in the glass–ceramic material. In contrast 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 aluminium and silicon, than in the 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 behaviour of the glass–ceramic and metallic parts of the SOFC. The test method presented here can act as a first fast and simple screening test to characterize the interaction of the metallic and glass–ceramic parts of an SOFC.

Keywords: Solid oxide fuel cells; Interconnect; Sealant; Interaction; Corrosion

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1. Introduction

Due to their high efficiency for energy conversion, their absence of moving or rotating parts, their compatibility with various fuels (hydrogen, methane, natural gases, waste gases, etc.) and their atmospheric friendliness solid oxide fuel cells (SOFCs) have a great potential for power generation either in stationary or in mobile applications (e.g. as auxiliary power units). The heart of a planar SOFC system is the stack containing the ceramic cells (MEA, membrane electrode assembly), the gas-distributing and current-collecting metallic bipolar plates (interconnects) and the glass or glass–ceramic sealant material for gas chamber separation.

To date, widespread research has mainly focused on one of the above-mentioned parts. That is to say 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 materials. In recent years, more and more work has been done on characterizing the interactions between the different SOFC parts either under artificial atmospheres or under realistic SOFC gases. Research work is being carried out with respect to reactions in the cell itself (e.g. the interaction of electrodes with the electrolyte under varying oxygen partial pressure conditions)

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or between stack parts. Horita et al. [1] investigated the reaction of Pyrex glass used as a sealant with either YSZ (yttria-stabilized zirconia, electrolyte) and calcium-doped lanthanum chromate (ceramic interconnect). Lahl et al. [2] described the interaction of an aluminosilicate glass sealant with the components on the anodic parts of the cell, e.g. YSZ and nickel oxide. Similar investigations were carried out by Larsen et al. [3]. Furthermore, Yang et al. studied the interaction between barium–calcium–aluminosilicate glasses and ferritic stainless steel interconnect material [4,5]. They found that at the edges of the sandwich samples (glass sealant between two metallic plates) barium-chromate phases were formed. Barium-chromate forms by combining the chromia or chromia vapour species from the chromia oxidation layer on the steel and the barium oxide from the sealant material. Both investigations were conducted under air conditions only for 1 h at 850 °C followed by 5 h at 750 °C. Thus the investigations can be referred to as short-term testing. In a subsequent paper Yang et al. [6] performed similar tests but for time periods up to 168 h (1 week) at 750 °C. Additionally, a steel material named Crofer22APU 1st specifically developed for SOFC applications [7] was characterized. The authors found enhanced chemical compatibility with their glass seal material (named G18) and the Crofer22APU 1st steel resulting in good bonding (4 h at 750 °C). 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. [8,9] created a novel method for evaluating the suitability of glass–ceramic sealants for metallic interconnects. They designed a sandwich test where the glass is applied within two square metallic plates. The top plate has a hole in the middle where a test gas can be added. On the outer side normally air is applied. Thus it is possible to perform a test under dual atmospheres. Additionally, the voltage can be measured. Test runs can vary from some hours up to long-term exposures. However, the test specimens are complex and the number of test stands is limited due to gas distribution and control equipment.

To date, there have been no reports on easy and simple mid-term or long-term investigation 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 [10], 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 h.

2. Materials and experimental procedure

2.1. Glass–ceramic material

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 [10]. Table 1 lists the chemical composition of the glass. The manufacturing of the material follows as described in detail in [11], 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 glass A.

The glass–ceramic for the tests used 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. Pre-crystallization should avoid undesired interactions between the sealant and the metal. Additionally it was possible to characterize the different adhesion behaviour.

2.2. Metallic materials

As the metallic part two high-chromium steels especially designed for SOFC applications were used. On the one hand, a pre-pilot material known as JS-3 developed at Research Centre Jülich [7] and, on the other hand, a commercial steel designated Crofer22APU 1st (ThyssenKrupp VDM, Werdohl, Germany) [12], which is industrially produced according to the JS-3 formula. Table 2 lists the chemical compositions of both materials. From Table 2 it is obvious that the main difference between the two metals is the amount of silica and alumina. In Crofer22APU 1st alumina and silica are detectable in dopant amount.

2.3. Metal/glass–ceramic specimens

To conduct the tests, metal plates of dimensions 10 mm × 20 mm were cut from metal sheets with a thickness

Table 1
Chemical composition of glass A (wt.%)

Oxide	Amount
BaO	∼40
CaO	∼8
Al_2O_3	∼2
SiO_2	∼35
B_2O_3	$\sum \sim$ 15
ZnO	
PbO	
V_2O_5	

Table 2
Chemical composition of the metallic materials (wt.%)

Element	Cr	Fe	C	Mn	Si	Al	Cu	P	Ti	La
Crofer22APU 1st[a]	20–24	Balance	0.03	0.30–0.80	0.50	0.12[b]	0.50	0.050	0.03–0.20	0.04–0.20
JS-3[b]	23.1	Balance	0.007	0.39	<0.01	<0.01	–	–	0.05	0.09

[a] Data from [12].

[b] Data from Central Department of Chemistry at Research Centre, Jülich.

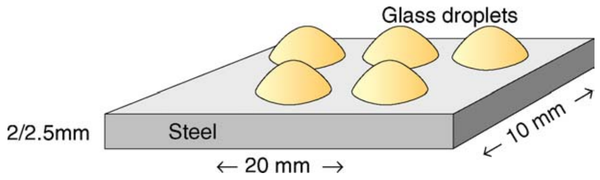

Fig. 1. Schematic overview of the metal/glass specimens.

of 2 or 2.5 mm. The plates were subsequently polished on one side and then cleaned with deionised water and ethanol. The glass paste was applied on the polished side by dispensing five droplets. Fig. 1 shows the specimens schematically. Besides these samples an additional type of specimens 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.

2.4. Test conditions

Three different atmospheres were chosen for the tests. Starting with ambient air, a second test run was carried out under humidified air (50% H_2O abs.) followed by a third under humidified hydrogen (3% H_2O 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 vapour or hydrogen may cause different forms of interactions within the metal bipolar plates and the glass–ceramic sealant (not yet published). Thus those two atmospheres should simulate these findings.

Humidification of the gases is obtained by bubbling the gas through water. The temperature of the water is controlled using a heater and is kept at such a temperature that the water vapour pressure is higher than the desired value. The humidified gas–water vapour mixture is passed through a condenser. This condenser is kept at a constant temperature using a thermostat. The temperature of the condenser corresponds to the exact water vapour pressure desired thus condensing the surplus of water from the gas. For 3% water vapour in hydrogen the corresponding temperature is 298 K. For 50% water vapour in air the condenser temperature is 356 K.

After applying the glass or glass–ceramic paste the samples were heated in air at 1 °C min^{-1} to 350 °C, followed by a dwell time of 1 h, a subsequent heating at 2 °C min^{-1} to 850 °C, followed by a dwell time of several hours for nucleation and to simulate the sealing of an SOFC stack. After this dwell time, the samples were cooled down to 800 °C and then the annealing time started under the aforementioned atmospheres. After times of 1, 5, 25, 150 and 500 h the samples were retained for characterization. Firstly, the adhesion was characterized (fast cooling down from 800 °C to room temperature due to retainment), secondly the samples were photographed and then cut, polished and prepared for SEM (LEO 1530-Gemini) investigations. Fig. 2 shows the cutting line of the samples to improve understanding of the following SEM cross-sectional micrographs.

2.5. Test combinations

The following test combinations were carried out:

Metal	Glass	Atmosphere	Duration (h)
Crofer22APU 1st	73	Air	1, 5, 25, 150, 500
Crofer22APU 1st	73 (pre-crystallized)	Air	1, 5, 25, 150, 500
Crofer22APU 1st	73	Air, 50% H_2O	1, 5, 25, 150, 500
Crofer22APU 1st	73 (pre-crystallized)	Air, 50% H_2O	1, 5, 25, 150, 500
Crofer22APU 1st	73	H_2, 3% H_2O	1, 5, 25, 150, 500
Crofer22APU 1st	73 (pre-crystallized)	H_2, 3% H_2O	1, 5, 25, 150, 500
JS-3	73	Air	1, 5, 25, 150, 500
JS-3	73 (pre-crystallized)	Air	1, 5, 25, 150, 500
JS-3	73	Air, 50% H_2O	1, 5, 25, 150, 500
JS-3	73 (pre-crystallized)	Air, 50% H_2O	1, 5, 25, 150, 500
JS-3	73	H_2, 3% H_2O	1, 5, 25, 150, 500
JS-3	73 (pre-crystallized)	H_2, 3% H_2O	1, 5, 25, 150, 500
Sandwich	73	Air	1, 5, 25, 150, 500
Sandwich	73 (pre-crystallized)	Air	1, 5, 25, 150, 500
Sandwich	73	Air, 50% H_2O	1, 5, 25, 150, 500
Sandwich	73 (pre-crystallized)	Air, 50% H_2O	1, 5, 25, 150, 500
Sandwich	73	H_2, 3% H_2O	1, 5, 25, 150, 500
Sandwich	73 (pre-crystallized)	H_2, 3% H_2O	1, 5, 25, 150, 500

Fundamental characterization was carried out with respect to the interaction reaction between the glass–ceramic material and the metallic part. Minor investigations concerned the formation of the oxide layers on the steel and the crystallization behaviour of the glass under the chosen atmospheric conditions. As noted in [7,14], Crofer22APU 1st and JS-3 are both chromate layer formers. The special elemental composition

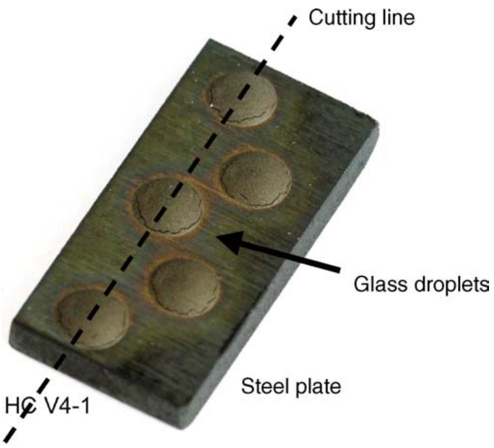

Fig. 2. Cutting line for SEM investigations of specimens.

of both metallic materials results in the formation of a double layer. A bottom layer of chromium oxide and a top layer of chromium–manganese-spinel. This double layer protects the steel from enhanced chromia evaporation which leads in an SOFC to cathode poisoning and subsequently to power degradation of a cell. The crystallites formed within glass A belong to the earth alkali-alumina–silicate group with compositional values varying between the single oxidic elements and various amounts of the tracer elements.

3. Results

3.1. Annealing under air

After retaining 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 samples retained 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. Fig. 3 shows as an example a photograph of the samples after 500 h of exposure. It is clear from Fig. 3 that 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. A detailed description of the interaction reactions can be found in [13]. Additionally, the adhesion on JS-3 is better than on Crofer22APU 1st. The yellowish colour of the samples is due to the formation of barium-chromate on top of the sealant. This finding was earlier reported by Yang et al. [4,5], Lahl et al. [2] and Geasee [13].

After 500 h of exposure no internal oxidation in the steel is visible. Fig. 4 shows as an example the SEM cross sections of samples of the combinations Crofer22APU 1st/glass A and JS-3/glass A (both glasses in non-pre-crystallized state). It is obvious from Fig. 4 that even at the edges of the sealant, e.g. at the triple-phase boundaries (sealant, metal, atmosphere), no internal corrosion is detectable. Only the oxide layer formed on the steel is present. A detailed view of the oxide layer formed shows for both material combinations, independent of the crystallization state of the glass at the start of the test, that the oxide layer formed is thin (approximately 1 μm) and consists of chromium, manganese and oxygen after short exposure times (1 h). After prolonged times (25 h) it does not become thicker but the separation into a two-layered structure is clearer. This finding holds for both the "free" steel surface and for the interaction zone of the glass–ceramic/steel.

3.2. Annealing under humidified air (50% abs.)

After conducting approximately 100 stack tests (short stacks = two cells per stack and power stacks) and various cell tests under varying conditions (atmospheres, temperatures, durations, ceramic or metal housing, etc.) at Research Centre Jülich it was concluded that an enhanced interaction between the glass–ceramic and the metal parts of an SOFC stack might be intensified either by moisture or by humid hydrogen. Thus after tests carried out under ambient air conditions two test runs were performed under humidified air and hydrogen.

Fig. 5 shows as an example the photograph of the combination of glass A and JS-3 after exposure times between 1 and 500 h. It can be seen that adhesion is good for all time periods and that the barium-chromate is formed even under

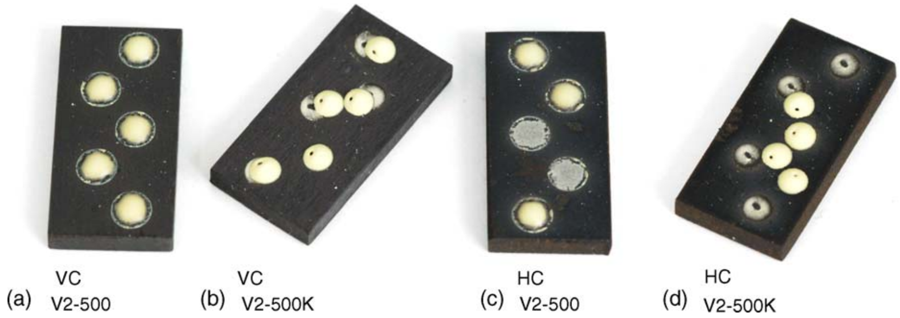

Fig. 3. Photograph of specimens exposed to air for 500 h: (a) JS-3, glass A; (b) JS-3, glass A, pre-crystallized; (c) Crofer22APU 1st, glass A; (d) Crofer22APU 1st, glass A, pre-crystallized.

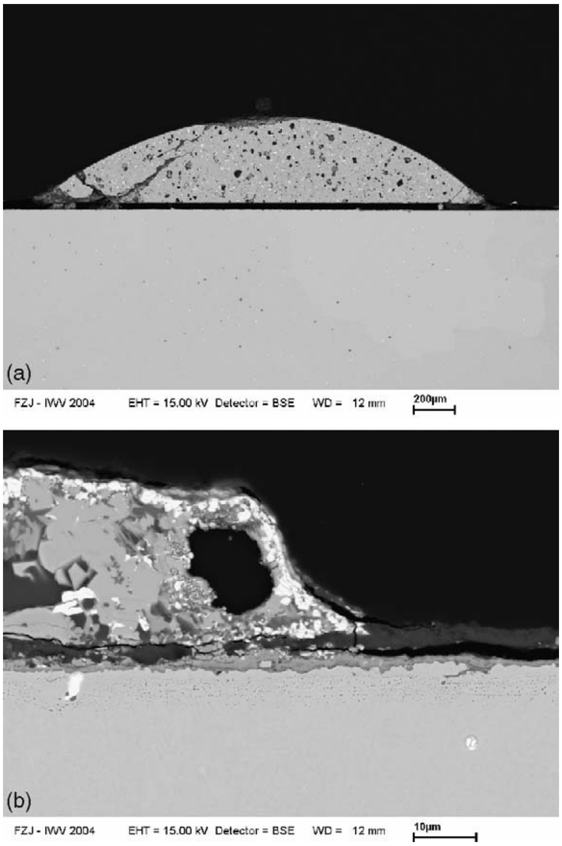

Fig. 4. SEM cross-sections of specimens annealed for 500 h under air: (a) Crofer22APU 1st/glass A (overview); (b) JS-3/glass A (detail from the triple-phase boundary); the gap between the steel and the glass results from sample preparation.

these atmospheric conditions. Analogous statements can be made for the combination of Crofer22APU 1st/glass A, but for the pre-crystallized glass–ceramic spalling off is present.

A comparison of the oxide layers formed between the free steel surface and the interaction zone glass–ceramic/steel shows at the free surface for JS-3 the existence of a double layer (Fig. 6b), but only a thin chromium- and manganese-containing single layer for the interaction zone (Fig. 6a). Additionally, the oxide layer thickness varies from 1 μm at the interaction zone to 3 μm on the free steel surface. Therefore it could be concluded that the interaction between glass–ceramic and metal to enhance adhesion influences the formation of the oxide layer. To date, no negative influence can be deduced under the given conditions because either there is no inner oxidation of the steel or the bonding between the glass–ceramic and the metal is good. Fig. 7 shows a top view of the sandwich sample annealed for 150 h. Even after these exposure durations no corrosion or internal oxidation in the steel is detectable. This is also true of the longest annealing time (500 h).

For the sample combinations with pre-crystallized glass–ceramic similar statements can be made.

3.3. Annealing under humidified hydrogen (3% abs.)

3.3.1. Short-term exposure (5 h)

After short exposure times in humidified hydrogen the oxide layer formed is very thin (<1 μm) for both steels and no internal oxidation within the steel material is detectable (Fig. 8). Due to the thin oxide layer no information about the layer structure (single- or double-layered) can be drawn. The bonding between glass–ceramic and metal is good for the glass–ceramic applied as an amorphous material but not for the pre-crystallized one.

3.3.2. Mid-term exposure (25–150 h)

After an exposure of 25 h first internal oxidation in the steel is visible. Fig. 9 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 approximately 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. For both steels, the oxide layer formed

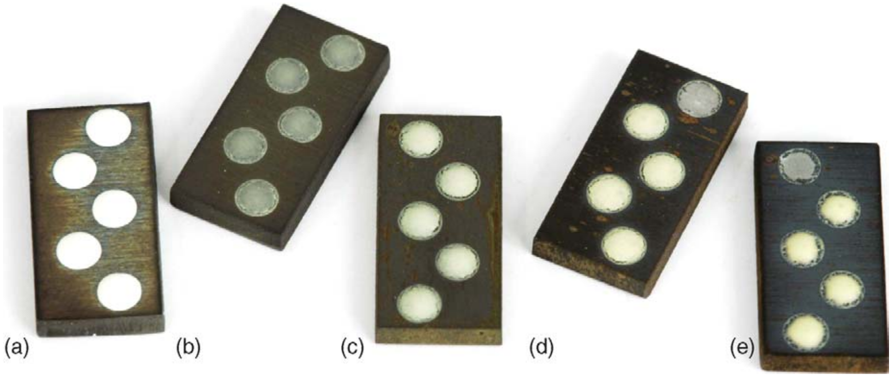

Fig. 5. Photograph of the JS-3/glass A combination exposed to humidified air: (a) 1 h; (b) 5 h; (c) 25 h; (d) 150 h; (e) 500 h.

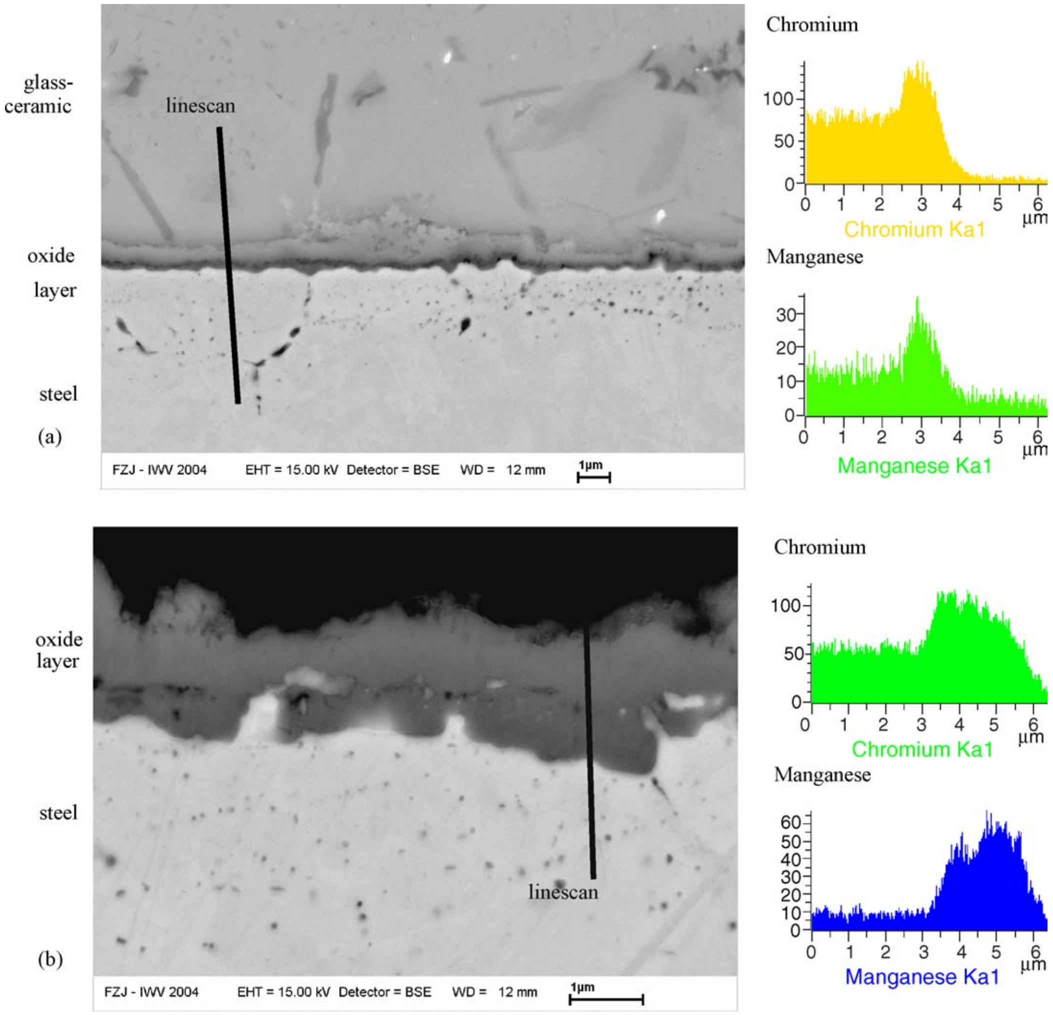

Fig. 6. SEM cross sections and line scans of the oxide layers of the JS-3/glass A combination after exposure to humidified air for 500 h: (a) interaction zone glass–ceramic/metal; (b) free steel surface (note the different magnifications).

has a thickness of 1–2 μm and is not double-layered but consists of manganese and chromium. After annealing times of 150 h all glass droplets spall off after being removed from the furnace.

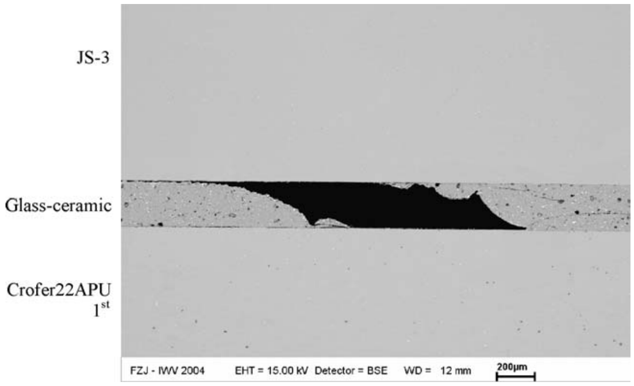

Fig. 7. SEM cross section of the sandwich sample annealed for 150 h in humidified air.

3.3.3. Long-term exposure (500 h)

Prolongation of annealing has no influence on the previously formed oxide layers. They are thin and not double-layered (SEM observation). However, the internal oxidation of the steel has progressed. Fig. 10 shows a cross section of the sandwich sample after 500 h in humidified hydrogen. It is obvious from Fig. 10 that either the scale of oxidation or the oxidation morphology is detrimentally different between the two steel materials. While JS-3 oxidizes, as previously stated, in volume with widths of approximately 100 μm and depths of 20 μm Crofer22APU 1st oxidation is more grain-boundary dominated and larger in scale. The oxidation width reaches 350 μm and the depth is up to 100 μm. In both cases the resulting oxide is chromia. Table 3 lists the chemical composition of both oxides detected via SEM-EDX. Based on the accuracy of the SEM-EDX measurement there is no difference in the oxide compositions. Both are predominantly chromia with lesser 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

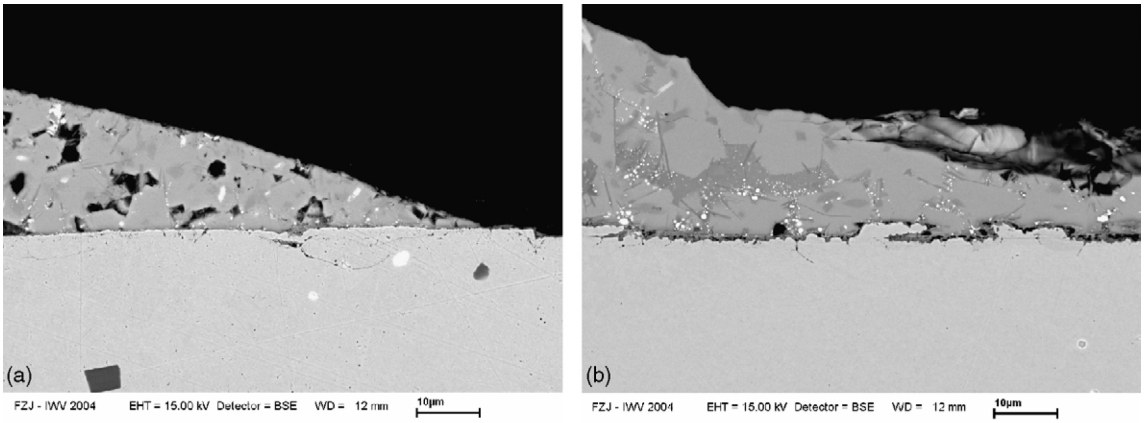

Fig. 8. SEM cross sections of samples annealed in humidified hydrogen for 5 h: (a) Crofer22APU 1st/glass A; (b) JS-3/glass A.

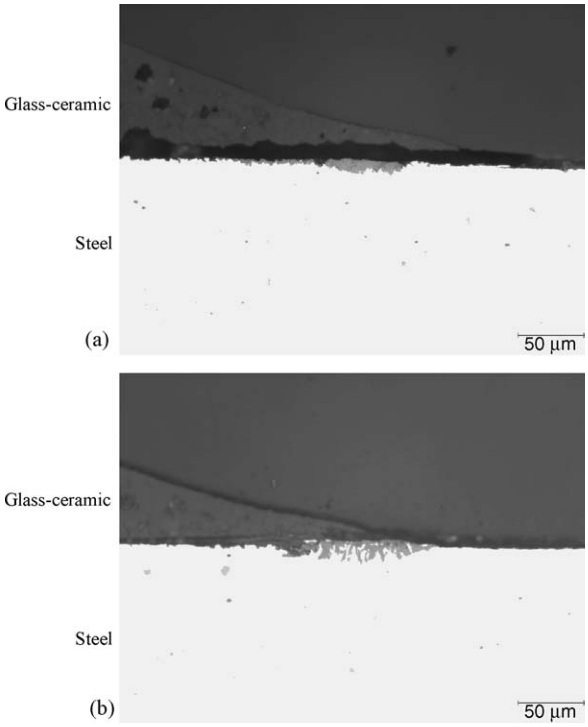

Fig. 9. Optical microscopy cross sections of samples annealed for 25 h in humidified hydrogen: (a) JS-3/glass A; (b) Crofer22APU 1st/glass A.

in the Crofer22APU 1st the steel surface bulges dramatically. Increases of up to 50 μm were observed.

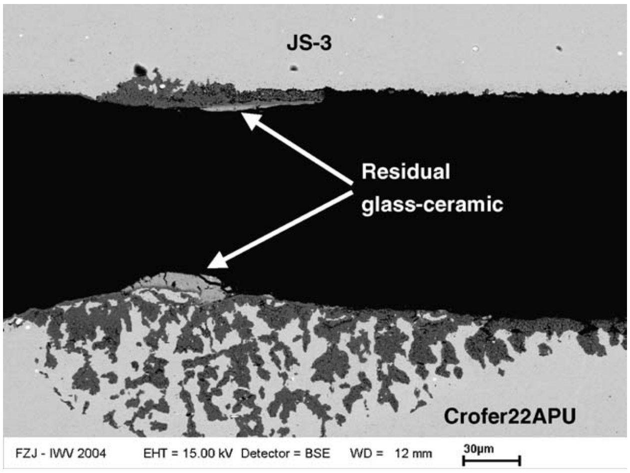

Fig. 10. SEM cross section of the sandwich sample exposed for 500 h in humidified hydrogen.

Table 3
Chemical composition of the oxides formed after 500 h in humidified hydrogen (SEM-EDX from Fig. 11) (wt.%)

Element	Cr	Mn	O	Others
Crofer22APU 1st	73	2	23	Rest
JS-3	75	2	23	Rest

A careful characterization was made of the grain-boundary-dominated oxidation of Crofer22APU 1st. Fig. 11a shows as an example the grain boundary oxidation with enhanced oxidation propagation into the steel sample. Fig. 11b shows the obvious grain boundary domination of the oxidation process followed by spreading into the metal grains. In Fig. 12 the result of a line scan of the oxidized grain boundary and the neighbouring metal grains is shown. The analytical result shows homogeneous distribution within the grains of iron, chromium, manganese and oxygen with depletion of the iron in the oxidation zone and vice versa an enrichment of the chromium, manganese and oxygen. Additionally, in the oxidation zone alumina and presumably silica can be detected. This leads to the conclusion that the aluminium and the silicon are enriched in the grain boundaries. It remains to be clarified whether the aluminium and silicon enrichment is a result of internal oxidation or whether this is the reason for the oxidation.

In Fig. 13 the result of a line scan of the tip of an internal oxidation is presented. Aluminium and oxygen are clearly detectable. The detection of silicon is less definite (thus not shown).

This result shows that aluminium is present at the grain boundary before the oxidation occurs.

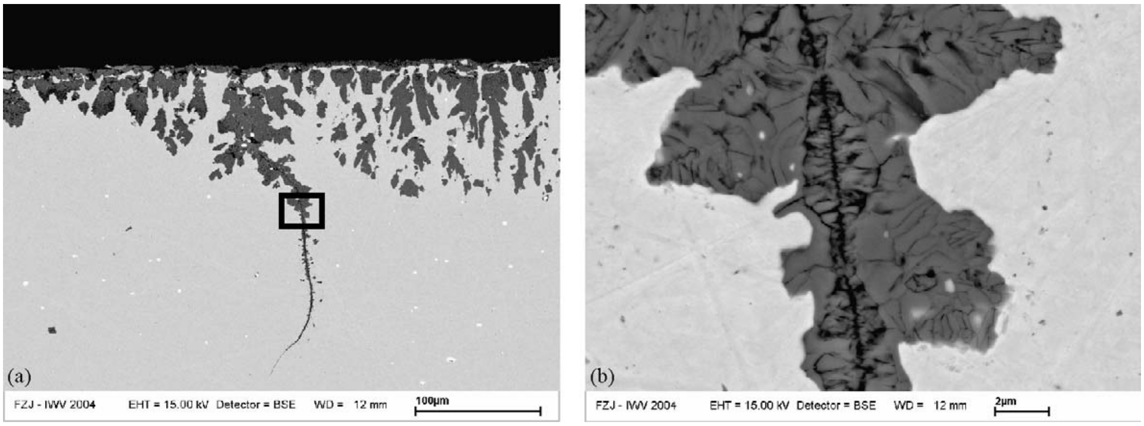

Fig. 11. SEM cross section of Crofer22APU 1st sample annealed for 500 h in humidified hydrogen: (a) overview of the grain-boundary-dominated internal oxidation and (b) higher magnification of the rectangle marked in picture (a).

Table 4
Listing of oxidation depth, adhesion and thickness of the oxide layer for the glass–ceramic/metal combinations

Metal/glass–ceramic combination	Atmosphere	Depth of internal oxidation after 500 h	Adhesion between glass–ceramic and metal	Thickness of oxide layer on the steel surface between steel and glass–ceramic after 500 h (μm)
JS-3/glass A	Air	None	Good	∼1
	Humidified air	None	Mostly good	1–2
	Humidified hydrogen	∼20 μm	Poor	2–3
Crofer22APU 1st/glass A	Air	None	Moderate	∼1
	Humidified air	None	Mostly good	1–2
	Humidified hydrogen	∼100 μm; oxidation peaks up to 250 μm	Poor	∼1

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

Table 4 summarizes the depth of internal oxidation, the adhesion properties and the thickness of the oxide layers formed under the aforementioned atmospheric conditions depending on the steel/glass–ceramic material combinations (only for the samples with non-pre-crystallized glass).

4. Discussion

4.1. Basics of the oxidation behaviour of the used steels in the test atmospheres

The examined metallic materials Crofer22APU 1st and JS-3 are high-chromium containing ferritic steels especially designed for use in solid oxide fuel cells [7,14,16]. Besides their physical properties their oxidation behaviour in SOFC-relevant atmospheres is of special interest. Both, the lab-scale material JS-3 and the commercial available Crofer22APU 1st are chromia formers. Although the mentioned ferritic steels are termed “chromia formers”, one has to have in mind, that during high temperature exposure most of the alloying elements will oxidize. In air and humidified air the minor alloying additions Mn, Al and Si and even the base element Fe can oxidize because the oxygen partial pressure of the environment (∼0.02 MPa) is higher than the dissociation pressure of the oxides of all mentioned elements.

In the humidified hydrogen (97% H_2, 3% H_2O) the oxygen partial pressure at 800 °C is approximately 10^{-23} MPa, which means that Cr, Mn, Al and Si may still oxidize, however, Fe is still stable in its metallic form because the dissociation pressure of the iron oxide is higher ($\sim 10^{-11}$ MPa) than the pO_2 of the chosen atmosphere.

Even if thermodynamic allows oxide formation of a certain element, kinetic factors determine whether its oxide(s) will form and, if yes, in which morphology they prevail. For the used ferritic steels oxidation of Fe does not play a major role because of the formation of the protective oxide scale. Mn can oxidize in the used environments and is mostly present in the form of a Cr–Mn-spinel on the top of the chromia scale [7,14,16]. This double-layer (chromia, Cr–Mn-spinel) ensures low chromium vapourization during operation under SOFC atmosphere conditions.

The oxides of the elements Al and Si posses dissociation pressures (Al: $\sim 10^{-36}$ MPa, Si: 10^{-41} MPa), which are lower than that of the chromia ($\sim 10^{-28}$ MPa). Consequently Si- and Al-oxide can mostly be found in form of internal precipitates beneath the chromia-rich layer in the steel matrix [7,14,16].

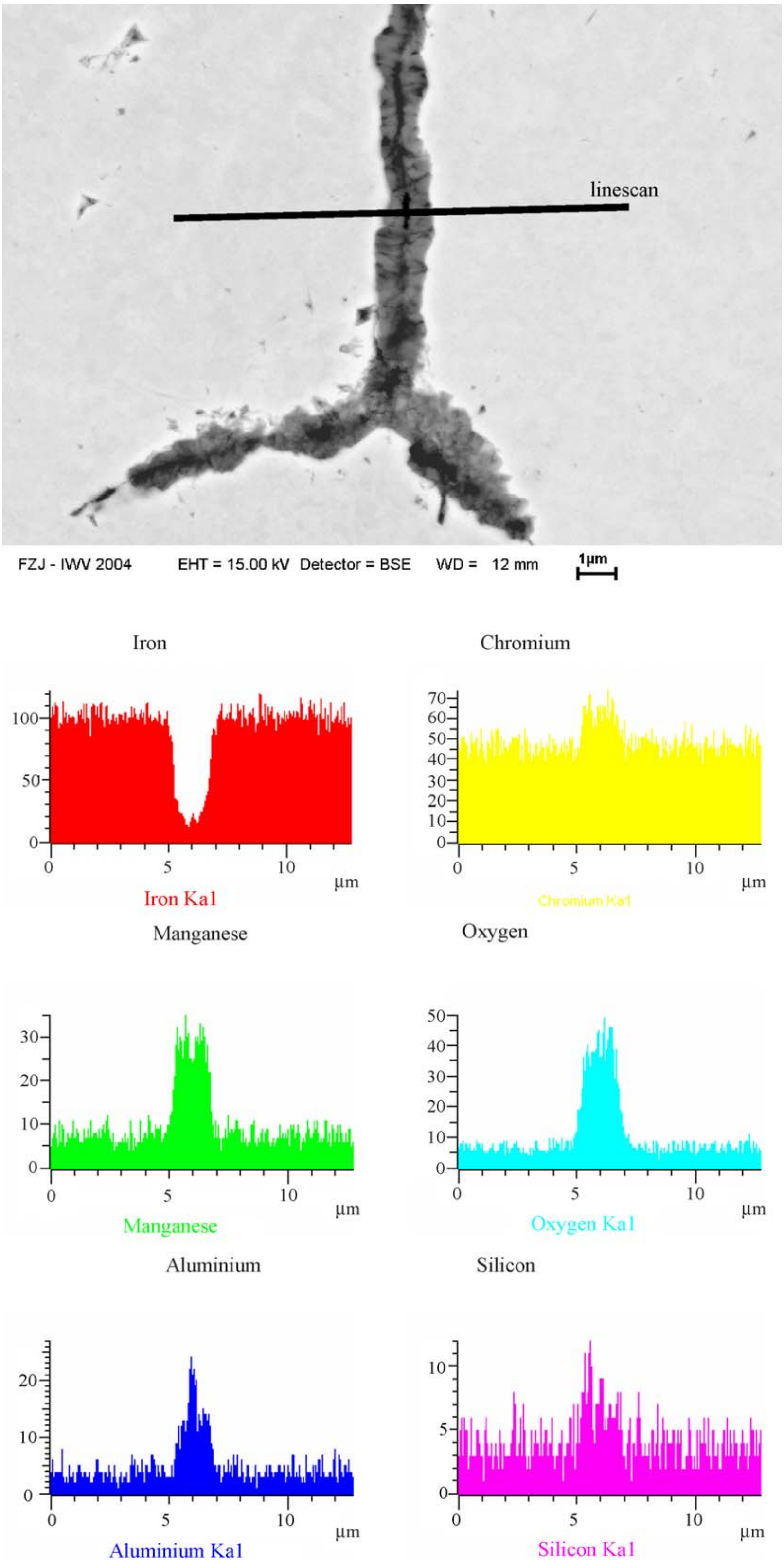

Fig. 12. SEM cross section and line scan of a sample annealed for 500 h in humidified hydrogen; EDX analysis of Fe, Cr, Mn, O, Al and Si.

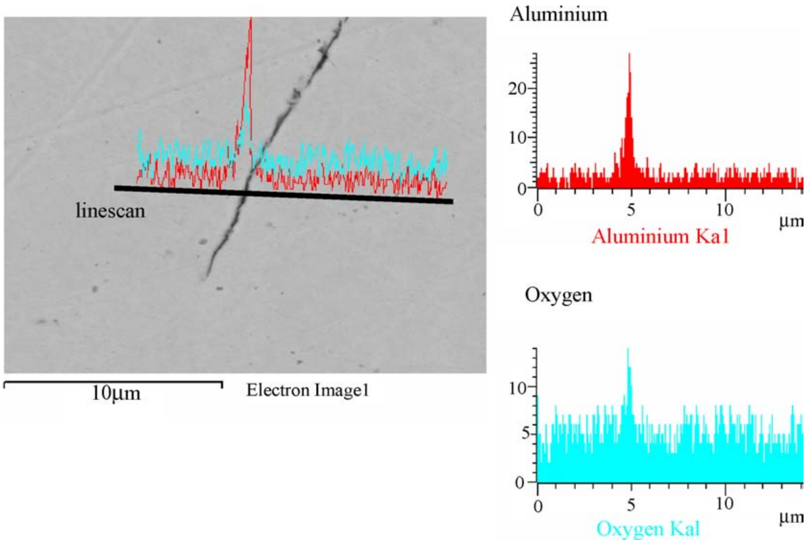

Fig. 13. SEM cross section and line scan of the oxidation peak.

4.2. *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, enhanced interdiffusion or double layer formation on the non-wetted steel surface 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–aluminium–silicate glass A could be used within an SOFC stack to seal the air compartment side.

4.3. *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 vapour 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 better usually 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 vapour, pO_2 4.06×10^{-22}) 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 in volume, Crofer22APU 1st reacts alongside the grain boundaries of the metal. SEM-EDX characterizations show that the tracer elements such as aluminium 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. Additionally the oxidation of aluminium and silicon are favoured due to their low dissociation pressure. Afterwards even manganese and chromium were oxidized (see above). The question whether both tracer elements or possibly only one of the two is necessary to support this grain boundary oriented 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 completely and not only at those zones where the glass–ceramic sealant is present. Also this reason is less likely.

2. If aluminium and silicon are localized at the grain boundaries and subsequently preferentially oxidized, the resulting greater volume due to the oxygen uptake and the lower density of the oxides formed 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 aluminium 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. [15].
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 imitate the oxidation.
5. If hydrogen/water vapour is necessary for internal metal oxidation it may be attributed to an interaction of hydrogen/water vapour with the double oxide layer to form hydroxides or other volatile species; possibly the layer is therefore not dense for oxygen migration under the chosen atmospheric conditions.

In fact, the existence of aluminium and silicon, the humidified hydrogen atmosphere (or corresponding the low pO_2) 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 the 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 the other hand, if the swelling starts from both sides of the interconnect, the gap between the metals may be bridged over and thus leading to short circuiting. Note that the swelling was approximately 30–50 μm after 500 h of exposure and the gap between the interconnects is only about 200 μm. For long-term operation of a stack this may lead to a problem.

Additionally, steel is easily diffused by hydrogen. Thus H_2 may migrate from the anode side of the bipolar plate to the cathodic side (if hydrogen is necessary for the reaction). If hydrogen reaches the cathode side and the oxide layer on the steel does not behave as a diffusion barrier for H_2, or hydrogen diffuses by another way (through the glass–ceramic, through the oxide scale, through cracks) the H_2 can influence the atmospheric conditions prevailing and thus leading to the observed oxidation reactions.

5. Conclusions and outlook

The annealing of sealed samples of a barium–calcium–aluminium–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 trace element-free steel (JS-3) was 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 in volume, Crofer22APU 1st forms chromia alongside the grain boundaries. The reaction depth and width for Crofer22APU 1st is approximately five times that of JS-3. The internal oxidation is dramatically promoted by the combination of minor steel constituents such as aluminium and silicon, the surrounding atmosphere and elements from the glass–ceramic. Due to the enhanced internal oxidation the steel swells. It should be noted 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.

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