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Journal of Power Sources 141 (2005) 102–107
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Short communication

A novel method to evaluate the suitability of glass sealant–alloy combinations under SOFC stack conditions

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Received 25 May 2004; received in revised form 13 August 2004; accepted 13 August 2004

Abstract

A novel test method has been developed to evaluate the suitability of combinations of sealing materials and alloys under simulated SOFC stack conditions. This method is based on test samples of two metallic sheets, joined together with a glass or glass–ceramic sealant. The outer side of the sample is exposed to ambient atmosphere, whereas the inner side can be exposed to different gas compositions. The whole set-up is placed in a furnace. Optionally, an external voltage can be applied across the sheets.

The background of the experimental design was the development of a methodology to investigate interaction phenomena between steel alloys and glass ceramic sealants under controlled conditions. Although exposure and oxidation experiments under atmospheric conditions did not show any indication of detrimental effects, corrosion was observed in actual stack experiments. The experimental set-up was thus designed in order to study the influence of single parameters on the interaction of alloy and sealant.

With this method the governing influences in simulated SOFC operation can be identified. Obviously, the presence of a dual hydrogen–air atmosphere induces enhanced corrosion in certain material combinations. The experiments presented here allow a systematic study of the materials in question and a rapid characterisation.

Keywords: SOFC; Glass sealants; Interconnect materials; Ferritic high-chromium alloys; Resistance measurements; Corrosion

1. Introduction

Solid oxide fuel cells (SOFC) are promising energy conversion systems with high conversion efficiencies and low carbon dioxide emissions. This is due to the direct conversion of chemical energy into electrical energy. Such a system, once it meets the targets for long-term durability and reliability, can compete with conventional energy conversion devices.

For the medium-term expectations, the potential long-life durability of planar SOFC stacks is more than 40,000 h. However, various stack components still suffer from degradation, which significantly limits the practical operation time. This can partly be explained by undesired chemical and physical interactions between the glass or glass–ceramic sealant, the alloy to be used for the interconnect and the manifold, and the surrounding gas atmosphere [1].

Glass–ceramic based materials from a BCAS (BaO–CaO–Al_2O_3–SiO_2) system are often used for joining dissimilar materials, i.e. ceramic cells, metallic manifolds, and metallic interconnects [1–3]. These joints should be both gastight and electrically insulating, which implies that the sealants should separate (a) the fuel gas in the inlet and outlet channels from the oxidising environment, i.e. the cathode compartment and outer side of the stack (ambient atmosphere), and (b) the oxidising gas in the inlet and outlet channels from the anode compartment (fuel gas) and the outer ambient environment. In addition to these properties, the glass sealant should possess a satisfactory matching of the thermal expansion coefficient with the cells and the chosen alloy, and it should also exhibit long-term stability under oxidising as well as dual environmental conditions at high temperatures.

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doi:10.1016/j.jpowsour.2004.08.053

Several studies evaluating glass and glass–ceramic sealants are based on determining the chemical and/or physical interactions between glasses and interconnect alloys [1–13]. Recent studies have shown that the presence of a dual atmosphere, i.e. hydrogen on one side of the sample and air on the other, can have a significant effect on the oxidation behaviour of the underlying alloy [14].

In this paper, a novel method is presented for evaluating the suitability of sealing material–alloy combinations under simulated conditions relevant for SOFC stacks. With this method several experimental parameters affecting stack life can be varied systematically allowing a systematic approach to the influence of each parameter on the physical and chemical interactions between the sealant and the alloy.

2. Experimental

2.1. Experimental set-up

Experiments were performed with sandwich samples based on two metallic sheets, which were joined together by glass paste applied by a dispenser. One of the sheets also contained a small hole allowing the desired gas composition to reach the inner part of the sample. In order to measure the electrical resistance of the joined couple, each sheet was connected to two Pt-wires, one to apply the desired external voltage over the sheets and the other to measure the current density. The samples were placed on top of a hermetically sealed alumina housing with four gas outlets. With this set-up a maximum of four samples could be tested simultaneously. A silver gasket was used to obtain sufficient gas tightness between the alumina housing and the sample.

After the sandwich samples were placed into the furnace, each sample was loaded with a weight of about 300 g. Joining of the metallic sheets and crystallisation of the glass sealant were carried out by a thermal cycle performed in air. The samples were heated to 850 °C at 1 °C min^{-1}. After reaching this temperature, a dwell time was set. This was followed by cooling the furnace down to 800 °C at 1 °C min^{-1}. During this temperature cycle organic solvents were removed, the glass was softened and a chemical interaction occurred between the glass sealant and the alloy resulting in sufficient bonding.

After the furnace reached the desired test temperature, in this case 800 °C, the inner part of the alumina housing was flushed (100 ml min^{-1} ATP) with the desired gas composition: on the inner side hydrogen saturated with 3 vol.% H_2O, and on the outer part of the samples air. Optionally, an external voltage typically prevailing in SOFC stacks could be applied. All data were obtained by dc methods using a current-control power supply type Gossen 24 K32R4 (Gossen-Metrawatt GmbH, Germany) and a computer-controlled data acquisition system including a datalogger type NetDAQ 2640A (Fluke, The Netherlands). Current density, external voltage, and consequently the electrical resistance were monitored continuously. If no external voltage was applied, the ohmic resistance was measured at regular intervals of approximately 24 h. A schematic set-up of the test unit is depicted in Fig. 1. After the total exposure time, the samples were cooled down to ambient temperature at a rate of 1 °C min^{-1}. During cooling the inner part of the samples was flushed with argon.

With respect to the electrical behaviour of the samples as a function of the exposure time, plots are presented with the specific resistance on the *Y*-axis and the exposure time on the *X*-axis. The specific resistance is calculated from the measured ohmic resistance between the two metallic sheets and corrected for the total surface area and thickness of the glass sealant.

2.2. Material

A series of experiments were performed with sandwich samples consisting of two metallic sheets from a ferritic-type high-chromium alloy (A1: Fe–23Cr). Metallic sheets with a thickness of 2.0–3.0 mm were cut into 50 mm × 50 mm squares, and a small hole (diameter: 10 mm) was drilled into

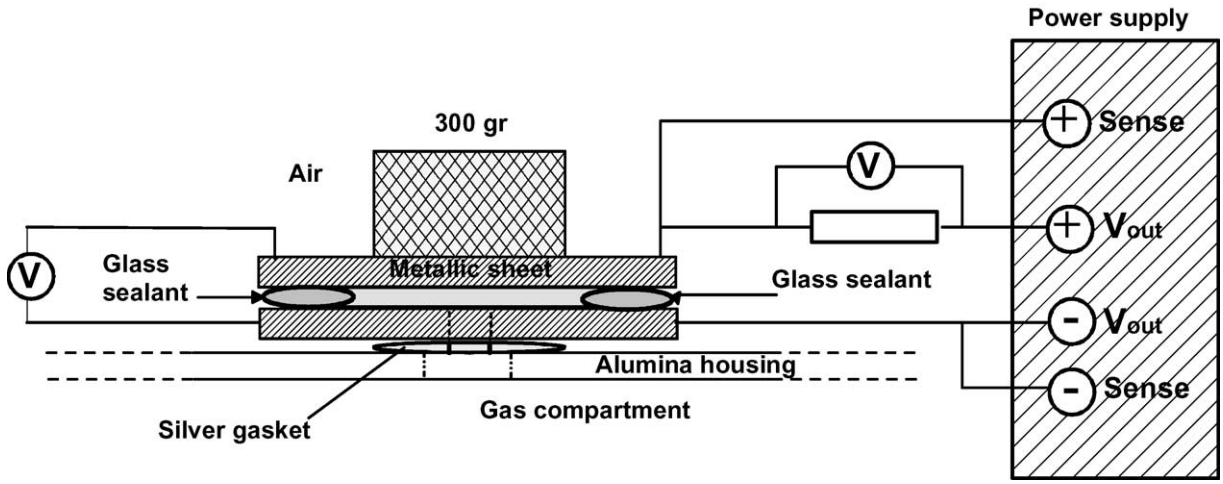

Fig. 1. Schematic view of the experimental set-up for electrical resistance measurements during high-temperature exposure in dual atmospheres.

Table 1
Chemical composition of the alloy A-1 used

Fe	Bal.
Cr	22.6
Mn	0.4
Ti	0.06
Si	0.1
Al	0.1
Re-el.	La-0.1
Ni	0.2

one sheet. The surface of the alloy sheets was subsequently ground, polished, and ultrasonically cleaned with ethanol and acetone to remove organic substances. Table 1 shows the chemical composition of the model alloy tested.

The glass sealant, indicated as type 73, is based on SiO_2 (35.3 wt.%), CaO (8.4 wt.%), BaO (40.8 wt.%), Al_2O_3 (2.5 wt.%), including minor additions of transition metal oxides to optimise the SOFC relevant physical and chemical properties. The glass paste was applied by a dispenser to the circumference of one sheet.

2.3. Experimental conditions

Experiments were performed under various conditions, i.e.:

- air–air (without an externally applied voltage);
- air–air (with an externally applied voltage of 800 mV);
- hydrogen (3 vol.% H_2O)–air (without external applied voltage);
- hydrogen (3 vol.% H_2O)–air (with external applied voltage of 800 mV);
- hydrogen–hydrogen (both 3 vol.% H_2O) (without external applied voltage).

2.4. Characterisation

Scanning electron microscopy (SEM) analyses of the surface morphology and cross-sections were performed using a LEO 1530 electron microscope (Gemini).

3. Results

3.1. Electrical resistance measurements

Conductivity measurements of samples exposed in air–air at 800 °C showed no obvious degradation of the electrical resistance of the glass sealant. After 400 h of exposure the specific resistance of the samples was still more than 1 kΩ m. This indicates that under these conditions no undesired electrical connection was formed between the metallic sheets. Similar experiments were performed applying an external voltage of 800 mV. The specific resistance remained sufficiently high. Based on these results, it can be concluded that after exposure in air for 400 h at 800 °C the insulation capacity

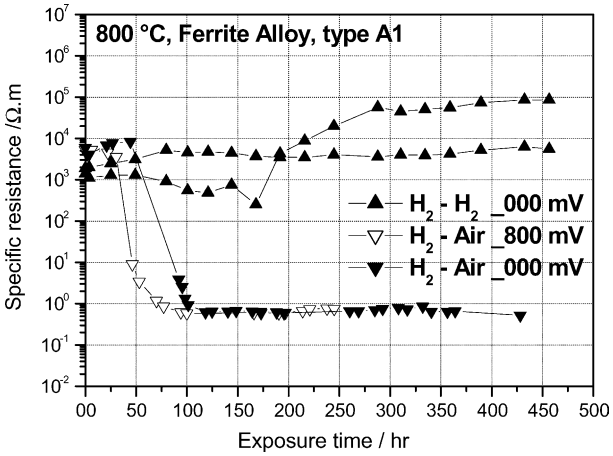

Fig. 2. Specific resistance of a ferritic alloy type A1 as a function of the exposure time.

of the glass sealant was still satisfactory. No additional effects occurred with an externally applied voltage. To investigate the effect of a dual gas atmosphere, a series of experiments were carried out with air on the outer side and hydrogen (3 vol.% H_2O) on the inner side of the sample. The specific resistance of the samples as a function of the exposure time is shown in Fig. 2. From this figure it is clear that after about 50 h of exposure the specific resistance was significantly reduced from almost 10 kΩ m to less than 1 Ω m. No obvious differences were observed between the conductivity of samples with or without an externally applied voltage. This indicates that the insulation capacity of the sample was significantly affected by the presence of a dual environment with hydrogen and air as the main gaseous reactants.

For reasons of completeness experiments were performed in hydrogen (3 vol.% H_2O). In this case, no external voltage was applied. The specific resistance as a function of the exposure time is shown in Fig. 2. Under these conditions, the specific resistance did not significantly change, indicating that under a hydrogen (3 vol.% H_2O) atmosphere the reaction processes were not changed in such a way that the resistance was reduced.

3.2. SEM analysis

Fig. 3a shows the surface morphology of the inner part of a sandwich sample exposed in air for 400 h at 800 °C (no external voltage applied). The outer surface of the alloy (top) consists mainly of an oxide rich in chromium and manganese. Near the three-phase boundary, i.e. air–glass–alloy, a relatively high amount of a bright crystalline phase was formed, rich in barium, chromium, and oxygen.

At the bottom part of this micrograph crystalline phases of the glass sealant are observed. Similar features were found with samples exposed in air but including an external applied voltage. No other oxidation products were formed which might finally lead to degradation of the electrical resistance between the two sheets.

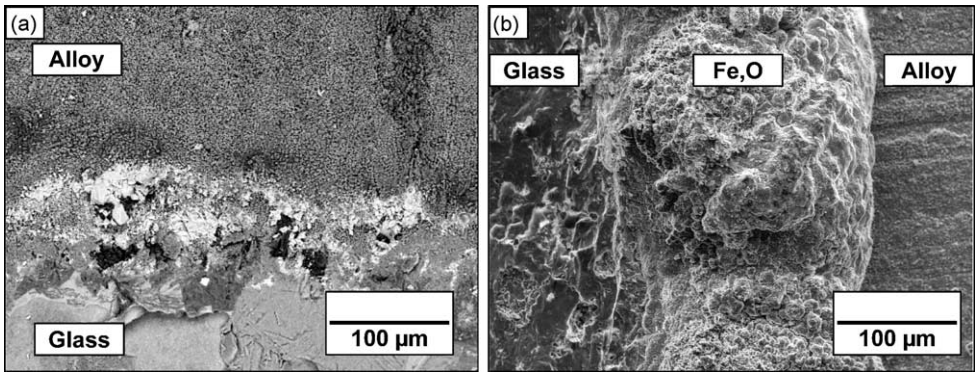

Fig. 3. SEM micrographs of the surface morphology of a ferritic alloy type A1 with glass sealant type 73 after 400 h of exposure at 800 °C, (a) in air–air (without externally applied voltage) and (b) in hydrogen (3 vol.% H_2O)–air (including an external voltage of 800 mV).

With respect to the sandwich sample exposed in a dual atmosphere consisting of hydrogen and air, a different surface morphology was observed. Along the glass edge, large iron-containing oxide nodules were present. Excessive oxide growth occurred, which finally could lead to "bridge formation" between the two metallic sheets. Fig. 3b shows a SEM micrograph of the surface morphology of Alloy A1 with glass sealant type 73 after 400 h of exposure in a dual atmosphere at 800 °C. In this case, an external voltage of 800 mV was applied. Furthermore, from SEM observations it was concluded that the presence of an external voltage of 800 mV did not obviously affect the formation of the various reaction products.

Sandwich samples were also tested in hydrogen, saturated with 3 vol.% H_2O. During 400 h of exposure at 800 °C no short-circuiting phenomena occurred, indicating that under these experimental conditions no highly conductive corrosion products were formed between the two metallic sheets. Removing the sheets from each other, it appeared that neither yellowish reaction products (barium chromate), nor any brownish corrosion products (iron-containing oxides) were formed near the three-phase boundary.

Fig. 4 shows the surface morphology of the alloy with glass sealant type 73 near the three-phase boundary. The outer metallic surface shows the formation of only small oxide particles (bottom part of Fig. 4a). Interesting to note is the presence of small cracks parallel to the three-phase boundary. The glass sealant, as shown in Fig. 4a (upper part) and b, displays a crystalline structure, with crystals rich in Ba, Si, and O, or Ba, Ca, Si, and O.

4. Discussion

To obtain more insight into the relation between the chosen experimental parameters simulating SOFC stack conditions and the chemical and physical compatibility of glass sealants with various ferritic, chromia-forming alloys, a novel test method was developed to investigate their interaction phenomena under controlled conditions.

In the first case, the experimental conditions were closely related to those expected in real SOFC devices, i.e. separating cathode chamber and oxidant inlet and outlet channels from the outer ambient environment.

Conductivity measurements performed in air revealed no electrical degradation. This means that during 400 h of exposure no highly conductive oxide products were formed adversely affecting the electrical insulation between the two metallic sheets. Furthermore, SEM analyses revealed the formation of a yellowish reaction product, rich in Ba, Cr and O,

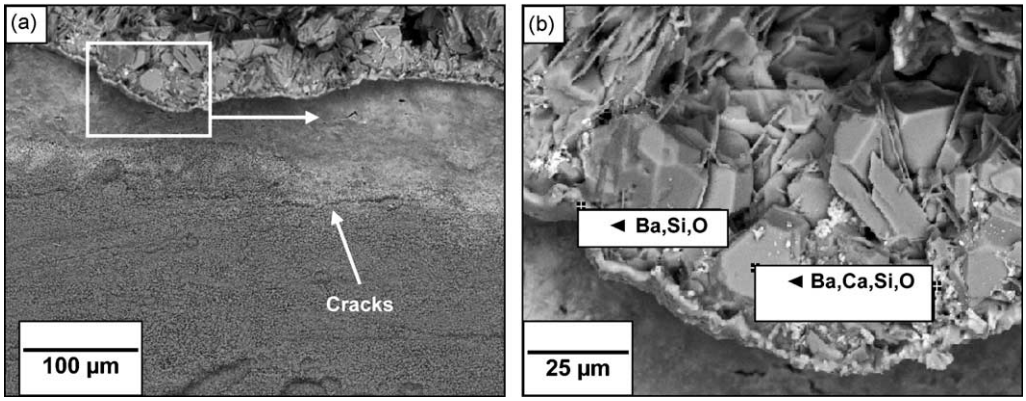

Fig. 4. SEM micrographs of the surface morphology of alloy A1 with glass sealant type 73 after 400 h of exposure in hydrogen at 800 °C. No external voltage was applied. Micrograph b shows a higher magnification of the glass edge as depicted in micrograph a.

along the edges of the glass sealant. The formation of this oxide can be explained by the presence of a chromium oxide scale which is in contact with the glass sealant containing BaO. Under oxidising conditions these species can form $BaCrO_4$. At the interface between the glass sealant and the alloy, a thin chromium-rich oxide layer was formed. Here, no extensive formation of $BaCrO_4$ was found.

From these observations, it was concluded that under purely oxidising conditions the glass sealant–alloy combination showed satisfactory interaction. Moreover, type 73 is a potential candidate to be used for stacks where the sealant has to separate the air in the channels and in the cathode compartment from the outer ambient environment.

In order to investigate the effect of an external voltage on the interaction between the glass sealant and the adjacent alloy, the experimental set-up was slightly modified. Here, realistic stack operation conditions including a constant load were simulated, where the glass sealant separates the oxidant channels and the cathode chamber from the outer ambient atmosphere. Conductivity measurements as well as surface morphological analyses of these samples showed that the results were similar to those observed under similar test conditions apart from an externally applied voltage. This means that with the above-mentioned alloy–sealant combinations the presence of an externally applied voltage of 800 mV is not required.

The use of sandwich samples with hydrogen (humidified with 3 vol.% H_2O) at the inner side and air at the outer part of the sample simulates that part of a stack where the glass sealant has to reliably prevent mixing of the oxidising atmosphere with the fuel gas in the inlet and outlet channels and that in the anode chamber. Also, in this case, no differences occurred between samples exposed with or without an externally applied voltage. Noticeably different to the former observations, with samples exposed in only air, was the fact that under these experimental conditions, including a dual atmosphere differences in the electrical and corrosion behaviour occurred. The samples already showed a substantial decrease of the specific resistance after short exposure times, indicating the presence of an electrical shunt between the two metallic sheets. Surface morphological analyses showed that in the case of short-circuiting significant amounts of voluminous corrosion products were formed, in addition to the formation of a Ba- and Cr-rich oxide. In particular, the formation of iron-rich oxide products, often found near the three-phase boundary, i.e. glass sealant–air–alloy, is worth noting. These fast-growing and highly conductive oxides finally result in "bridge formation" between the two metallic sheets. The iron-rich oxide products were not found near the three-phase boundary of glass sealant–hydrogen–alloy.

These results show that with the given experimental conditions including a dual gas atmosphere of hydrogen and air, the electrical properties and corrosion behaviour of the sandwich samples strongly depend on the chosen test parameters. Therefore, care has to be taken with respect to a thorough consideration of test parameters simulating the conditions prevailing in real SOFC stacks. Alloy–glass sealant combinations, which showed an excellent behaviour under purely oxidising conditions, can still be very susceptible to internal and external oxide formation, the latter resulting in short-circuiting, under a dual atmosphere. Moreover, to create model studies simulating complete SOFC devices, which can be performed with this novel method, it is important to make a critical analysis of the experimental conditions as present in these SOFC devices.

For comparison reasons, tests were also made in hydrogen only with 3 vol.% water vapour, but without an externally applied voltage. Conductivity measurements showed that the specific resistance of the two alloys was not obviously altered during 400 h of exposure at 800 °C, indicating that no short-circuiting had taken place. Here, no fast-growing external oxide products were observed, but crack formation did occur in the alloy near the three-phase boundary.

5. Conclusions

- A novel test method was developed to evaluate the compatibility of suitable "glass or glass–ceramic sealants"–"ferritic chromia-forming alloys" combinations under various realistic SOFC stack conditions.
- Significant differences occurred between the electrical properties and chemical behaviour of "sandwich" samples when exposed in only ambient atmosphere or in a dual environment simulating SOFC stack conditions.
- Carefully selected test conditions can simulate real SOFC stack conditions, and, as a result, the electrical, physical, and chemical behaviour of investigated samples is closer to that of materials used in real SOFC stacks.
- Before performing model experiments to evaluate the behaviour of materials (combinations) in SOFC devices, it is recommended that a critical evaluation should be made of the experimental conditions prevailing in SOFC devices.

Acknowledgements

The authors would like to thank the Central Department of Technology (Forschungszentrum Jülich GmbH, Germany), in particular Mr. A. Cramer, for the preparation of the sandwich samples. In addition, the authors gratefully acknowledge Dr. P. Batfalsky, Dr. D. Sebold, and Dr. E. Wessel for their assistance in SEM sample preparation and analyses, Mr. H. Wesemeyer for performing the resistance experiments, and the members of the TFK Group for their fruitful discussions.

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