GLASS-CERAMIC COMPOSITE
AS A NEW SEALING MATERIAL FOR SOFCs

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ABSTRACT

A composite material consisting of BaO-2SiO₂ (BS₂) as crystalline component in a CaO-MgO-Al₂O₃-SiO₂ glass matrix was evaluated as sealing material for solid oxide fuel cell stacks. Microstructural measurements using XRD and EDX indicated a reaction of the barium disilicate to barium aluminosilicate BaO-Al₂O₃·2SiO₂ (celsian). Dilatometric studies were performed on sintered composites. Although the CTE is lower than required, a good joining behavior and thermal cycling behavior with high chromium ferritic steels were obtained. Investigations of the chemical stability of the composite sealant under simulated SOFC conditions in a dual atmosphere revealed a good compatibility with the steel.

INTRODUCTION

During the last decade, crystallizing glass sealants have been used for the joining of solid oxide fuel cell (SOFC) stacks (1-5). An amorphous glass powder is applied onto the interconnect and cell plates. When heating up, the glass becomes viscous and flows. As a result, the cells are connected and at the same time a gas-tight and electrically insulating joint is achieved. During the heat treatment, the glass starts to crystallize and forms a glass-ceramic seal. This has the advantage of an enhanced stability against reducing and humid atmospheres. Another important process taking place during the joining procedure is the adhesion of the glass ceramics to the steel surface. The glass dissolves the oxide scale of the steel. By this interfacial reaction, interlocking is achieved. Once the glass is fully crystallized, this bonding process comes to an end. It is understandable that crystallization and dissolution are conflicting objectives: A rapidly formed glass ceramic would yield a joint with poor adhesion to the steel surface, on the other hand, slow crystallization is unfavorable due to the higher reactivity and possible corrosion at the steel interface and, furthermore, due to the long processing times required for joining (6).

The newly developed sealing material presented in this study consists of a pre-crystallized phase which is added to a glass matrix.

Matching the coefficient of thermal expansion (CTE) to the other stack components (CTE...
~ 10-12·10^{-6} \text{ K}^{-1}\) is usually an important requirement for developing glass-ceramic sealants. The CTE of glasses is usually lower than the CTE of the corresponding crystalline phases. The described composite material offers the advantage that the overall CTE can be previously determined – according to a simple mixing rule – by the relatively high amounts of the crystalline phase and a low one of the glass matrix. A high crystallization velocity of the glass matrix itself is not mandatory, as the pre-crystallized powder additives act as nucleating agents in these cases. Especially the alkaline earth silicates show CTEs well adapted to the other stack components. In this study, barium disilicate was chosen as pre-crystallized additive for the composite material. Spontaneous barium disilicate formation has been observed with previously investigated sealant compositions containing high BaO contents. This led to barium chromate formation at the steel interface, which was detrimental to sticking. The new approach allows to avoid the formation of barium chromate, especially at the three phase boundary (TPB) of steel – glass – air, by selecting a glass matrix formulated on the basis of the system CaO-Al_{2}O_{3}-MgO-SiO_{2}, i.e., without any barium oxide. With the new material, a characterization of the physical properties of the composite material itself as well as joining tests and investigations of chemical stability were performed.

**EXPERIMENTAL**

The composite material consists of a crystalline powder of barium disilicate (BS2) and a glass matrix of the CaO-Al_{2}O_{3}-MgO-SiO_{2} system (CAMS). The glasses were melted from a batch of pure carbonates and oxides in an inductively heated platinum crucible at 1480°C. The raw materials were distributed by Merck KGaA (Darmstadt, Germany) and had a grade of purity higher than 99%. After two hours, the melt was quenched by pouring it into ice water, rinsed with acetone and dried in a heating chamber at 60°C. For a better homogenization of the glass, the melting procedure was carried out twice. The glass frits for the glass matrix were wet-milled in acetone in an agate ball mill to a median particle size of 15 μm. The chemical composition was analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES); the resulting composition for glass type ‘V7’ is shown in table 1.

| Table 1. Chemical compositions of the glass matrix in wt% |
|------------|------------|-------------|--------------|--------------|------------|-------------|-------------|
| SiO₂       | CaO        | MgO         | Al₂O₃        | B₂O₃         | V₂O₅      | Li₂O        | Co₂O₃       |
| V7         | 27         | 25          | 7           | 14.8         | 20         | 3           | 0.2         | 3           |

Crystalline powder of BS2 was obtained by heating frits to 1250°C, followed by controlled cooling to room temperature with 5 K/min. The crystallized material was milled in an agate ball mill and sieved to a particle size fraction of 25 to 63 μm. X-ray diffraction measurements were carried out on the powder. For dilatometric measurements, a bar was pressed to a shape of 25 x 5 x 5 mm³ and sintered at 1250°C for 10 h. Dilatometric measurements were performed with a double sample Linseis L75 dilatometer at a heating rate of 3 K/min. Different mixtures with additions of 5, 10 and 20 wt% of ceramic component to the glass matrix powder were prepared as candidates for sealing materials. The powders were blended to a paste, using ethyl cellulose as binder in terpineole. For joining experiments, the paste was then dispensed to a steel surface by robot tracking. A high chromium containing ferritic steel was used in this study, the...
The chemical composition of which is given in table 2. This steel was developed in particular for high temperature applications at Forschungszentrum Jülich (7) and is now manufactured by ThyssenKrupp VDM, Germany under the product label Crofer22APU. The surfaces of the steel coupons (50 x 50 x 3 mm³) were ground using BN grit (125 μm). Before dispensing the sealant frit, the steel samples were cleaned in ethanol in an ultrasonic bath for 10 minutes and then rinsed with acetone. For so-called “sandwiched” samples, the glass paste was applied to the outer contour of one of the metallic sheets.

Table 2. Chemical composition of the ferritic steel in wt% (8).

|   | Cr  | Fe  | C   | Mn | Si  | Al  | Cu  | P   | Ti   | La  |
|---|-----|-----|-----|----|-----|-----|-----|-----|------|-----|
| Crofer22APU| 20- | bal | 0.03| 0.30-| 0.80| 0.12| 0.50| 0.05| 0.03- | 0.04-|
|24   |     |     |     |     |     |     |     |     | 0.20 | 0.20|

The joining of the samples was carried out by placing a dead load of 300 g on top of a second steel plate and heating this sandwich specimen in air up to 850°C with a rate of 2 K/min in air. After a dwell time of several hours, the samples were cooled to room temperature at a rate of 2 K/min and the gas-tightness was checked by He leakage detection (UL200, Inficon).

In order to investigate the interactions between steel and glass-ceramic composite under atmospheric SOFC stack conditions, electrical resistance measurements were carried out. The sandwiched samples were exposed to a dual atmosphere: The inner cavity between the two joined coupons to humidified hydrogen atmosphere (H₂ - 3% H₂O), and the outer side to air. The electrical resistance between the two metallic plates was recorded during the exposure for 400 h. More information about this method of electrical resistance measurements can be found in (9). After exposure, the samples were epoxy-mounted and cross-sectioned. The cross-sections were analyzed by optical and scanning electron microscopy (Cambridge Stereoscan 360) with energy dispersive X-ray analysis (Oxford EDX) at an operating voltage of 20 kV.

RESULTS

Dilatometric Measurements

The CTE was measured on sintered bar shaped samples for the crystalline component BS₂ itself as well as for the composite sealing material, consisting of 10% BS₂ and 90% V7 (BS₂/V7-10/90). In the temperature range between 600 and 800°C, a value of 12.4·10⁻⁶ K⁻¹ was measured for the pure BS₂. For the composite material BS₂/V7-10/90, a value of 8.9·10⁻⁶ K⁻¹ was recorded at 700°C.

X-ray Diffraction Analysis

The crystalline component barium silicate was analyzed in terms of the phase content in the synthesized state. The results are shown in figure 1. Three binary phases of the system BaO-SiO₂ were related to the diffraction pattern. The major phase was detected to be sanbornite BaSi₂O₅.
The analysis was carried out on the composite sealing material, consisting of 10% BS$_2$ and 90% V7 after a thermal treatment of 850°C for one hour, followed by soaking at 800°C for 100 hours. Beside celsian (BaAl$_2$Si$_2$O$_8$) as the major phase, anorthite (CaAl$_2$Si$_2$O$_8$), diopside (CaMgSi$_2$O$_6$) and monticellite (CaMgSiO$_4$) were also detected. The initially used binary barium silicates could not be detected in the composite material anymore.

![XRD analysis of the crystalline component BS$_2$ as synthesized.](image)

**Joining Tests**

In order to determine the suitability of glass V7 based composites as a sealing material, joining tests were carried out with varying additions of crystalline compound, ranging from 5 up to 20 wt% of BS$_2$. Best results were obtained for 10% BS$_2$ and 90% V7. Low He leakage rates were measured for sandwiched samples of BS$_2$/V7-10/90 even after 50 thermal cycles. With higher portions of crystalline phase added, the viscosity during joining was too high and the achieved overall height shrinkage did not meet the geometrical requirements for our specific design of SOFC stacks. The gas tightness of composite materials with additions of less than 10% of crystalline compounds was poor, He leakage rates in the range of $10^{-3}$ mbar·l·s$^{-1}$ were measured for 5% BS$_2$ and 95% V7.

**Microstructural Analysis**

The phase formation after joining was analyzed on cross-sections by EDX. In figure 2, a SEM image of a cross-section of a sandwiched sample of composite material V7 with 10% BS$_2$ is shown.

The microstructure of the glass-ceramic sealant includes a high number of small crystallites, which can be seen in between the large particles of the crystalline compound as bright white clusters. Both very fine and large pores are found, with the growth of crystallites occurring in the large voids. In the lower part of the image to the right, the interface to the steel is visible. A thick and distinct layer of chromium oxide of around 3 μm is formed at the interface between glass-ceramic material and steel. The interfacial zone between glass-ceramic and steel surface shows, however, a good adhesion of the
composite material to the steel surface. The protective oxide scale of the steel is not penetrated or dissolved by the glass matrix, as it is usually observed for glass-ceramic sealants of the system BaO-CaO-SiO₂ (6).

EDX spectra were recorded at the points marked in fig. 2b. The crystalline compound consists of aluminum besides silicium, barium and oxygen (point 1). The relative amounts of elements match with the stoichiometry of celsian (BaO·Al₂O₃·2SiO₂). The dark gray crystals are detected to consist mainly of calcium, silicium and oxygen with varying amounts of Al (point 2). The light gray crystals were analyzed to be calcia-magnesia-silicates, although the quantities could not be associated with a single phase of the system (point 3).

**Electrical Resistance Measurements**

The electrical resistance of a sandwiched sample of Crofer22APU joined with composite sealing material BS₂/V7-10/90 did not change significantly change during exposure to the fuel cell atmospheres over 400 h (see figure 3).

Figure 3. Electrical resistance measurements as function of time for sandwiched samples of Crofer22APU with different glass compositions, exposed to a dual atmosphere.
After exposure, the samples were checked for gas tightness. The He leakage rate was below $10^{-9}$ mbar·s$^{-1}$. The samples were cross-sectioned and analyzed by SEM. In Figure 4, the three phase boundaries (TPB) of the joint to the different gas atmospheres are shown.

![Figure 4. SEM micrograph of the TPB of sandwiched sample of Crofer22APU joined with BS2/V7-10/90 a) air side b) 3% H₂O-H₂.](image)

On the air side of the sample, a dense layer of magnesium chromate was formed. Cracking of the layer can be assumed to be a result of the metallographical preparation of the sample. On the hydrogen side, no interfacial reaction can be observed. An open porosity is visible at the inner side of the sample. At the interface to the glass sealant, a thick chromia rich layer is formed on the steel. Besides the formation of alumina dendrites, no morphological changes of the steel interface are observed.

**DISCUSSION**

The main advantages expected when adding a crystalline compound to a glass sealant are:

- an improvement of strength of the material itself,
- an increase of the overall coefficient of thermal expansion CTE due to the high CTE of the crystalline phase and
- an enhanced chemical stability of the joining material by including an inert phase.

The material discussed here could not fulfill these expectations in all of these points.

Pure barium disilicate has a coefficient of thermal expansion which matches with the other stack components of Jülich F-design type planar, anode substrate cells (10). During the joining process, a phase conversion reaction of the crystalline component occurs. BS$_2$ is infiltrated by aluminum from the glass matrix and forms the thermodynamically favored ternary phase celsian BaO·Al$_2$O$_3$·SiO$_2$. The coefficient of thermal expansion is given in literature as $8 \times 10^{-6}$ K$^{-1}$ (11). As a consequence of this transformation, the desired increase in CTE of the composite material cannot be achieved.
Nevertheless, the material indeed shows excellent joining properties with sandwiched samples using steel coupons. A good wetting behavior and adhesion to the steel is observed. The samples withstand thermal cycling tests up to 50 times without any change of gas tightness. The chemical stability - as investigated by resistance measurements of sandwiched samples in a fuel cell alike dual atmosphere - is good. After exposure, no detrimental interactions could be found at the TPB glass-steel-atmosphere. As the glass matrix composition is free of barium, the formation of barium chromate at the TPB is avoided. Instead, on the air side of the sample a formation of a magnesium chromium oxide compound takes place. Thus, due to the high amount of nucleating centers, the addition of the pre-crystallized phases leads to a fast crystallization of the composite, and the amount of residual glass phase is too small to continue the formation of any magnesium chromium oxide compounds.

CONCLUSIONS

The newly developed glass-ceramic composites seem to be an excellent alternative sealing material for the joining of SOFC stacks. Beside good adhesion to the steel, a gas-tight and chemically compatible joint is formed. For the time being, the investigations have been performed at a laboratory scale only. In the future, the functionality of these new materials will be tested in stack assemblies.

With the prospect of realizing other chemically inert composites, crystalline additives like 2CaO·BaO·3SiO₂ or ceramic powders like ZrO₂ will be evaluated in future work.

ACKNOWLEDGMENTS

The authors would like to thank Mr. A. Cramer and Mr. K. Fischer for the preparation of the sandwiched samples, Mr. K. Watermeyer and Mrs. R. Göddertz for their assistance in SEM sample preparation, Mr. V. A. C. Haanappel and Mr. H. Wesemeyer for conducting the electrical resistance tests. In addition, the authors gratefully acknowledge the members of the glass sealant development group for their fruitful discussions.

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