ALUMINOSILICATE GLASS CERAMICS AS SEALANT IN SOFC STACKS

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ABSTRACT
The potential of aluminosilicate glass ceramics based on the AO-SiO2-Al2O3-B2O3 system (A = Ba, Ca, Mg) was investigated by systematic fundamental investigations. 13 different compositions were considered to determine also the influence of different Al2O3 concentrations and of nucleating agents in the MgO containing sealants. Glasses were obtained by the quenching of melts. Their characteristic temperatures, crystallization, and crystallization kinetics were determined. Electrical conductivities and component volatilities were additionally obtained for the sealants. Extensive studies revealed the chemical interactions at the interface between the sealants and the SOFC component materials, Ni and 8YSZ for the anode, 8YSZ for the electrolyte, as well as the oxide dispersion strengthened (ODS) alloy Cr5Fe1Y2O3 and a ferritic steel for the interconnect. The results showed that aluminosilicate glass ceramics have a high potential for the development of sealants for SOFC. Guidelines for the development are given.

INTRODUCTION
Gas tight materials are required for the sealing of the different components of planar SOFC to prevent gas leakage. Besides the gas tightness, these materials should show chemical stability to oxidizing and reducing atmospheres as well as to the component materials with which they come in contact. Further requirements are the insulating properties, matching thermal expansion coefficients, good wetting behavior during soldering and relaxation of stresses either through creep or viscous flow at operating temperatures. Several glass and glass ceramic systems were investigated as candidate materials for sealants (1-8).

Glass ceramics formed by controlled crystallization from glass can in principle meet most of these requirements by suitably choosing the components. As compared to glasses, they show superior mechanical properties and a greater flexibility for the adjustment of suitable thermal expansion coefficients, TECs. Further, it is expected that diffusion processes in glass ceramics are less than in glasses of the same chemical composition due
to the inherent difference in structure and bonding. It may also be pointed out that if a 
glass is used as sealant, during thermal cyclic operation of SOFC, it would be 
crystallized, which may not be controlled crystallization and, therefore, may lead to 
unpredictable behavior of the sealant depending on the operation time and temperature of 
the SOFC.

To develop a good sealant on the basis of glass ceramics, a series of samples of basic 
composition AO·SiO₂·Al₂O₃·B₂O₃ (A = Ba, Ca, Mg) (Table 1) was synthesized. Small 
amounts of B₂O₃ were added to reduce the glass transition temperature Tₐ. The content of 
Al₂O₃, an intermediate oxide, was varied between 5 mol% and 10 mol%. Moreover, 
additions of nucleating agents such as TiO₂, ZrO₂, Cr₂O₃, and Ni were tried in MgO 
based glasses in order to get more insight into the controlled crystallization process and to 
explore their potential for the suppression of undesired phases. The aluminosilicate 
samples were characterized by the determination of different properties, and their 
chemical interactions with the SOFC components determined in order to allow 
predictions concerning their potential use as sealant in SOFC. The component materials 
considered were Ni and 8YSZ for the anode, 8YSZ for the electrolyte, and the oxide 
dispersion strengthened (ODS) alloy Cr5Fe1Y2O3 and a ferritic steel with 18 mass% Cr 
for the interconnect.

EXPERIMENTAL

The glass compositions considered here together with their label are given in Table 1. 
The glasses were prepared from stoichiometric amounts of different constituent oxides or 
carbonates which were mixed in a ball mill, melted, and quenched. Samples 1-8, 12, and 
13 (Table 1) were quenched in water. The other samples were splat cooled between two 
steel plates to obtain flakes. The chemical analysis of the final products was carried out 
by inductively coupled plasma - optical emission spectroscopy, ICP-OES. The 
compositions determined are given in Table 1.

Phase analysis was conducted by X-ray diffraction analysis, XRD, (Philips 1050, 
CuKα, as well as STOE, CoKα. The chemical composition of the phases was obtained by 
scanning electron microscopy with energy dispersive X-ray analysis, SEM/EDX 
(CAMSCAN / Tracor Northern) and transmission electron microscopy with EDX, 
TEM/EDX (Philips). The thermal analyzer Netzsch STA 429 and the dilatometer Netzsch 
402 ED were used for differential thermal analysis, DTA, and for the determination of the 
thermal expansion coefficient, TEC, of the samples.

The chemical interactions between the sealants and the materials of the SOFC 
components were investigated by annealing the two materials in contact with each other 
under oxidizing and reducing conditions. Oxidizing conditions mean annealing under 
ambient air. Reducing conditions were adjusted by using initially a gas mixture composed 
of Ar with 4% H₂ which was humidified by passing a water bath at 84 °C and 
subsequently a condenser at 56 °C leading to a H₂O/H₂ ratio of 4.
RESULTS AND DISCUSSION

Characterization of the Glass Ceramics

The compositions of the samples in Table 1 were derived from weighed quantities and agreed with the results of the chemical analysis within the analytical uncertainty of 1% to 3%. The XRD analysis of the as prepared samples showed the amorphous nature of the glass. The glass transition $T_g$, crystallization $T_c$, and melting temperatures $T_m$ were obtained as shown in Table 2 by heating up the glass powder samples (medium grain size about 13 μm) with a rate of 10 K min$^{-1}$. Figure 1 shows some DTA diagrams as an example.

Table I: Glass compositions (at %) with label.

| Glass | BaO | CaO | MgO | SiO$_2$ | Al$_2$O$_3$ | B$_2$O$_3$ | TiO$_2$ | ZrO$_2$ | Cr$_2$O$_3$ | Ni | Label |
|-------|-----|-----|-----|---------|-------------|------------|---------|---------|------------|----|--------|
| 1     | 45  |     |     | 45      | 5           | 5          |         |         |            |    | BAS    |
| 2     | 45  |     |     | 45      | 5           | 5          |         |         |            |    | CAS    |
| 3     | 45  |     |     | 45      | 5           | 5          |         |         |            |    | MAS    |
| 4     | 40  |     |     | 45      | 10          | 5          |         |         |            |    | MAS10  |
| 5     | 38  |     |     | 45      | 10          | 5          | 2       |         |            |    | MAST10 |
| 6     | 38  |     |     | 45      | 10          | 5          | 2       |         |            |    | MASTZ10|
| 7     | 43  |     |     | 45      | 5           | 5          | 2       |         |            |    | MAST5  |
| 8     | 43  |     |     | 45      | 5           | 5          | 2       |         |            |    | MASTZ5 |
| 9     | 35.6|     |     | 43.1    | 12.8        | 3.6        | 4,9     |         |            |    | MAST12 |
| 10    | 43.7|     |     | 44.6    | 6.4         | 3.4        |         |         |            | 1.9|MASN6  |
| 11    | 46.2|     |     | 42.9    | 6.6         | 3.7        |         |         |            | 0.6|MASC6  |
| 12    | 33  |     |     | 45      | 10          | 5          | 7       |         |            |    | MAS7T10|
| 13    | 38  |     |     | 45      | 10          | 5          |         |         |            | 2  | MASN10 |

Table II Characteristic transformation temperature $T_g$, crystallisation temperature $T_c$, and peak temperature $T_p$ and activation energy of crystal growth of the investigated glasses in °C.

| Glass | $T_g$ | $T_c$ | $T_m$ | $T_p$ | $E_A$ [kJ/mol] |
|-------|-------|-------|-------|-------|----------------|
| 1     | 628   | 737   | 810   | 827   | 332            |
| 2     | 700   | 814   | 846   | 921   | 413            |
| 3     | 717   | 838   | ----- | 921   | 420            |
| 4     | 720   | 860   | 925   | 962   | 343            |
| 5     | 707   | 856   | 890   | 954   | 403            |
| 6     | 721   | 859   | 938   | 973   | 311            |
| 7     | 712   | 830   | 880   | 913   | 444            |
| 8     | 723   | 845   | ----- | 931   | 410            |
| 9     | 710   | 858   | ----- | 955   | 408            |
| 10    | 735   | ----- | 892   | 939   | 622            |
| 11    | 738   | ----- | 897   | 946   | 498            |
| 12    | 701   | 871   | 922   | 950   | 428            |
| 13    | 732   | 917   | 960   | 990   | 590            |

*) $T_p$ is the temperature of the exotherm crystallization peak.
Information on the crystallization kinetics was obtained by annealing the samples at temperatures of 900 °C and 1000 °C over time periods between 12 h and 1000 h. The phases formed were identified by XRD. The major phases determined in the glasses given in parenthesis are BaSiO₃, BaAl₂Si₂O₈ (BAS), CaSiO₃, CaAl₂Si₂O₈ (CAS), as well as MgSiO₃ and Mg₂Al₄Si₅O₁₈ (all MgO containing glasses). The formation of the Mg₂Al₄Si₅O₁₈ phase is detrimental for practical application as sealant due to its very low TEC of 2 × 10⁻⁶ K⁻¹ as compared to the major phases of the glass ceramics (e.g. 9 K⁻¹ - 12 × 10⁻⁶ K⁻¹ for MgSiO₃ and CaSiO₃). The formation of Mg₂Al₄Si₅O₁₈ is diminished in sealants containing 5 mol% Al₂O₃. The Mg₂Al₄Si₅O₁₈ formation can be suppressed by using the sealants MASC6 and MASN6 with grain sizes larger than 20 μm and MAST5 using lumps (grain size about 4 mm). The degree of suppression increases with increasing grain size. Sealant MAS shows this suppression for grain sizes smaller than 10 μm.

In addition, activation energies of crystal growth \( E_A \) were obtained by DTA as described in Ref. 4 (Table 2). They are of interest for practical application: The very low value for BAS means fast crystal growth whereas this growth is hindered for sealants such as MASN6 and MASC6 with high \( E_A \) values and crystallization temperatures. High \( E_A \) values render possible a good wetting during the soldering process. The different \( E_A \) values can be explained by the different field strengths of ions and by the fact whether an ion acts as network former or modifier. Ba²⁺ exhibits for example a very low field strength as compared to Ca²⁺ and Mg²⁺. Al acts for example at low concentrations as network former (relative high \( E_A \)) and at high concentration as modifier (relative low \( E_A \)).
The very low value of the glass transition temperature of the sealant BAS together with its low $E_a$ value means a very fast crystallization of this glass which could be shown by the determination of the percentage of crystallization in different samples using XRD after the same heat treatment (annealing at 900 °C and 1000 °C up to 1000 h). The glass BAS gets practically 100% crystallized at all temperatures after very short time periods. The crystallization of the other glasses amounts to between 50% and 100%.

The TEC of the sealant BAS is the highest due to the low field strength of the Ba$^{2+}$ ion. TiO$_2$ additions reduce the TEC due to the very high field strength of Ti$^{4+}$ (cf. Figure 2). The TEC is also influenced by the degree of crystallization after the applied annealing of the glass rods used in the measurements.

![Figure 2. Plot of thermal expansion for glass ceramics obtained from glasses BAS, CAS, MAS, MAS10, MAST10, and MASZ10, MAS7T10 and MASN10 after heat treating the glasses at 1000°C for 24h.](image)

Estimates of the vaporization of the sealant components in typical anode and cathode atmospheres show a high volatility of B$_2$O$_3$ at both sides of the cell and of SiO$_2$ at the anode side. The high volatility may be controlled by small free surface of the sealant in the stack. The presence of Na or K in sealants enhances dramatically the chromium vaporization from metallic interconnects by the formation of the very volatile Na$_2$CrO$_4$(g) and K$_2$CrO$_4$(g) species. It is generally known that the chromium vaporization leads to polarization losses due to the blocking of the active sites for the oxygen reduction at the cathode side (9).

Chemical Interactions between the Sealants and the SOFC Component Materials

The chemical interactions between the different glass ceramics and the SOFC components were studied by the annealing of powder mixtures as well as diffusion couples over different time periods under reducing and oxidizing conditions as well as by their subsequent characterization using XRD, ceramography, and analytical electron microscopy (SEM/EDX, TEM/EDX). Oxidizing and reducing conditions will be indicated in the following description of the results by (ox) and (red), respectively. No
reaction products between Ni and the sealants BAS and CAS were identified (ox and red) unlike between the Mg containing sealants and Ni where the (Mg,Ni)$_2$SiO$_4$ phase was often determined (ox and red). ZrSiO$_4$ was determined as reaction product between 8YSZ and the Mg containing glasses (ox and red). CAS in contact with 8YSZ gives rise to the formation of the Ca$_3$Zr(Si$_2$O$_9$)O$_2$ phase (ox) or monoclinic ZrO$_2$ (red). The following reaction phases were detected between Cr$_5$Fe$_1$Y$_2$O$_3$ and the glass ceramics given in parenthesis: BaCrO$_3$ (BAS) for (ox) unlike for (red), Ca$_3$Cr$_2$(SiO$_4$)$_3$ (CAS) for (ox and red), as well as the spinel (Mg,Fe)(Cr,Al)$_2$O$_4$ (Mg containing sealants) for (ox) and (red). The spinel (Fe,Mg)(Cr,Fe)$_2$O$_4$ was formed between the steel and the Mg containing sealants (ox). BaCrO$_3$ and Ba$_3$Fe$_2$Zr$_5$ were formed in powder mixtures of BAS and the steel (ox). CAS and steel formed Ca$_3$Cr$_2$(Si$_4$O$_9$)$_3$ (ox) and CaFeSiO$_4$ (red). Clearly it can be stated that the reactivity of the MgO containing sealants is significantly lower as compared to those containing BaO and CaO.

The preparation of interconnect/glass/8YSZ diffusion couples with good adhesion at the glass/interconnect interface was difficult at 1000 °C. Adherence for this interface was obtained for slurries of small MAS grains (<10 μm) as well as by the use of thin glass plates (thickness about 1 mm) for the samples MAST5, MASN6, and MASC6. The good adherence for the latter 3 sealants might be explained by the high activation energies of crystal growth leading to good wetting during the heat up procedure for the soldering due to the retarded crystallization. Moreover, the formation of the Mg$_2$Al$_4$Si$_5$O$_{18}$ phase is hindered under these conditions. A significantly improved adherence also for other sealants was obtained at 900 °C. The Mg$_2$Al$_4$Si$_5$O$_{18}$ phase formation is hindered here due to the low temperature. No experiments were carried out with slurries at 900 °C. The different adherence described above can be explained by the formation of the Mg$_2$Al$_4$Si$_5$O$_{18}$ phase which may lead to failure of the bond due to the already mentioned difference in the TECs (cf. Section 3.1). It seems that pre-oxidation of the interconnect alloy improves the adherence at the interconnect/sealant interface significantly as shown for a Cr$_5$Fe$_1$Y$_2$O$_3$/MASZ5 or MAST5/8YSZ diffusion couple at 1000 °C. The adherence at the glass/8YSZ interface was excellent for all glasses at 900 °C and 1000 °C.

The annealing experiments showed that the diffusion of Cr into the sealants is the highest. Results from 20 diffusion couples with 6 different glasses annealed at temperatures of 900 °C and 1000 °C up to 500 h showed that the diffusion coefficients of chromium range from about $10^{-12}$ cm$^2$ s$^{-1}$ at 1000 °C and short annealing time (≤50 h) up to $10^{-14}$ cm$^2$ s$^{-1}$ at 900 °C and long annealing time (up to 500 h). The diffusion coefficients of chromium generally decrease at constant temperature with increasing diffusion time if the same diffusion couple is considered. This can be explained by the increasing crystallization of the glass thereby diminishing the mobility of the cations in the sealant. The diffusion couple with the pre-oxidized alloy shows a significantly reduced chromium diffusion into the sealant besides the improved adherence mentioned above.

Figures 3 and 4 show as an example diffusion profiles of different species at the same interface MASC6/Cr$_5$Fe$_1$Y$_2$O$_3$ after different time periods. The profile in Fig. 4 belongs to the interface shown in Figure 5. The profiles indicate a high affinity between the Mg and
Figure 3. Diffusion profile of diffusion couple MASC6/ODS after annealing at 1000°C for 100 h

Cr cations which can be explained by the formation of MgCr\(_2\)O\(_4\) in the reaction layer at the interface. With increasing time Si also diffuses into this layer. Figure 5 shows the formation of a reaction layer.

A similar reaction layer was also observed at the MASN6/Cr5Fe1Y2O3 interface. A parabolic growth of the thickness of the two reaction layers was observed at the beginning. After about 20 h the thickness remained constant in practical terms. Rate constants of 5.5 \(10^{12}\) cm\(^2\) s\(^{-1}\) for sealant MASC6 and of 8.4 \(10^{12}\) cm\(^2\) s\(^{-1}\) for sealant MASN6 resulted for the initial growth of the reaction layer. The practically constant thickness of the reaction layer can be explained by a reduction in the cation mobilities by phase formation, saturation effects, and crystallization of the glass.

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It is interesting to note that the diffusion couple with the sealant BAS shows melting at the sealant/steel interface with detrimental corrosion attack of the alloy after annealing at 1000 °C for 1000 h under reducing conditions. FeO is present under these conditions which forms systems with the other components at the interface which have low eutectic temperatures. Severe interactions were also observed at the CAS/8YSZ interface leading to the diffusion of Ca into the 8YSZ and the diffusion of Y into the sealant.

Figure 5. SEM micrograph of diffusion couple MASC6/ODS after annealing at 1000°C for 1100 h.

Figure 6. Resistivity curves of the diffusion couples MASZ10/Steel, MAS10/Steel, MASN6/Steel, MASN/ODS, MASC6/Steel, and MASC6/ODS during annealing at 900°C and applying of voltage.

A high ohmic resistance was found by electrical conductivity measurements for a sealant sandwiched between two metallic plates made of Cr5Fe1Y2O3. The measurements were carried out at 1000 °C by applying a potential difference of 1 V over a time period of 1000 h and 1250 h. The results are shown in Figure 6. The initial increase of the
resistance can be explained by the crystallization of the sealant. Specific resistances between 1 and 20 MΩ cm were estimated by taking into account the thickness of the sealant layer and the area of the metallic plates. The resistances measured do not lead to electrical losses in practical terms.

CONCLUSIONS

Aluminosilicate glass ceramics have a high potential for the development of appropriate sealants for SOFCs. The following findings are useful in the sealant development:

The BaO containing sealants showed a significantly higher TEC, faster and more extensive crystallization, as well as lower Tg and Tc values as compared to the CaO and MgO containing glasses. The reactivity of the BaO and CaO containing glasses with typical SOFC component materials is significantly higher than that of the glasses with MgO. These reactivities can be detrimental.

Extensive investigations of MgO containing glasses with different Al2O3 concentrations as well as with and without nucleating agents were carried out. They showed that the detrimental formation of the Mg2Al4Si5O18 phase present in these sealants can be suppressed using low Al2O3 concentrations as well as appropriate grain sizes and nucleating agents. Ni and Cr2O3 nucleating agents yield high activation energies of crystal growth and high crystallization temperatures which are advantageous for a good wetting of the SOFC components and a good adherence. Pre-oxidation of the metallic interconnect improves the adherence.

Glass ceramics show very low cation mobilities thereby giving rise to a high specific electrical resistance and to low diffusion coefficients which are advantageous for SOFC applications.

The volatility of B2O3 and SiO2 in sealants is high. Na and K in sealants can increase the chromium volatility from metallic interconnect significantly thereby enhancing the electrical degradation in SOFC due to chromium reduction.

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