THE STABILITY OF THE SEALING GLASS AF 45 IN H₂/H₂O - AND O₂/N₂ - ATMOSPHERES

C. Günther, G. Hofer und W. Kleinlein

Siemens AG
Freyeslebenstr. 1
D - 91058 Erlangen
Germany

ABSTRACT

The commercially available AF 45 - (SiO₂-B₂O₃-BaO-Al₂O₃-As₂O₃) glass has been successfully used for sealing SOFC - stacks operating at temperatures between 850 and 950°C. This solder shows low viscosity at lower temperatures. At temperatures between 800 and 1000°C, it crystallizes in a number of possible -modifications of celsian and SiO₂. These crystallographic modifications depend on the time-temperature path chosen and the reaction of the glass with the surrounding atmosphere. The crystallization increases the viscosity sufficiently to insure a gas - tight seal. X - ray diffraction analysis of the solder after stack - operation shows a fully or almost fully crystallized state of the material. From this, it could be concluded that part of the glass-forming agent, most likely B₂O₃ is lost. Thermodynamic calculations performed for reaction of AF45-glass with H₂, H₂/H₂O-, O₂-gases and air yield a number of volatile gas - species as reaction products which could be responsible for the removal of B₂O₃ and As₂O₃ and also the formation of pores.

INTRODUCTION

The composition of the glass AF 45 is given in Table I. It was soon recognised that during the thermal soldering cycle and also during operation of the SOFC - stack, As₂O₃ and B₂O₃ are lost from the AF45 - solder. A pungent garlic smell emanating
Table I: Composition of the AF45* - Solder

| Oxide     | Wt.% | Md.% | Wt.% | Md.% | Metal    | Wt.% | Md.% |
|-----------|------|------|------|------|----------|------|------|
| B_2O_3    | 14.0 | 15.4 | 0    | 0    | B        | 7.8  | 15.4 |
| Al_2O_3   | 11.0 | 8.2  | 12.9 | 9.8  | Al       | 10.5 | 8.2  |
| SiO_2**   | 50.5 | 64.2 | 59.1 | 76.1 | Si       | 42.4 | 64.2 |
| As_2O_3   | 0.5  | 0.2  | 28.1 | 14.2 | As       | 0.7  | 0.2  |
| BaO       | 24.0 | 12.0 | 0    | 0    | Ba       | 38.6 | 12.0 |

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** 0.5% of unidentified material was added to SiO_2 in order to facilitate the equilibrium calculations.

from the cold traps of the stacks indicated that AsH_3 has been formed (2). WDX analysis confirmed that most of the boron has also disappeared. There is a possibility that the partial pressures of the gaseous B-, and As - species like B(OH)_3, BO(OH), As_2 and AsH_3 are responsible for the pores observed in the AF45 seal after operation (Fig. 7). The chemical composition of the solder is changed after the removal of B and As to 76.1 Mol.% SiO_2, 14.2 Mol.% BaO and 9.8 Mol.% Al_2O_3. This composition is shown in the isothermal section of a ternary phase diagram (Fig. 1) at the point marked AF45-As-B (read: AF45 minus As, minus B). This phase diagram was derived using data given in "Phase Diagrams for Ceramists" (4).

AF45 - glass solder appeared black near the H_2 - channel and yellow near the air-channel after stack operation at 850°C for 3500h. X-ray diffraction diagrams were taken of powdered samples of the black and yellow materials and are shown in Fig. 2. This figure also displays the x-ray diffraction pattern of a powdered sample of the initial AF45 material. The large peak at a Bragg-angle of 2θ = 11.450° is due to paraffin within the vaseline used to fix the powder on the sample holder. Both, the black and the yellow material are fully crystallized and have the same x-ray diffraction patterns. Analysis of the patterns gave a mixture of 61 Mol.% celsian in the "high-temperature modification (JCPDS-No.: 28-124) and 39 Mol.% SiO_2 as cristobalite (JCPDS-No.: 39-1425). This composition is plotted as a point on the tie-line between SiO_2 and BaO*Al_2O_3*2SiO_2 in Fig. 1. It is quite near the point AF45-As-B. The differences in color may be due to differences in the concentration of color centers.

Another x-ray analysis was performed on AF45 sandwiched between two 1cm square and 1mm thick samples of CrFe_5(Y_2O_3)_3 - material (bipolar plate - BIP, interconnector), heat - treated in air for 32.5h at 1000°C (cooling rate 2K/min) and then broken in the middle of the AF45. One side was crystallized, the other not. The crystallized side yielded 80% of α - or β - BaO*Al_2O_3*2SiO_2 -(celsian), (JCPDS-No.: 12-725 or 12-726), and 20% cristobalite. This composition is also plotted in Fig. 1.
The Gibbs free energy minimization program ChemSage (1) was used for investigating the reactions of AF45 with various gas-atmospheres. For these thermodynamic calculations, only quasi-binary data were available (3). No free energy data were found for quasi-ternary compounds like celsian. For this reason, for instance, the calculations with this program do not find the quasi-ternary equilibrium of SiO$_2$-celsian-BaO•2SiO$_2$ (Fig. 1), but the equilibrium SiO$_2$-mullite-BaO•2SiO$_2$. In these calculations, 65 different phases and 114 different species were considered. The model for these calculations is the reaction of 1 mole of AF45 with a large surplus of gas (2000 moles), so that the partial pressures of the species may be compared at virtually constant H$_2$- and H$_2$O-activities. Even with the above mentioned restrictions, it is worthwhile to look at the results of these thermodynamic calculations to find out if there are quasi-binary species that could be responsible for the B- and As-transport away from the solder.

Fig. 3 shows the As- and Fig. 4 B-containing species produced by the H$_2$/H$_2$O-reaction with AF45. The gas-species with the highest partial pressure is B(OH)$_3$, in the temperature range of interest for the SOFC between 850 and 950°C. The partial pressure of this compound is almost constant in this temperature range at about $10^{-4}$ bar. The partial pressure of gaseous SiO at 850°C, extrapolated from Fig. 4, is $6.04\times10^{-16}$ bar. The As-containing gas-species with the highest partial pressure is As$_2$. Its partial pressure is about $10^{-4}$ bar and constant in the temperature range of interest. These pressures are surely sufficient for the transport of B and As from the AF45, if they are compared with those of the chromium-containing species responsible for Cr-transport as discussed by Hilpert et al. (5).

The reaction of 2000 moles of H$_2$ with AF45 forms again B- and As-containing gas-species (Fig. 5). B$_2$(OH)$_3$ is the species with the highest vapour pressure for this reaction. Its temperature-dependency between 850 and 950°C is reasonably small and its pressure level only slightly lower than that of B(OH)$_3$. Some of the species are identical to those of the AF45-H$_2$/H$_2$O-reaction, but with different partial pressures.

Only the two gas-species BO$_2$ and B$_2$O$_3$ are found with the thermodynamic analysis for the reaction of AF45 with air (Fig. 6) at pressure levels that are 3 to 5 orders of magnitude lower than those of the H$_2$/H$_2$O-reactions. But we have, in addition, relatively high partial pressures for the nitrous gases NO, NO$_2$ and N$_2$O. The reaction of AF45 with pure O$_2$ gives the same temperature-pressure-relationships for BO$_2$ and B$_2$O$_3$ as shown in Fig. 6 but, of course, no nitrous gases.
At last, a look shall be taken at the solid phases determined by this analysis. The amounts (in mole) of these phases are listed in Table II. We see that the phases SiO2(Q), BaO∗2SiO2 and mullite are the most stable phases, keeping in mind the lack of thermodynamic data of quasi-ternary phases for the BaO-\(\text{Al}_2\text{O}_3\)-SiO2-

Table II: Summary of the concentration of solid phases in equilibrium with the gas species at a particular temperature.

| T (°C) | 800  | 850  | 900  | 950  | 1000 | 1050 | 1100 | 1150 | 1200 |
|-------|------|------|------|------|------|------|------|------|------|
| mol   |      |      |      |      |      |      |      |      |      |
| SiO2(Q) | 0.403 | 0.403 | 0.403 | 0.403 | 0.403 | 0.403 | 0.403 | 0.403 | 0.403 |
| BaO* | 0.1196 | 0.1196 | 0.1196 | 0.1196 | 0.348 | 0.348 | 0.348 | 0.348 | 0.348 |
| 9Al2O3* | 0.00316 | 0.00316 | 0.00316 | 0.00316 | 0.0275 | 0.0275 | 0.0275 | 0.0275 | 0.0275 |
| 3Al2O3* | 0.403 | 0.403 | 0.403 | 0.403 | 0.403 | 0.403 | 0.403 | 0.403 | 0.403 |
| 2SiO2 | 0.332 | 0.1196 | 0.369 | 0.1196 | 0.332 | 0.1196 | 0.332 | 0.1196 | 0.332 |
| Mullite | 0.00916 | 0.00916 | 0.00916 | 0.00916 | 0.0275 | 0.0275 | 0.0275 | 0.0275 | 0.0275 |
| mol   |      |      |      |      |      |      |      |      |      |
| SiO2(Q) | 0.403 | 0.403 | 0.403 | 0.403 | 0.403 | 0.403 | 0.403 | 0.403 | 0.403 |
| BaO* | 0.1196 | 0.1196 | 0.1196 | 0.1196 | 0.348 | 0.348 | 0.348 | 0.348 | 0.348 |
| 2Bi2O3 | 0.0038 | 0.0038 | 0.0038 | 0.0038 | 0.0275 | 0.0275 | 0.0275 | 0.0275 | 0.0275 |
| 2B2O3 | 0.403 | 0.403 | 0.403 | 0.403 | 0.403 | 0.403 | 0.403 | 0.403 | 0.403 |
| 2SiO2 | 0.332 | 0.1196 | 0.369 | 0.1196 | 0.332 | 0.1196 | 0.332 | 0.1196 | 0.332 |

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system. Whereas the boron is structurally bound up to high temperatures in solid phases for the reactions of AF45 with H₂ and air, the boron-containing phase disappears between 950 and 1000°C and mullite comes into play during the reaction of AF45 with H₂/H₂O - mixtures. 9Al₂O₃•2B₂O₃ is evaporating, only gaseous species of boron are left at 1000°C and above.

It is worthwhile noting here the amounts of the three phases left at 1000°C for the reaction of AF45 with H₂/H₂O - mixtures given in Table II:
0.348 moles SiO₂(Q), 0.1196 moles BaO•2SiO₂ and 0.0275 moles 3Al₂O₃•2SiO₂ (mullite).

From these phase compositions, the amounts of the constituents of this quasi-ternary phase diagram, are computed:
9.8 Mol.% Al₂O₃, 76.1 Mol.% SiO₂ and 14.2 Mol.% BaO.
This is exactly the composition we would expect (point AF45-As-B in Fig. 1).

The evaporation of a solid phase at a certain temperature could be another cause for the formation of the observed pores. Whether such a reaction exists or not can only be determined with calculations using more complete data. Up to now we have no explanation for the formation of different pore sizes seen in Fig. 7.

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Fig 1. System BaO - Al₂O₃ - SiO₂ derived from Phase Diagrams for Ceramists (4).
Fig. 2. X-ray diffraction diagrams of AF45-glass in the as-delivered state and in the state after stack operation of 3500h at 850°C, cooling rate 0.55K/min.
Fig. 3. Partial pressures of As-containing species as a function of the reciprocal absolute temperature produced by the reaction of 1 mole of AF45 with 1000 moles of H₂ and 1000 moles of H₂O.
Fig. 4. Partial pressures of B-containing gas species as a function of the reciprocal absolute temperature produced by the reaction of 1 mole of AF45 with 1000 moles of H₂ and 1000 moles of H₂O.
Fig. 5. Partial pressures of B- and As-containing gas-species as a function of the reciprocal absolute temperature produced by the reaction of 1 mole of AF45 with 2000 moles of H2.
Fig. 6. Partial pressures of B - and N - containing gas - species as a function of the reciprocal absolute temperature produced by the reaction of 1 mole of AF45 with 2000 moles of air.

Fig. 7. Section through a single SOFC showing pores in part of the AF45 - solder.