EFFECTS OF HYDROGEN ON THE INTERACTIONS OF FUEL CELL SEALING GLASSES WITH INTERCONNECT ALLOYS

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ABSTRACT

In situ X-ray diffraction was used to study the interactions of the PNNL G18 fuel cell sealing glasses with the oxides that form on candidate interconnect alloys and with the ebrite alloy. Experiments under 4% hydrogen and air at temperatures up to 1000 °C showed that both sealants react rapidly with alumina and chromia, but not with NiO. The crystallization of the high-CTE phase BaCrO₄ was noted for G18 in contact with chromia or ebrite under air, but reducing conditions inhibit the crystallization. The reactions in all cases begin within a few hours at temperatures above 800 °C and go to completion or near completion after ~12 h.

INTRODUCTION

The fuel cell design might include rigid glass or glass-ceramic seals [1–6] or compressive seals in which a compressive load on a pliable material such as mica provides the seal [3,5,7]. Regardless of design, the seal is required to meet rather stringent thermomechanical, thermochemical, and electrical requirements, as summarized in a recent review by Fergus [8].

The sealing glasses, or glass-ceramics, have been focused on the alkaline earth aluminosilicates, borosilicates, and lanthanide alumino borosilicates [1,2,4,5,7]. The patented sealing glass compositions developed at the Pacific Northwest National Laboratories are Ba-Al-Si-O compositions (the primary one denoted G18) with boron additions to control viscosity, the glass transition temperature, and wetting behavior [5,9]. Many potential glass compositions are based on the fundamental glass science of the PNNL compositions.

The problems associated with the interaction of the sealing glasses and oxidation resistant alloys have come to the forefront of the sealing problem [1,4,6,10]. It is clear that the glass will react with the surface oxide layer in some of the glass-metal seals, but will be relatively inert in others [6,11].

The present work was undertaken to establish the fundamental materials behavior during the interaction of the sealing glass with the surface oxides and ebrite. Of particular importance is the crystallization behavior at short times, on the order of the time scale used to seal the fuel cell stack during the initial manufacturing stage. Of course, changes in the seal phase composition with time are also important, but rather more straightforward to investigate.

EXPERIMENTAL

The G18 sealant was prepared with a molar composition of 35% SiO₂, 9.4% B₂O₃, 5.2% Al₂O₃, 1.2% ZrO₂, 0.9% MgO, 12.6% CaO, and 35.8% BaO. Glass batches of 300 g were prepared from...
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analytical grade chemicals by melting at 1400 °C for 45 to 90 min in a platinum crucible. The glasses were sufficiently fluid to be homogenized by swirling the crucible at 15 min intervals. The glasses were poured into a steel mold and annealed, and then milled in a McCrone micronizing mill to an average particle size (d<sub>50</sub>) of 10 µm.

A custom high-temperature diffraction furnace, described by Misture [12] was used for the high-temperature X-ray diffraction (HTXRD) measurements. The HTXRD measurements were made using Co or Cu radiation and a Braun position-sensitive detector that was scanned over an appropriate angular range to measure the peaks of interest.

The measurements were made under static air or under a mixture of dry He + 4% H₂, depending on the experiment. All heating rates were 30 K/min, and the temperature was calibrated against the NIST temperature standards GM759 and GM760 [13,14]. Therefore, the temperature accuracy is on the order of ±10 ºC. The specimens were prepared by lightly mixing the sealant powder with the alloy or oxide of interest in an alumina mortar and pestle under ethanol. The HTXRD specimen was prepared as a thin layer of powder (approximately 50 µm thick) on Pt sample holders.

RESULTS AND DISCUSSION

The global results for the G18 sealant under air and hydrogen are shown in Table I. All phase identification and quantification was performed using Rietveld analysis, which is particularly useful for diffraction data with many overlapping lines. The data in Table I are based on in situ diffraction data, and therefore do not represent equilibrium phase assemblages. Previous work on G18 and a range of other BCAS sealants includes the crystallization behavior of G18 in pure form [15,16].

As shown in Table I, the phase evolution in G18 in the presence of alumina differs from that of pure G18 in that BaAl<sub>2</sub>O<sub>4</sub> forms as a major phase. Figure 1 shows the isothermal HTXRD data for a mixture of G18 + 25 wt% alumina at 900 ºC in air, demonstrating that the BaAl<sub>2</sub>O<sub>4</sub> phase begins to crystallize within ~2 h of the start of the experiment. Hexacelsian is the other major phase that forms, and a minor fraction of BaSiO<sub>3</sub> forms as well. A large reservoir of alumina therefore favors crystallization of the Al-rich hexacelsian phase (instead of BaSiO<sub>3</sub>) and the subsequent crystallization of BaAl<sub>2</sub>O<sub>4</sub>, which is silica-free. It is important to note that the BaAl<sub>2</sub>O<sub>4</sub> grows rapidly up to the end of the 12-hour experiment, suggesting that equilibration of the sealant in contact with alumina will take significantly longer than 12 h. In the presence of 4% H₂ gas, the crystallization behavior of the G18 + alumina system does not change, as indicated in Table I.

The thermal expansion coefficient for BaAl<sub>2</sub>O<sub>4</sub> has been reported from diffraction data, and the equivalent bulk thermal expansion coefficient (CTE) is 9.6 × 10⁻⁶ K⁻¹ over the range of 20 to 1000 ºC. The target CTE for the sealant is between that of the stabilized zirconia electrolyte and the interconnect, approximately 11 × 10⁻⁶ K⁻¹ [5,16]. Therefore, the expansion of the BaAl<sub>2</sub>O<sub>4</sub> phase is a reasonable (but not ideal) match to the target CTE for the sealant, and represents a technologically viable microstructure.
As indicated in Table I, the presence of NiO has little effect on the reaction products of G18, under air or hydrogen. Of course, the NiO is reduced to Ni metal under hydrogen, as expected, but the presence of Ni metal does not change the oxide phases formed. The dynamics of crystallization are shown in Figure 2, for both air and 4% H₂. As shown in Figure 2, (Ba,Ca)₂SiO₄, hexacelsian, and BaSiO₃ equilibrate under hydrogen near the end of the 12-hour experiment. Under air, however, the (Ba,Ca)₂SiO₄ phase continues to grow at the expense of BaSiO₃. Given the stable oxidation states of the Ba, Ca, and Si ions, it appears that a complex mechanism causes the preference for the (Ba,Ca)₂SiO₄ phase under air versus hydrogen.

Adding chromia to G18 results in a vastly different phase assemblage when heating in air, which is a well-known reaction [6,8,17]. Table I summarizes the results as a function of temperature,

Table I. Comparison of phases formed in the G18 sealant under air and 4% H₂, based on non-isothermal HTXRD measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phases Formed under Static Air</th>
</tr>
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<tbody>
<tr>
<td>Pure Glass</td>
<td>800 °C: BaSiO₃ [major] + (Ba,Ca)₂SiO₄ [minor]; 850 °C: BaSiO₃ [major, melts lower than 1000 °C] + (Ba,Ca)₂SiO₄ [major] + hexacelsian [major]; 900 °C: BaSiO₃ [major, melts lower than 1000 °C] + hexacelsian [major]; 950 °C: hexacelsian [major] + (Ba,Ca)₂SiO₄ [major]; 1000 °C: hexacelsian [major]</td>
</tr>
<tr>
<td>Glass + Al₂O₃</td>
<td>800 °C: BaSiO₃ [major]; 850 °C: BaSiO₃ [major]; 900 °C: BaAl₂O₄ [major] + hexacelsian [major]; 950 °C: hexacelsian [major]; 1000 °C: hexacelsian [major]</td>
</tr>
<tr>
<td>Glass + NiO</td>
<td>800 °C: BaSiO₃ [major]; 850 °C: BaSiO₃ [major, melts below 1000°C] + (Ba,Ca)₂SiO₄ [major, melts below 1000°C] + hexacelsian [major]; 900 °C: hexacelsian [minor, melts by 1100 °C] + melt</td>
</tr>
<tr>
<td>Glass + Cr₂O₃</td>
<td>800 °C: BaCrO₄ [major]; 850 °C: BaCrO₄ [major] + hexacelsian [minor]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Phases Formed under 4% H₂</th>
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<tbody>
<tr>
<td>Pure Glass</td>
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<tr>
<td>Glass + Al₂O₃</td>
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<td>Glass + NiO</td>
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<tr>
<td>Glass + Cr₂O₃</td>
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<td>Glass + Ebrite</td>
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with BaCrO$_4$ and a minor fraction of hexacelsian as major phases. BaCrO$_4$ is well known to have a very large thermal expansion [18], with an equivalent bulk CTE of $2.4 \times 10^{-5}$ K$^{-1}$ resulting in mechanical failures at the glass-interconnect interface [5,6,17].

The dynamics of the phase formation demonstrate the high reactivity of chromium in the system, as shown in Figure 3 for G18 + ebrite. Note that BaCrO$_4$ crystallizes very rapidly, indeed even more rapidly than the BaSiO$_3$ phase crystallizes from pure G18 glass. In contrast to pure G18, the presence of chromium promotes the formation of BaCrO$_4$, followed by the formation of a small fraction of hexacelsian. Both BaSiO$_3$ and (Ba,Ca)$_2$SiO$_4$ are inhibited when chromia is present, presumably as a result of the Ba being incorporated into the chromate phase.

When exposed to 4% H$_2$ at 900 ºC, the G18 + chromia system crystallizes phases that are entirely different than in air, but the same as those that crystallize from pure G18. Most notable is the absence of BaCrO$_4$ when heating under hydrogen, as noted Table I. Perusal of an Ellingham diagram indicates that Cr$_2$O$_3$ will reduce to Cr metal at 900 ºC under 4% H$_2$ if the water content is low, however, the present experiments did not include drying the H$_2$/He gas mixture, and the water content is unknown. Although there was no evidence of Cr metal during the experiments, the absence of BaCrO$_4$ indicates that the oxygen partial pressure is low enough to reduce Cr$^{6+}$ to lower valence, preventing crystallization of BaCrO$_4$.

The presence of an iron source in the ebrite alloy results in crystallization of Fe$_2$O$_3$ (hematite) as a result of oxidation of the ebrite alloy. Figure 3 also shows the dynamics of the crystallization of hematite. It is interesting to note that crystallization of BaSiO$_3$ from the sealing glass is only the
first step in the reaction sequence, followed by reaction with the chromium from the ebrite to form BaCrO₄.

The primary effect of the presence of ebrite in air is therefore inhibiting the growth of (Ba,Ca)₂SiO₄ while forming BaCrO₄ and Fe₂O₃.

As indicated in Table I, the reactions of G18 and ebrite under 4% hydrogen are identical to the reactions of G18 in air. Therefore, the presence of hydrogen inhibits the formation of the surface oxides on the ebrite, preventing the crystallization of BaCrO₄ and Fe₂O₃.

CONCLUSION

Of the candidate alloy interconnect surface oxides (Ni, Cr, Al), both Al and Cr change the phase evolution sequence in G18. Introducing Cr₂O₃ results in the formation of BaCrO₄ and suppression of BaSiO₃ and (Ba,Ca)₂SiO₄ when under oxidizing conditions. However, BaCrO₄ phase does not crystallize when exposed to 4% hydrogen, because the hexavalent chromium ion is not stable under strongly reducing conditions. For alumina, the G18 forms a major fraction of BaAl₂O₄ at the expense of (Ba,Ca)₂SiO₄, regardless of oxidizing or reducing conditions.

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REFERENCES


