A BRAZE SYSTEM FOR SEALING METAL-SUPPORTED SOFCs

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ABSTRACT

A composite braze material for sealing and interconnecting metal-supported SOFCs, comprising Ag-Cu-Ti braze alloy and particulate Al<sub>2</sub>TiO<sub>5</sub> filler is used to produce metal/braze/metal and metal/braze/YSZ joints. The addition of Al<sub>2</sub>TiO<sub>5</sub> to the braze lowers the coefficient of thermal expansion (CTE) of the resulting composite sufficiently so as to produce joints in which the YSZ does not crack due to CTE mismatch. Optimization of the active element (Ti) level is discussed with regard to its effect on electrolyte conductivity. Electronic conductivity and shear strength of the braze alloy were determined before and after oxidation at 700°C in air. Both properties remain acceptable after oxidation. A braze joint was also tested in a dual atmosphere Air/H<sub>2</sub>, 3wt% H<sub>2</sub>O environment at 700°C. After this exposure, the joint remains hermetically sealed and no significant degradation of the joint was observed.

INTRODUCTION

Sealing of SOFCs represents a significant technical barrier to their widespread adoption for power generation. Many seal types have been explored, including glass- and braze-based rigid seals, and mica-based compressive seals. Each type has drawbacks that have precluded the emergence of a dominant seal technology. In this work, we describe a modified braze material developed at LBNL that is especially well-suited to sealing and interconnecting metal-supported SOFCs for which yttria-stabilized zirconia (YSZ) is one of the sealing surfaces.

Brazing to ceramics, including YSZ, is usually accomplished by metalizing the ceramic surface prior to brazing, or by including an active element in the braze material that reacts with the ceramic surface thereafter promoting wetting of the surface by the braze. Typical active elements include Ti, Zr, Hf, V, Nb, etc. Many commercial brazes are available with an active element added. Of these, precious-metal-based alloys are most promising, as the braze must withstand fuel and oxidizing atmospheres at high temperature in an operating SOFC. Cost constraints further narrow the field of interesting materials to the Ag-based active braze alloys.

The coefficient of thermal expansion (CTE) of most braze materials is in the range 16-21 ppm/K, with Ag-based alloys at the higher end of this range. The CTE of YSZ is 10.5 ppm/K. This CTE mismatch is sufficient to cause cracking in a YSZ joining member after brazing with typical alloys. Such cracking is clearly detrimental to the gas-sealing
and strength of the joint, and therefore unacceptable. In this work, we report the use of a low-CTE particulate filler that is added to the braze alloy, resulting in a braze composite mixture with a reduced bulk CTE that is better-matched to that of YSZ. Such a modified braze is successfully employed to produce crack-free joints between 430 stainless steel and YSZ. The base braze alloy has also been exposed to simulated operating conditions, and the effects of this exposure on the quality of the braze joint are discussed.

EXPERIMENTAL TECHNIQUES

Brazing was accomplished in a vacuum furnace. Typical heating and cooling rates were 10°C/min to 50°C above the alloy liquidus temperature, with a 5-minute hold at this temperature. YSZ substrates were prepared by sintering YSZ (Tosoh 8Y) at 1400°C in air. Pure silver (~325 mesh, Aldrich) was used in powder form and pure Ticusil (68.8Ag-26.7Cu-4.5Ti, Morgan Advanced Ceramics) was used in foil or paste form. Braze mixtures with Al₂TiO₅ (29 μm median, Aldrich) and/or TiH₂ (1-3μm, Alfa Aesar) were prepared by mixing the filler powders with Ticusil paste under IPA.

Cross-section images were obtained by impregnating the sample in epoxy resin, sectioning with a diamond wafering blade, and carefully polishing to 1μm grit size. Images were recorded with an optical microscope (Keyence VH8000) or SEM (Hitachi S4300).

Samples were prepared for AC impedance analysis by sputtering thin Au electrodes which were then covered with Au paste and Pt mesh leads. Samples were tested in air using a 4-point probe and Solartron SI 1255.

TGA (TA Instruments) was performed on small pieces of braze that were removed from a braze/YSZ joint.

Samples for conductivity evaluation were prepared by brazing long, thin strips of braze composite onto YSZ substrates. Conductivity was determined using a 4-point probe method while passing DC current (1-4 amps).

Brazed metal/braze/metal lap joints were prepared with 430 steel substrates. Failure testing was accomplished in tensile mode under load control on an Instron 810 Materials Test System.

RESULTS AND DISCUSSION

We have produced YSZ/Braze/430 SS joints using brazes based on Ticusil. Figure 1a shows a cross-section of one such joint using pure Ticusil foil as the braze material. The braze material spreads and wets both the YSZ and steel substrate well, producing a high-quality, nonporous joint. Thin reaction layers are present at the braze/YSZ and braze/steel interfaces; we surmise these reaction layers are Ti-rich. Large cracks are visible in the YSZ substrate, arising from coefficient of thermal expansion (CTE) mismatch between the braze material and the ceramic.
One method of avoiding cracking when brazing to a ceramic is to modify the CTE of the braze material. The addition of ceramic or carbon particles to braze materials has been previously demonstrated as a means of reducing the bulk CTE of the resulting braze composite (1,2,3). In most reported cases, Al$_2$O$_3$ was the ceramic of choice for both the particulate filler and joining member, and the Al$_2$O$_3$ joining member was free of cracks after brazing. In contrast, we have found that YSZ still cracks after brazing with Al$_2$O$_3$-filled Ticusil. This difference is probably because Al$_2$O$_3$ is stronger than YSZ. Therefore, we presume a better CTE match is necessary to ensure a crack-free YSZ joining member after brazing. A better CTE match can be generated by increasing the amount of filler particles or by using filler particles that have a very low CTE. The latter scenario is
desirable, as the addition of very high particulate loadings could compromise the conductivity, strength, or non-porous nature of the composite braze. The table below indicates the CTE for selected materials. On this basis, Al$_2$TiO$_5$ is clearly a better candidate to reduce the overall CTE of an alloy/ceramic composite braze material.

Table 1. Coefficients of thermal expansion for selected materials.

| Material   | CTE (ppm/K) |
|------------|-------------|
| Ticusil    | 18.5        |
| YSZ        | 10.5        |
| Al$_2$O$_3$| 7           |
| Al$_2$TiO$_5$ | 1.5      |

Braze mixtures of various Al$_2$TiO$_5$ loadings were used to braze YSZ to 430 SS. Cross-section images of the resulting joints are shown in Figures 1b-f. All samples shown in the images displayed good bonding to both the YSZ and steel surfaces. The joints are free of major defects, and there does not appear to be any porosity in the joints. For Al$_2$TiO$_5$ levels ≤15 v%, significant cracking in the YSZ disk occurs. No cracking was observed for the 20 v% and 25 v% samples. This suggests that the higher levels of filling are sufficient to reasonably match the bulk CTE of the braze joint to that of YSZ. A reaction layer is clearly visible as a gray area surrounding each filler particle. Reaction layers on the steel and YSZ surfaces are also visible. The thickness of these reaction layers decreases with increasing filler level, suggesting that the reactive element (Ti) is used up in the reaction with the filler particles. Higher levels of filling (30 v% and 35 v%) resulted in a poor bond to the YSZ disk. This is likely due to reaction of the Al$_2$TiO$_5$ surface with Ti in the braze alloy, leaving too little Ti to produce a strong bond with the YSZ brazing surface. Addition of TiH$_2$ to the braze mixture (1:1w based on weight of Al$_2$TiO$_5$) mitigated this problem, allowing successful joints to be produced with >25 v% Al$_2$TiO$_5$ filler.

We observed that the entire surface of some of the YSZ samples was darkened after the brazing operation. This darkening was accompanied by electronic conductivity on the YSZ surface. We surmise this is due to migration of Ti from the braze joint across the YSZ surface during brazing, accompanied by nonstoichiometry in the underlying YSZ (4). After oxidizing the samples (>300°C in air), they became electronically insulating, presumably by oxidation of the Ti surface layer to TiO$_2$. Of the samples shown in Figure 1, only those with Al$_2$TiO$_5$ content ≤10 vol% displayed the surface conductivity and darkening. For higher filler levels, the excess Ti was used up in forming the surface reaction layer on the filler particles, and was therefore not available to migrate across the YSZ surface. Addition of TiH$_2$, as indicated above, improved the wetting of the braze material, but also provided excess Ti that migrated across the YSZ surface. Optimization of the Ti and TiH$_2$ loading is necessary in order to produce a braze material that wets well yet does not contain excess Ti. This is an important issue, as the Ti-rich surface layer comprises a high-impedance barrier on the YSZ surface that is expected to dramatically affect fuel cell performance. A sample that experienced a high degree of Ti migration over the YSZ surface during brazing was analyzed with AC impedance. The Nyquist plot consisted of two semicircles that were assigned to the Ti-rich surface species (low frequency) and YSZ in the bulk of the sample (high frequency). As shown in Figure 2,
Gold electrodes for AC impedance, applied after brazing

Ti-containing surface layer produced during brazing

Figure 2. (Left) Schematic of sample geometry for impedance testing. (Right) Temperature-dependence of the conductivity for YSZ standard and YSZ sample that had experienced Ti migration during brazing.

the conductivity of the YSZ in the bulk of the sample was nearly identical to that observed for an external YSZ reference (Tosoh 8Y, sintered at 1400°C). This suggests that Ti has not migrated into the interior of the sample during brazing or AC Impedance testing. The total impedance for the sample, including the Ti-rich surface layer, is about three orders of magnitude lower than that of pure YSZ. Therefore, any YSZ that is contaminated with Ti by the brazing process cannot be expected to contribute to the electrochemical function of the fuel cell. Similarly low total conductivity was obtained when using Zr as the active brazing element in a Ag/Zr-hydride braze mixture. In that case, however, the impedance of the sample bulk YSZ increased substantially, suggesting that Zr had migrated into the interior of the sample.

Concern has been expressed in the literature regarding the stability of precious metal-based brazes in oxidizing atmospheres (5,6,7). In particular, Ag-Cu-Ti brazes have been shown to oxidize relatively quickly at similar conditions to the air side in a working SOFC (6,7). We have explored the impact of oxidation of Ticusil on those materials properties that are relevant to SOFC sealing and interconnect.

TGA was used to determine the minimum time required for complete oxidation of the Cu and Ti constituents in the braze materials at 700°C in air. Figure 3 shows that all compositions experienced a rapid initial oxidation weight gain, after which the sample weight stabilizes. The initial weight gains correspond well to those expected for complete oxidation of the Cu and Ti: 10% for Ticusil, 9.5% for filled Ticusil, and 2% for Ag/3w% Ti. This data indicates that initial oxidation is complete within 50-100 hours, and provides a guideline for the protocol used to determine the effect of oxidation on relevant materials properties.
Figure 3. TGA traces for various braze materials exposed to flowing air at 700°C.

Figure 4. Conductivity of selected braze samples after holding in 700°C air for various times. Ticusil (diamonds), Ticusil/25vol% Al₂TiO₅ (squares).
In the case that the braze material functions as an interconnect between adjacent cells in a stack, the electronic conductivity of the material must be high and remain so over the lifetime of the device. Figure 4 shows the dependence of braze conductivity on oxidation time. Comparison of the as-brazed samples (0 hours data) indicates that addition of Al$_2$TiO$_5$ filler material reduces the conductivity of the composite braze material only slightly. Upon 50 hours of oxidation, the conductivity of both samples is reduced about 50%, yet remains sufficiently high for use in a SOFC. Further oxidation time does not statistically affect the conductivity, agreeing well with the oxidation timescale established by TGA, above. We predict therefore that oxidation of a Ticusil-based braze will not limit current collection over the lifetime of a SOFC device operating at 700°C.

In the case that a braze provides mechanical connection between adjacent cells, it must maintain a high strength over the lifetime of the device. The cells being developed at LBNL utilize metallic current collectors and cell-to-cell joint housings. Therefore a metal/braze/metal lap joint provides a relevant model geometry for strength testing. Such joints were produced by brazing 430SS metal strips (500µm thick) to each other using various braze composites. The samples were then subjected to various thermal treatments before pull-testing to determine shear strength. As-brazed Ticusil/25v% Al$_2$TiO$_5$/1:1wt TiH$_2$ failed in the braze material at 48MPa, which is a much higher load than can be expected in a fuel cell under normal conditions. Unfilled Ticusil joints were tested as-brazed, after 50 hours oxidation at 700°C, and after 40 rapid thermal cycles (100 to 700°C, 3 minutes per cycle). In all cases the metal strips failed, leaving the brazed area intact. We therefore conclude that Ticusil-based joints connecting metal to metal are very strong, and remain so after oxidation or thermal cycling.

![Figure 5. Schematic of sample geometry for dual atmosphere and vacuum-leak testing.](image)

Previous work has indicated that silver is stable in oxidizing conditions, yet unstable when in contact with both air and fuel atmospheres at high temperature, such as in an operating SOFC. (8) The authors report that at temperatures above 500°C, voids were produced in a silver tube separating air and fuel, presumably due to the combination of hydrogen and oxygen to produce steam within the silver. Catastrophic failure occurred at 700°C. We have tested Ticusil under similar conditions, but did not observe failure or void formation within the braze joint. Pure Ticusil was used to braze an Al$_2$O$_3$ sheet onto a 430SS washer, which had been previously gold-brazed onto a Swagelock fitting suitable for mounting on a gas/vacuum manifold. A schematic of the setup is shown in...
The setup was checked for vacuum-tightness after which flowing hydrogen/3 wt% water was introduced to the interior of the sample. The sample was then held at 700°C for 125 hours. After this conditioning, vacuum-tightness of the setup was again confirmed, indicating hermetic failure of the braze joints did not occur. The sample was then cross-sectioned and polished. An image of the Ticusil braze joint is shown in Figure 6. Clearly, the braze material is free of voids and exposure to the dual atmosphere environment has not visibly degraded the quality of the joint. We speculate that the robustness of Ticusil relative to pure silver may be due to favorable microstructure or mechanical properties introduced by the presence of Cu and Ti in the braze alloy. Similar tests for vacuum-tightness and stability in dual atmospheres are under way for samples where a YSZ plate replaces the Al₂O₃ plate shown in Figures 5 and 6.

CONCLUSIONS

The use of a very-low-CTE material, Al₂TiO₅, as a braze filler has enabled the production of crack-free steel/braze/YSZ joints based on commercially-available Ticusil braze alloy. It was found that filler loadings >20v% lowered the CTE of the composite braze material sufficiently so as to prevent cracking in the YSZ joining member. Filler loadings higher than 25v% were possible if additional reactive element, in the form of Ti-hydride for instance, was added to promote wetting of the ceramic filler and joining member surfaces by the braze alloy. It was found that the level of active brazing element must be carefully controlled: excess active element migrates out of the joint area and contaminates the YSZ surface with a high-impedance layer that would be detrimental to fuel cell performance.

Complete oxidation of the Cu and Ti in Ag-based brazes was found to occur within the first 50-100 hours of exposure to air at 700°C. Electronic conductivity and shear strength
were determined before and after oxidation. Both properties exceeded the requirements for reliable fuel cell operation even after complete oxidation of the Cu and Ti species in the braze. An Al$_2$O$_3$/Ticusil/steel joint was also exposed to fuel on one side and air on the other at 700°C. No significant damage to the braze alloy or joint was observed after exposure.

Based on these observations, we believe that silver-based brazed alloys filled with low-CTE particulates are suitable candidates for use as the seal or interconnect in SOFCs operating at 700°C.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the assistance of James Wu for vacuum brazing and Grace Lau for cross-section sample preparation. This work was supported in part by the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

REFERENCES

1. M. Zhu and D. D. L. Chung, *J. Mat. Sci.*, 32, 5321 (1997).
2. T. Makino and M. Shinkai, US Patent 6,742,700 (2004).
3. M. Shinkai and M. Kida, US Patent 6,565,621 (2003).
4. W. B. Hanson, K. I. Ironside and J. A. Fernie, *Acta Mater.*, 48, 4673 (2000).
5. J. P. Rice, D. M. Paxton and K. S. Weil, in *Proceedings of the 26th Annual Conference on Composites, Advanced Ceramics, Materials and Structures*, B. H.-T. Lin and M. Singh, Editors, p. 809, American Ceramic Society, Westerville, OH, (2002).
6. D. B. Lee, J. H. Woo and S. W. Park, *Mat. Sci. Eng.*, A 268, 202 (1999).
7. A. J. Moorhead and H.-E. Kim, *J. Mat. Sci.*, 26, 4067 (1991).
8. P. Sing, Z. Yang, V. Viswanathan, and J. W. Stevenson, *J. Mat. Eng. Performance*, 13, 287 (2004).