A braze system for sealing metal-supported solid oxide fuel cells

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Abstract

A composite braze, consisting of Ag–Cu–Ti braze alloy and particulate Al_2TiO_5 filler, was used to produce metal/braze/metal and metal/braze/YSZ joints to seal and interconnect metal-supported SOFC membranes. The addition of Al_2TiO_5 to the braze alloy 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 reactive element (Ti) loading is discussed with regard to its effect on electrolyte conductivity. Electronic conductivity, sealing ability, and strength of the braze alloy remain acceptable after complete oxidation at 700 °C in air. Joints were also tested in air/fuel dual atmosphere environment at 700 °C. After this exposure, the joint remains hermetically sealed, and no significant degradation of the joint was observed. This is in contrast to a free-standing foil of the braze alloy, which failed upon dual atmosphere exposure. The composite braze material was used to seal a metal-supported thin-film YSZ cell. The sealed cell was thermally cycled 30 times very rapidly without any deterioration of the open circuit voltage.
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Keywords: Solid oxide fuel cell; Braze; Seal; Coefficient of thermal expansion; Thermal cycling

1. 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 metal or mica-based compressive seals [1]. Each type has drawbacks that have precluded the emergence of a dominant seal technology. In this work, we describe a modified braze material that is especially well-suited to sealing and interconnecting metal-supported SOFCs for which yttria-stabilized zirconia (YSZ) is one of the sealing surfaces.

The requirements for a braze material that joins ceramic and/or metal parts in a solid oxide fuel cell are that it (i) wets and bonds to the joining members, (ii) provides a crack-free joint after brazing and during use, (iii) provides a joint with no interconnected porosity, (iv) is stable when simultaneously exposed to fuel and oxidizing atmosphere, (v) does not contain entities that could contaminate the other materials of the fuel cell and, in the case that the braze is part of the current path, (vi) has a high electrical conductivity. Fig. 1 shows the application of

braze to seal and join a metal-supported SOFC cell to a metallic interconnect. The braze must seal at the electrolyte and interconnect surfaces and provide electrical connection and a strong bond between the metal support and metal interconnect. In this paper we report a modified Ag-based braze that fullfils all of these requirements.

Brazing is widely used to join materials by means of an alloy that melts upon heating and reacts with the surface of the materials to be joined, creating a bond upon cooling and solidification of the braze alloy. A suitable braze wets the surfaces of the materials to be joined, and allows them to be joined without physically changing them. To accomplish this, brazes generally melt at a low temperature relative to the melting points of the materials being joined. The heating and cooling are usually, although not necessarily, carried out in vacuum or inert atmosphere. This is a complication for the application of brazing to SOFCs because many interesting cathode catalyst materials decompose in such an environment. Recent work indicates that this incompatibility may be addressed by carrying out the brazing operation in air [2–4]. Alternatively, the cathode catalyst can be infiltrated into the cathode structure after brazing is complete [5].

Brazes are often based on metals such as Ag, Au, Cu, Ni, Ti, Pd, Pt, Cr, and alloys thereof. Brazes can also include small fractions of a wide variety of other elements that are added to

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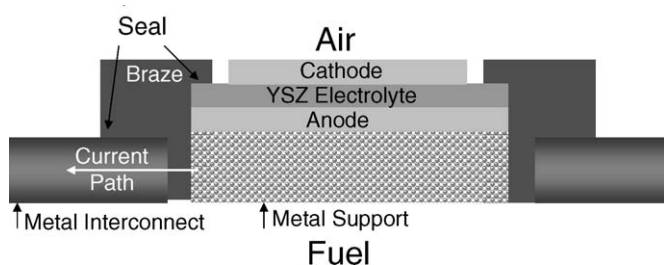 *E-mail address:* mctucker@lbl.gov (M.C. Tucker).

Fig. 1. Schematic of metal-supported SOFC cell brazed to metal interconnect.

tune various properties of the resulting alloy. Brazing can be used effectively to join similar or dissimilar materials, i.e., metals to metals, ceramics to ceramics, and metals to ceramics. In the case of brazing to ceramics, it is usually necessary to treat their surface so that the braze wets the ceramic and a strong bond is achieved. This can be accomplished in several ways, including plating a metal film onto the ceramic before the brazing [6], or including an element in the braze alloy that reacts with the ceramic surface during the braze operation [7]. The reactive element is often Ti, Hf, Zr, V, or Nb. Many commercial braze alloys include the reactive element as an integral part of the braze alloy. Of these, precious metal-based alloys are most promising for use in SOFCs, as the braze must withstand fuel and oxidizing atmospheres at high temperature. 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^{-1}, with Ag-based alloys at the higher end of this range. The CTE of YSZ is 10.5 ppm K^{-1}. This CTE mismatch is sufficient to cause cracking in a YSZ joining member after brazing. Even if a crack-free joint can be produced, thermal cycling of the joint during operation will produce cracks at the braze/YSZ interface. Such cracking is clearly detrimental to the gas-sealing, strength and lifetime of the joint, and is therefore unacceptable. There are many strategies for minimizing the thermal stress in a brazed joint. For instance, the brazed joint can include a metal foil or mesh that either has a low CTE, thus reducing the bulk CTE of the joint, or has a low Young's modulus so as to accommodate mechanical strain [8–11]. The addition of cladding metals or foil members to the joint may, however, have undesirable consequences for thickness, lifetime, oxidation stability, chemical stability, etc., of the joint.

Another strategy is to fill the braze joint with particles that have a lower CTE than the braze alloy, resulting in a composite braze material with a bulk CTE that is more closely matched to that of the joining members. Ishikawa et al. disclosed a joint wherein the gap between two fitted bonding members is filled with a hard solder and a particulate filler, resulting in a composite joint material after soldering [12]. The volume fraction of the particulate filler is specified to be 30–90% of the total composite filler. Makino and Shinkai, described an alumina-filled braze with a CTE reduced enough to avoid cracks in an alumina joining member [13]. The surface of the ceramic particles required metal-plating to enhance wetting with the braze material, and the particulate alumina filler fills up to 90% of the joint volume.

High loading of particulate filler is necessary if the CTE of the particles is only moderately different than that of the alloy. This high volume fraction may lead to undesirable reduction of ductility, electrical and thermal conductivity, etc., of the resulting joint. Shinkai and Kida disclosed a bonding system in which a hard solder is filled with at least two types of particulates differing in wettability with the solder [14]. For instance, some of the particulates can have a metallized surface while the others have a native surface. They show that at least 25% of the filler particles should have good wetting with the solder (i.e., by having a metallized surface), or else bond strength of the joint will suffer. The resulting joints have a degree of porosity, associated with the addition of the particle that has low wettability with the solder. Such porosity may adversely affect the gas-tightness of the resulting joint. We see that in the case of ceramic filling particles, metallization is deemed necessary to produce good wettability; this can be a costly and time-consuming step.

Zhu and Chung reported the use of uncoated carbon fibers as a filler in silver-based brazing materials [15]. The joint strength between 304 stainless steel and alumina was maximized using 12 vol% carbon fiber filler. A Ti-rich reaction layer was observed at the braze/carbon and braze/Al_2O_3 interfaces. The improved joint strength was attributed to modification of the alumina/braze reaction layer, reduction of the braze CTE, strengthening of the braze, and decrease of the braze microhardness due to addition of the carbon fibers. This work illustrates the role of titanium management in creating a strong joint to ceramic surfaces, and the use of an untreated filler material to modify the titanium content at the braze/ceramic interface. The use of carbon fiber strongly limits the utility of the prepared joint, as the carbon fibers will oxidize at temperatures well below the operation temperature of, e.g., solid oxide fuel cells or gas turbine parts.

We report here a composite braze material consisting of a Ag-based braze alloy and a very low CTE particulate filler. Addition of a reactive element promotes wetting of the particle with the braze alloy. The low CTE of the filler allows significant reduction of the composite CTE for even the relatively low loadings of less than 30 vol% filler. Thus, the desirable thermal, mechanical, and electrical properties of the braze alloy are largely retained in the composite. The composite braze is successfully employed to produce crack-free sealed joints between ferritic stainless steel and YSZ. The joints were exposed to fuel cell operating conditions and thermally cycled without failure.

2. Experimental methods

2.1. Brazing

Brazing was accomplished in a vacuum furnace. Typical heating and cooling rates were $10\,^{\circ}C\,min^{-1}$ to $880\,^{\circ}C$ with a 5-min hold at this temperature. YSZ and stainless steel substrate surfaces were washed in water and acetone before brazing, with no other specific surface treatment. YSZ substrates were prepared by sintering YSZ (Tosoh 8Y) at $1400\,^{\circ}C$ in air. Pure Ticusil (68.8Ag–26.7Cu–4.5Ti, Morgan Advanced Ceramics) was used in foil or powder form. Braze mixtures with Al_2TiO_5 (29 μm median, Aldrich) and TiH_2 (1–3 μm, Alfa Aesar) were prepared
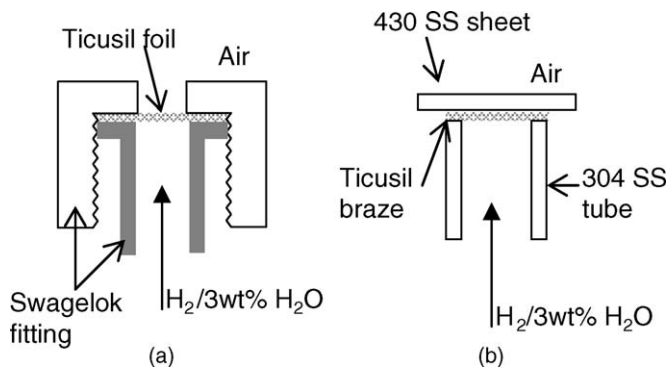
Fig. 2. Schematic of test fixture for dual atmosphere testing. (a) Free-standing foil and (b) brazed joint.

by mixing the filler powders with Ticusil powder under IPA or terpineol. Joints were free-standing with no external load applied during brazing.

2.2. Analysis

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

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

Thermogravimetric analysis (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 A).

Brazed metal/braze/metal butt joints were prepared with 430 steel strip substrates. The joining surface of the substrates was 1 cm wide and 0.7 mm thick. A gap of <500 μm between these surfaces was filled with braze alloy. Failure testing was accomplished at room temperature in tensile mode under load control with an Instron 810 Materials Test System. Specimens were tested in the as-brazed geometry, with no notch or other features introduced.

2.3. Dual atmosphere exposure

Pure Ag and Ticusil foils were compressed in Swagelock fittings suitable for mounting on a gas/vacuum manifold for dual atmosphere exposure. A schematic of the setup is shown in Fig. 2a. The setup was checked for vacuum-tightness after which flowing H_2/3 wt% H_2O was introduced at atmospheric pressure to the interior of the sample with ambient air exterior to the sample. The sample was then held at 700 °C for 125 h. After this conditioning, vacuum-tightness of the foil was not

achieved for this configuration. Brazed joints of the geometry shown in Fig. 2b were similarly conditioned for 300 h. No weight or mechanical loading was applied to the joint during brazing or dual atmosphere exposure. In this case, vacuum-tightness was achieved after exposure.

2.4. Thermal cycling

Anode-supported tubular cells for thermal cycling testing were produced by co-sintering a NiO-YSZ tube with a thin YSZ layer applied by aerosol spraying. Co-sintering occurred at 1400 °C in air, after which the cell was reduced in 4%H_2/Ar at 800 °C for 10 h prior to brazing. Reducing the NiO to Ni before brazing is necessary to avoid oxidation of Ti in the braze mixture. Metal-supported tubular cells were prepared by proprietary technology. The metal-supported cell consisted essentially of a highly porous metal supporting a ∼30 μm thick dense YSZ electrolyte on the outside of the tube. These cells were brazed to metal housings (17-4PH stainless steel) using pure Ticusil. A layer of 25 vol% Al_2TiO_5/Ticusil with 1:1 wt TiH_2:Al_2TiO_5 was used to seal against the metal housing and YSZ electrolyte film. Rapid thermal cycling with 3%H_2O/H_2 fed to the interior of the cell was achieved by moving the cells in and out of a furnace held at 735 °C. The cells were allowed more than 3 min in or out of the furnace to ensure thermal equilibration. Thermal equilibration with the environment was confirmed with a thermocouple mounted on the surface of the metal housing. Maximum heating and cooling rates were ∼500 °C min^{-1}, and the minimum temperature was below 100 °C for each cycle.

3. Results and discussion

3.1. The use of Ag-based braze in a SOFC environment

Considering the requirements for a braze joint in an operating SOFC, including cost targets, the Ag-based family of braze materials is quite promising. Ticusil (68.8Ag–26.7Cu–4.5Ti) is a commercially available braze alloy that finds use in brazing to ceramic joining members. Ticusil has a high loading of Ti, which reacts with the ceramic surface and promotes wetting of the braze alloy. The presence of Cu reduces the melting point of the braze alloy significantly. It also reduces the CTE somewhat and increases the Young's modulus and strength without significantly reducing the electrical or thermal conductivity.

Concern has been expressed in the literature regarding the stability of precious metal-based brazes in oxidizing atmospheres [16–18]. In particular, Ag–Cu–Ti brazes have been shown to oxidize relatively quickly at similar conditions to the air side in a working SOFC [17,18]. We have explored the impact of oxidation of Ticusil on those materials properties that are relevant to SOFC sealing and interconnection. Oxidation of the Cu and Ti is expected in the presence of air at SOFC operating conditions. Oxidation at 700 °C in air was assessed by TGA. Fig. 3 shows the weight gain for brazed Ticusil. The dashed line represents the weight gain expected for complete oxidation of Ti and Cu. Complete oxidation occurs rapidly after which the sample weight stabilizes. These data provided a guideline for the
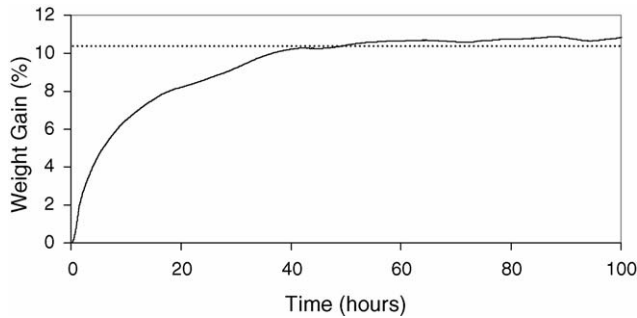
Fig. 3. TGA data for brazed Ticusil in flowing air at 700 °C. The dashed line represents theoretical weight gain for complete oxidation of Ti and Cu.

protocol used to determine the effect of oxidation on relevant materials properties.

Fig. 4 shows an image and element maps of a stainless steel/Ticusil/Al$_2$O$_3$ joint that was oxidized in air at 700 °C for 125 h. There are two distinct regions of braze: the area of the braze joint nearest the air interface is clearly oxidized, while the thin section between the alumina and steel remains unoxidized. The oxidation front moved about 500 μm during the 150 h oxidation, indicating an overall oxidation rate of 4 μm h^{-1} at 700 °C. We have oxidized Ticusil numerous times in various sample geometries and found this oxidation rate to be typical. The element maps reveal that the Ag and Cu are fairly homogeneously distributed throughout the joint, with the exception of a Cu-rich area at the free (air) surface of the braze. The microstructure is characterized by Cu-poor regions that are presumably at the Ag–Cu eutectic composition, surrounded by Cu-rich regions. The Ti has segregated to the surfaces of the steel and alumina, promoting wetting of those surfaces by the braze alloy. Oxidation does not dramatically affect the element distributions.

In the case that the braze joint provides electrical connection between the cell and interconnect as shown in Fig. 1, the electronic conductivity of the braze must be high, and remain so over the lifetime of the device. Fig. 5 shows the dependence of braze conductivity on oxidation time. Comparison of the as-brazed samples (0 h data) indicates that addition of Al$_2$TiO$_5$ filler material (discussed in Section 3.2) reduces the conductivity of the composite braze material only slightly. Upon 50 h of oxidation, the conductivity of both samples is reduced about 50%, yet remains sufficiently high for use in a SOFC. Further oxidation does not statistically affect the conductivity, agreeing well with the rapid 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.

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 [19]. 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 reproduced these results for Ag and Ticusil foils using the compression fitting test fixture shown in Fig. 2a. Extensive
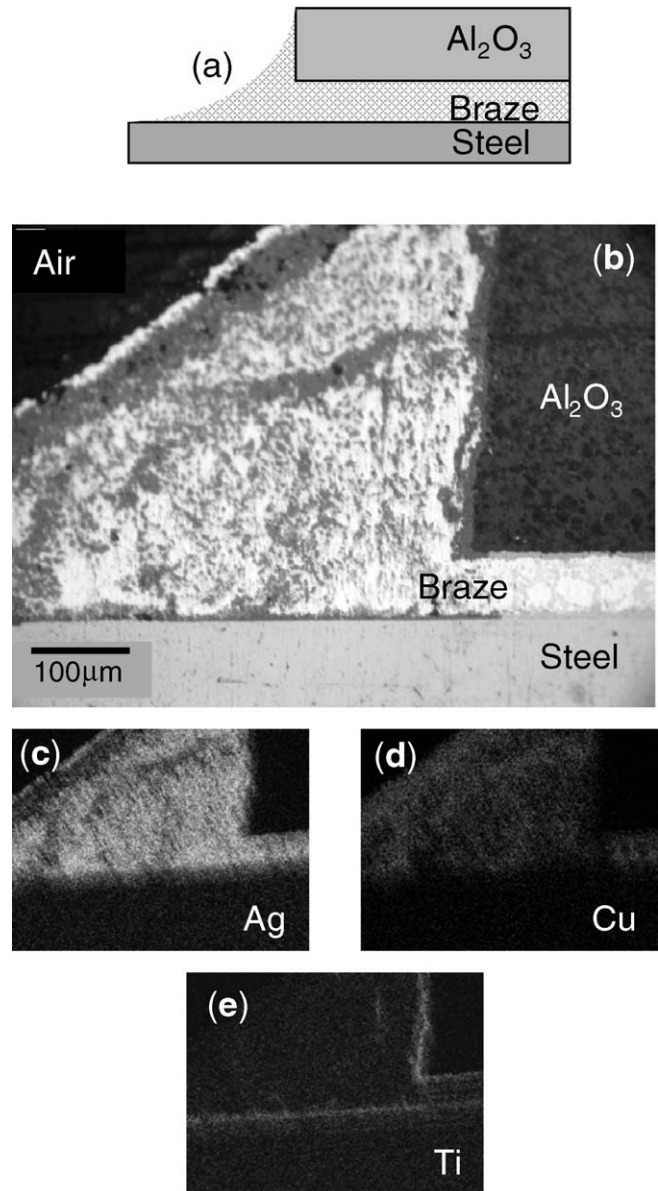

Fig. 4. Cross-section image and element maps of a Al$_2$O$_3$/Ticusil/430 stainless steel joint after oxidation for 125 h at 700 °C in air. (a) Schematic of joint, (b) SEM image of polished cross-section, (c) Ag map, (d) Cu map and (e) Ti map.
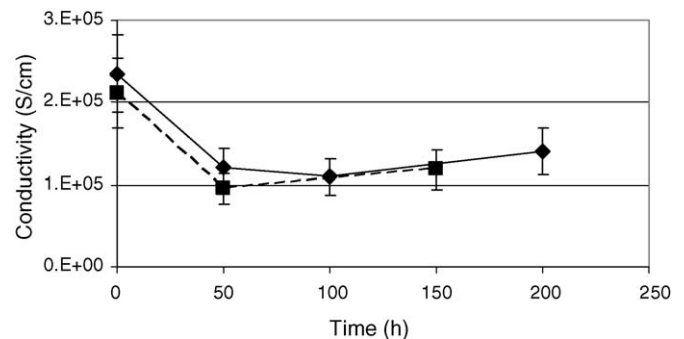

Fig. 5. Conductivity as a function of oxidation time in air at 700 °C for pure Ticusil (diamonds) and Ticusil with 25 vol% Al$_2$TiO$_5$ filler (squares).
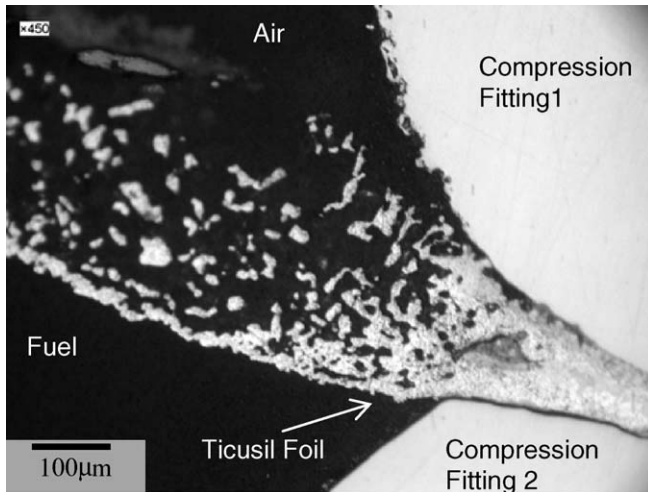
Fig. 6. Cross-section image of Ticusil foil after exposure to air and fuel ($97\%H_2/3\%H_2O$) dual atmosphere for 125 h at 700 °C.

void formation was observed for both foils after exposure to dual atmosphere at 700 °C. The cross-section image in Fig. 6 shows the Ticusil foil after dual atmosphere exposure. The left side of the image shows a region where the foil was free-standing. The bright areas in the image are regions of intact Ticusil and the dark areas are void space. The foil was ~250 μm thick before testing, and expanded considerably due to extensive void formation within the foil. On the right side of the image, the foil is compressed between the mating surfaces of the fitting. Both oxygen and hydrogen have high permeability through Ag, [20,21] so we surmise this region of the foil experienced similar hydrogen, oxygen, and steam pressures as the free-standing region of foil. Yet, the compressed region of foil does not contain any voids after exposure. We speculate this is because contact with the compression fitting provides mechanical constraint of the foil sufficient to counteract the steam pressure developed within the foil. In essence, steam bubbles cannot form if the foil is prevented from deforming.

Brazed Ticusil joints were produced between thin-wall stainless steel tubes and stainless steel sheets so as to allow exposure to fuel on the inside of the tube/joint and air on the outside (Fig. 2b). The resulting dimension of the Ticusil joint separating the two atmospheres is comparable to the thickness of the foils tested above and tubes tested in Reference [13]. Pure Ticusil joints were tested with simulated low-utilization and high-utilization fuel streams ($3\%H_2O/97\%H_2$ and $85\% H_2O/15\%H_2$, respectively). A sample with 25 vol% Al_2TiO_5 filler, discussed in Section 3.2, was also tested with low-utilization fuel stream. All joints passed a vacuum test for gas-tightness after dual atmosphere exposure. Fig. 7 shows cross-sections of the exposed joints. Neither catastrophic failure nor significant void formation was observed for any joint tested. We speculate this is because the steel joining members provide mechanical constraint for the Ticusil joint. No external loading or weight was applied to the joint, so sufficient mechanical constraint is provided simply by contact between the braze and joining surfaces. Essentially, the bond between the braze and the stainless steel prevents the braze from deforming in the presence of internal steam pressure. The
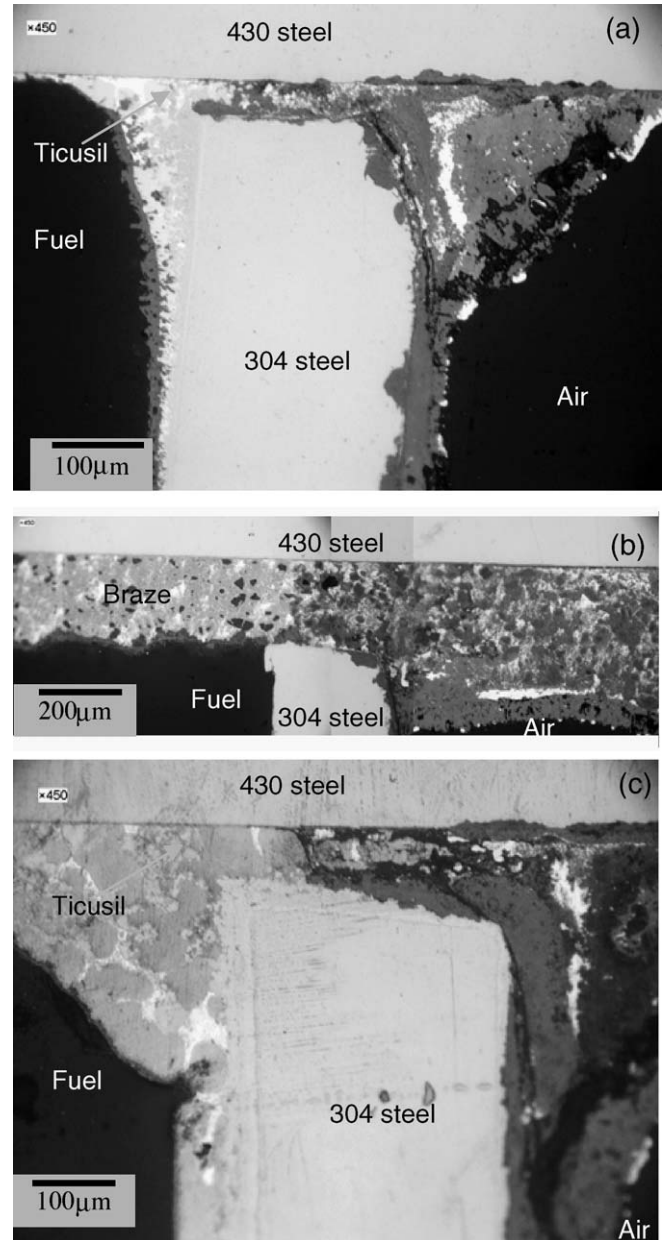

Fig. 7. Cross-section image of 430 stainless steel plate/Ticusil/304 stainless steel tube joints after exposure to air and fuel dual atmosphere for 300 h at 700 °C. (a) Pure Ticusil, fuel is $97\%H_2/3\%H_2O$, (b) Ticusil has 25 vol% Al_2TiO_5 filler, fuel is $97\%H_2/3\%H_2O$ and (c) pure Ticusil, fuel is simulated high fuel utilization $15\%H_2/85\%H_2O$.

Ticusil near the air side of the joint has clearly oxidized. Thin and thick oxide scales are present on the 430 and 304 steel surfaces, respectively, after exposure to air. The fuel side of the Ticusil joint remains unoxidized. This is somewhat surprising, considering that the oxidation rate determined in Section 3.1 would lead us to expect the oxidation front to travel ~1200 μm during 300 h of exposure at 700 °C. The presence of fuel on one side of the joint clearly prevents the oxidation front from crossing the entire joint. We expect this will be beneficial for maintaining a strong, conductive, gas-tight joint in an operating SOFC.

If the braze joint provides mechanical connection between adjacent cells, it must maintain a high strength over the lifetime

of the device. The cells being developed in the present work utilize metallic supports, current collectors and cell-to-cell joint housings. Therefore a metal/braze/metal butt joint provides a relevant model geometry for strength testing. Such joints were produced by brazing 430SS metal strips (500 μm thick) to each other using various braze composites. Some samples were then subjected to complete oxidation at 700 °C in air before pull-testing to determine failure strength. As-brazed Ticusil/25 vol% Al_2TiO_5/1:1 wt TiH_2 failed in the braze material at 48 MPa, which is a much higher load than can be expected in a fuel cell under normal conditions. Unfilled Ticusil joints were tested as-brazed, and after complete oxidation at 700 °C. The as-brazed joints failed at ∼76 MPa in the metal strips, not in the brazed area, indicating that the braze joint is stronger than the metal substrate. The fully oxidized sample failed within the braze at ∼6 MPa. This represents a worst-case failure strength. As indicated above, the presence of fuel prevents the joint from complete oxidation. Therefore failure strength in an operating cell is expected to be closer to the high as-brazed strength and therefore sufficient for maintaining sealing. We therefore conclude that Ticusil-based joints connecting metal to metal are very strong, and remain so after oxidation. A stainless steel tube that was capped by a braze joint to stainless steel sheet was also tested for sealing ability after complete oxidation at 700 °C. The vacuum leak rate was negligible after oxidation.

These results demonstrate that Ticusil can provide a strong, conductive joint that is stable and robust when exposed to the SOFC operating environment at 700 °C. To further utilize Ticusil as a seal in an operating SOFC, it must be modified so as to match the CTE to that of YSZ.

3.2. Matching the braze CTE to that of YSZ

Fig. 8a shows a cross-section of a brazed YSZ/430SS joint using pure Ticusil foil. The braze spreads and wets both the YSZ and steel substrate well, producing a high-quality, nonporous joint. Thin Ti-rich reaction layers are present at the braze/YSZ and braze/steel interfaces. Large cracks are visible in the YSZ substrate, arising from CTE mismatch between the braze mate-
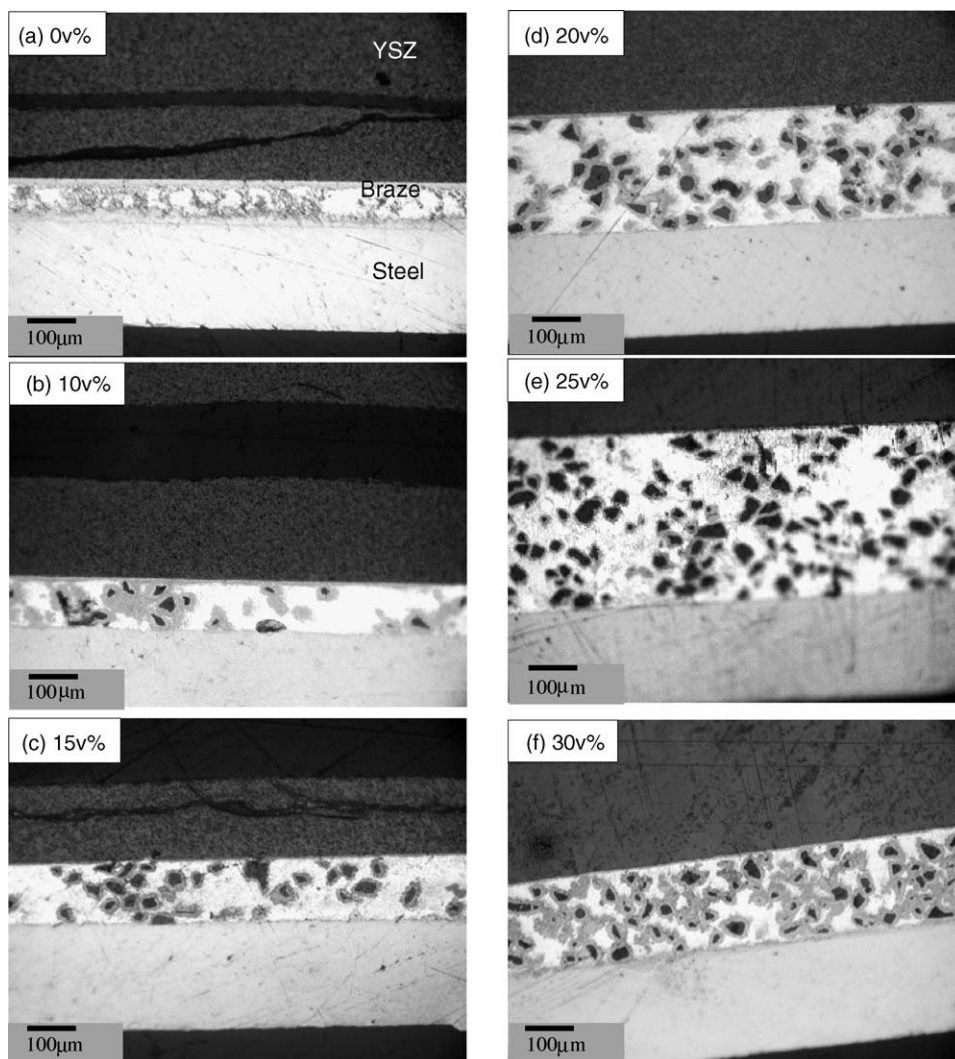

Fig. 8. (a–d) Cross-section images of YSZ/braze/430 stainless steel joints after brazing. The braze composite is Ticusil filled with Al_2TiO_5 at the volume loading indicated in each image. The braze composites shown in (e) and (f) had additional loading of TiH_2 at 1:1wt Al_2TiO_5:TiH_2.

Table 1
Coefficients of thermal expansion for selected materials

Material	CTE (ppm K^{-1})
Ticusil	18.5
430SS	10.4
17-4PH SS	10.8
YSZ	10.5
Al_2O_3	~7
Al_2TiO_5	~1

rial and the ceramic. Such cracks are also present for Ticusil brazed to YSZ with no steel joining member.

Previous work has demonstrated the addition of particulate filler to brazes to modify the CTE of the resulting braze composite [12–15]. In most reported cases, Al_2O_3 was the ceramic of choice for both the particulate filler and joining member, and the Al_2O_3 joining member was free of cracks after brazing. In contrast, we have found that YSZ still cracks after brazing with Al_2O_3-filled Ticusil. This difference is probably because a YSZ joining member is weaker than an Al_2O_3 one. In fact, we have been able to produce some Al_2O_3/pure Ticusil/430SS joints with a crack-free Al_2O_3 member, whereas all YSZ/pure Ticusil/430SS joints we have produced display cracks in the 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 high particulate loadings could compromise the conductivity, strength, or nonporous nature of the composite braze. Table 1 indicates the CTE for selected materials. On this basis, Al_2TiO_5 is clearly a better candidate to reduce the overall CTE of an alloy/ceramic composite braze material. Furthermore, Al_2TiO_5 is expected to be stable at metal-supported SOFC operating conditions [22].

Braze mixtures of various Al_2TiO_5 loadings were used to braze YSZ to 430SS. Cross-section images of the resulting joints are shown in Fig. 8b–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_2TiO_5 levels less than 15 vol%, significant cracking in the YSZ disk occurs. No cracking was observed for the 20–30 vol% Al_2TiO_5 braze samples. This suggests that the higher levels of filling are sufficient to reasonably match the bulk CTE of the braze material 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, as the reactive element (Ti) also segregates to the surface of the filler particles. Higher levels of filling (>20 vol%) require the addition of TiH_2 to the braze mixture to compensate for the amount of Ti that reacts with the filler particle surface. Without this additional TiH_2, a poorly bonded joint results.

After the brazing operation, a dark band on the YSZ is sometimes produced around the braze joint. In particular this band is present for low levels of Al_2TiO_5 filler or high levels of filler accompanied by TiH_2 addition. We surmise this is due to migration of excess Ti from the braze joint across the YSZ surface during brazing, accompanied by nonstoichiometry in the underlying YSZ [7]. Because Ti migration out of the joint area is undesirable for reasons discussed below, optimization of the Ti and TiH_2 loading is necessary to produce a braze material that wets the YSZ and Al_2TiO_5 surfaces well yet does not contain excess Ti. The dark band extended more than 1 cm away from the braze material in some cases, and was accompanied by electronic conductivity on the YSZ surface. After oxidizing the samples (>300 °C in air), the dark area became white and electronically insulating, presumably by oxidation of the Ti surface layer to TiO_2. Minimization of Ti migration is an important issue, as the Ti-rich surface layer presents 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 Fig. 9, the conductiv-
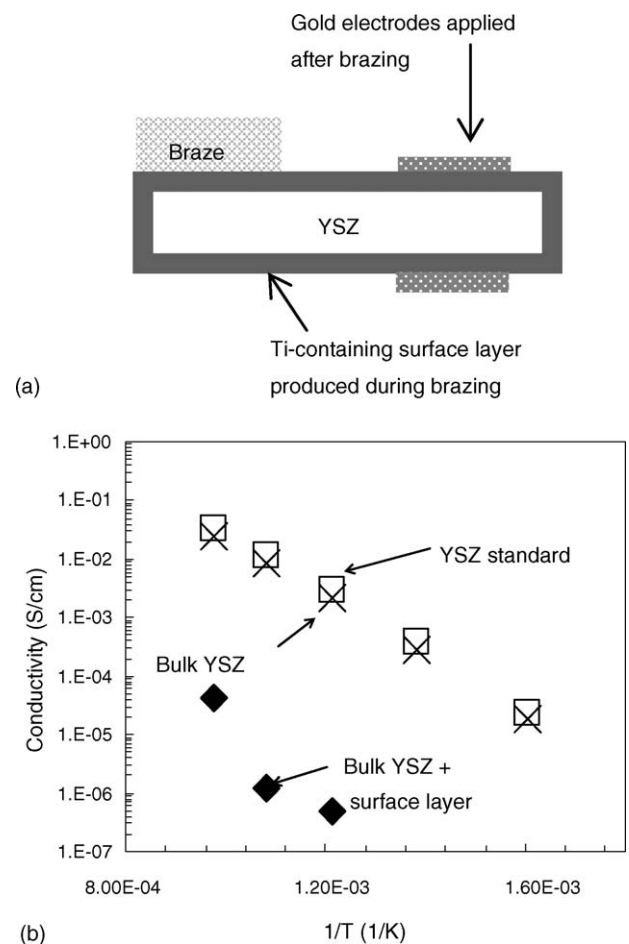

Fig. 9. The effect of Ti migration on electrolyte conductivity. (a) Schematic of sample geometry. (b) Conductivity determined by ac impedance for the entire sample including surface film (diamonds), the interior/bulk of the sample only (crosses), and an external YSZ standard (squares).

ity 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.

The amount of reactive element included in the braze mixture can be optimized according to the amount of filler particle and joining member surface area to be treated; we have successfully produced joints with good bonding and minimal Ti migration outside of the joint area.

3.3. Thermal cycling

Addition of Al_2TiO_5 to Ticusil results in a braze composite with a CTE that is matched to YSZ well enough to allow crack-free joints to be prepared. Thermal cycling provides a more aggressive test of the CTE match. We have brazed 25 vol% Al_2TiO_5-Ticusil onto dense YSZ and porous Ni-YSZ substrates and exposed these joints to thermal cycling. The YSZ/braze joint was cycled very rapidly from 100 to 700 °C 20 times in air, with maximum heating and cooling rates ~500 °C min^{-1}. The Ni-YSZ/braze joint was cycled 60 times between 350 and 700 °C at 10 °C min^{-1} in 4%H$_2$/96%Ar to prevent the Ni from oxidizing. Cross-sections of the joints are shown in Fig. 10. There is no cracking or delamination at the interface, suggesting that the CTEs are well-matched. We have also thermally cycled tubular cells that were braze-sealed to stainless steel housings. Pure Ticusil was used to join the cell to the housing, and 25 vol% Al_2TiO_5–Ticusil was used to seal against the housing and YSZ electrolyte. Two cells with thin-film YSZ electrolyte layers ~30 μm thick were tested: Ni-YSZ supported, and stainless steel-supported. The cells were cycled between 735 °C and
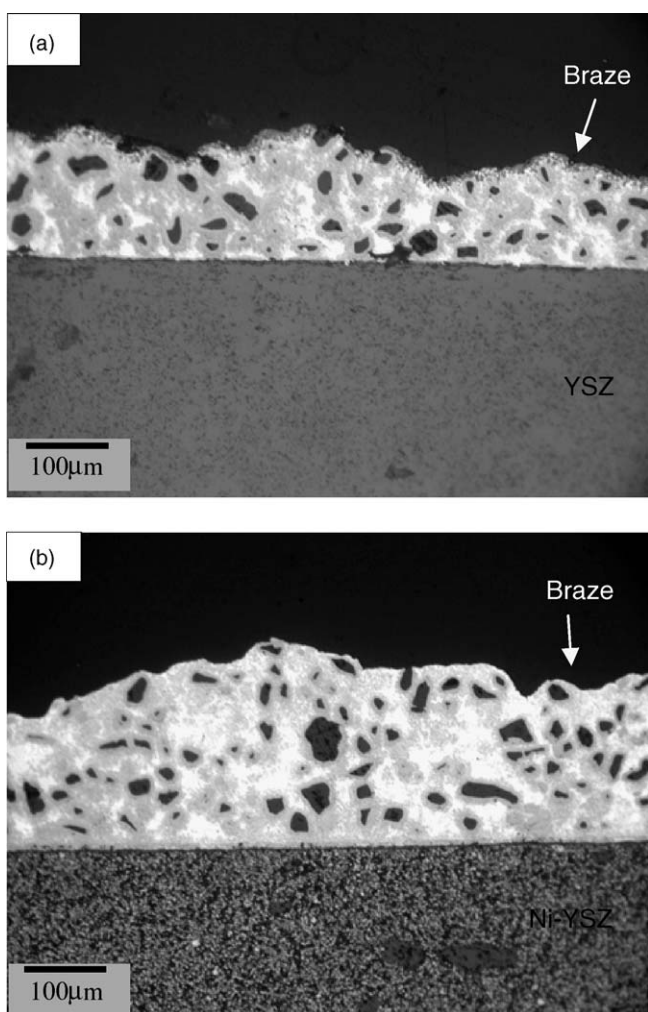

Fig. 10. Cross-section images of Ticusil/25 vol% Al_2TiO_5-filled joints after thermal cycling. (a) YSZ substrate, 20 very rapid cycles in air 100–700 °C. (b) Ni-YSZ substrate, 60 cycles 350–700 °C at 10 °C min^{-1} in 4%H$_2$/argon.
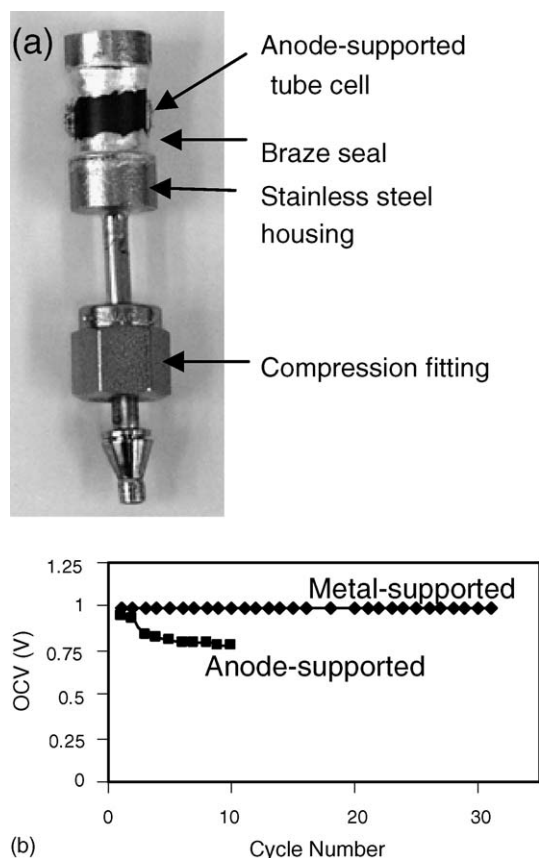

Fig. 11. (a) Anode-supported tubular cell brazed to 17-4PH stainless steel housing with compression fitting manifold for fuel flow. Identical fittings and geometry were used for metal-supported tube cell (not shown). (b) Open circuit potential after thermal cycling very rapidly in air between 735 °C and about 100 °C. Fuel is H$_2$/3%H$_2$O. Ni-YSZ anode-supported tubular cell (squares) and metal-supported tubular cell (diamonds) with thin-film YSZ electrolyte. Cells were joined to stainless steel housing with pure Ticusil and then Ticusil with 25 vol% Al_2TiO_5 filler was used to seal against the housing and YSZ electrolyte.

about 100 °C at ~500 °C min^{-1} maximum heating and cooling rate by moving them in and out of a furnace held at 735 °C. Fig. 11 shows the open-circuit potential (OCP) of both cells as a function of thermal cycle number. The anode-supported cell displayed a large drop in open circuit voltage (OCV) after the second cycle, followed by very gradual decay. After testing there were visible cracks in the cell wall, but none in the vicinity of the joint. A bubble test confirmed that the joint was not leaking. The brazed joint is clearly much more robust towards rapid thermal cycling than the anode-supported cell itself. The stainless steel-supported cell displayed no decay at all in OCV during rapid thermal cycling. This indicates the steel-supported cell is more robust than the anode-supported cell and furthermore that the YSZ-braze composite seal is CTE-matched well enough to tolerate very rapid thermal cycling without cracking or delamination.

4. Conclusions

Ticusil (68.8Ag–26.7Cu–4.5Ti) braze alloy was tested for its utility as a seal/joint for SOFCs operating near 700 °C. Ticusil oxidizes rapidly in air at 700 °C, but after complete oxidation the strength, sealing ability, and conductivity of the braze remain sufficiently high. Ticusil joints were exposed to fuel/air dual atmosphere. After exposure the joints was robust and free of voids, even though free-standing Ticusil foil was found to fail after similar exposure. We speculate this is because the joining members provide mechanical constraint against void formation in the braze alloy.

Ticusil was filled with a very-low-CTE material, Al_2TiO_5, to reduce the bulk CTE of the resulting composite braze, and more closely match it to the CTE of YSZ. This enabled the production of crack-free steel/braze/YSZ joints. It was found that filler loading of 20–30 vol% was sufficient to prevent cracking in the YSZ joining member. Addition of reactive element, for instance in the form TiH_2, assured wetting of the Al_2TiO_5 particles and YSZ by the braze alloy. It was found that the loading of active brazing element must be carefully controlled: excess active element migrates out of the joint area, contaminating the YSZ surface with a high-impedance layer that would be detrimental to fuel cell performance.

Al_2TiO_5-filled Ticusil/YSZ joints were found to be exceptionally robust towards thermal cycling. Even after very rapid cycling no delamination or cracking was observed in the vicinity of the joint. This enabled 30 rapid thermal cycles of a braze-sealed metal-supported tubular cell with no loss of open circuit potential.

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

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