NEW BRAZE MATERIAL FOR PLANAR SOLID OXIDE FUEL CELL APPLICATIONS

By

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A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

Materials Science and Engineering—Doctor of Philosophy

ABSTRACT

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Solid oxide fuel cells (SOFC) are power generation devices that can convert the chemical energy from a wide range of fuels and energy-carriers directly into electricity with high efficiency. One of the major challenges for the viability of commercial SOFC devices is the development of suitable sealing technologies for the separation of the air and fuel in the system at high temperature (~750°C). Silver-copper oxide reactive air brazes (RAB) are the most widely used SOFC brazes. However, the conventional Ag-4 wt.% Cu composition has a high wetting angle of ~45° in air on yttria-stabilized-zirconia (YSZ) that leads to manufacturing defects (denoted as Type I pores). Also, many reactive elements that oxidize during brazing to promote braze wetting (such as CuO) are easily reduced by SOFC fuels. This results in Type II pores that decrease the braze interfacial strength and provide a quick path for H₂ invasion into the braze (where the H₂ reacts with diffused O₂ to form gaseous water pockets, denoted as Type III pores).

In the present work, two approaches were proposed to replace the current RAB brazing system by either designing a new, silver-free braze or to develop a CuO-free, silver-based braze. For the first approach, an integrated computational-experimental method was used. Thermo-Calc[®] was utilized to fast screen through hundreds of alloy systems to identify candidate braze compositions. Material compositions, melting ranges, mechanical properties, oxidation resistance, as well as wetting characteristics of these candidate alloys were analyzed. Substrate

surface pre-treatments, active element additions, and novel brazing schemes were also investigated. Unfortunately, the current study failed to find a suitable silver-free braze for SOFC applications.

In the second approach to find a CuO-free, silver-based SOFC braze, a novel silvernickel brazing method was developed. It was demonstrated that transient porous nickel interlayers, instead of reactive element additions, can be used to promote Ag wetting on YSZ and produce high-quality YSZ-stainless steel braze joints. Mechanical tests on these reactiveelement-free, silver-based SOFC braze joints, both before and after 500 hours of 750°C oxidation in air, show that the braze and braze interface strength are higher than the underlying YSZ|NiO-YSZ substrate. The microstructural and compositional evolution of SS|Ag-Ni|YSZ braze joints exposed to dual atmosphere (air on one side and 4%H₂-96%N₂ on the other side) for 300 hours of isothermal 750 °C aging and 300 25°C/min 35-830 °C rapid thermal cycles were compared to a Ag-3CuO braze joint. The Ag-Ni brazes remained pore free and well bonded, suggesting that Ag-Ni brazes may be more suitable for long term SOFC operation than Ag-CuO brazes. Other applications inspired by the silver-nickel wetting process are also explored. Copyright by QUAN ZHOU 2019 This dissertation is dedicated to my family. Thank you for your belief in education.

ACKNOWLEDGEMENTS

This work was supported by the Department of Energy under Award Number DE-FE0023315. Microscopy and mechanical testing were conducted at the Michigan State Composites Center, which is supported by the NSF Major Instrumentation Program and Michigan State University.

I would like to express my sincere gratitude to both of my advisors, Dr. Thomas R. Bieler and Dr. Jason D. Nicholas, for their patience and guidance throughout the course of my doctoral study. Their passion and enthusiasm for science and education was the greatest support for this dissertation. I am also deeply thankful for the countless discussions and arguments with them, which helped shape my research and also this dissertation. I'm also grateful for the many opportunities they provided for me to present my work at multiple conferences, which opened my eyes and helped establish my own professional network.

I would also like to thank my dissertation committee members Dr. Andre Lee, and Dr. Patrick Kwon, for their valuable suggestions for my dissertation work. I also want to thank the weekly metal group meetings with Dr. Martin Crimp, Dr. Carl Boehlert, and Dr. Philip Eisenlohr, as well as the weekly meetings with Dr. Nicholas' group members. Discussions from these meetings have helped me overcome a lot of hardships in this work. I would also thank Dr. Yue Qi and her group members for their collaboration on the computational part of this work.

I would like to thank Robert W. Nichols from Delphi Technologies PLC, Bryan A. Gillispie and Rick Kerr from Aptiv PLC for their assistance with testing samples, raw materials, and the dual-atmosphere tests. Their consistent support on experiment and samples was crucial in finishing this work.

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I also want to thank my fellow graduate students and all my friends for their support. My thanks also go to a couple of undergraduate students that have worked with me over these years on different projects. I've had a lot of fun playing with you in the labs and it was my pleasure working with you.

Finally, I want to express my deepest gratitude to my parents and my wife Yuewen (Jenny) for their unwavering belief in education that led to my doctoral study, for their selfless love and understanding all these years, and for their company in the darkest hours.

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CHAPTER 1

Introduction and Literature Review

1.1 Rationale

Fuel cells are energy generation devices that can convert chemical energy directly in to electrical energy. Compared to traditional power generation methods, fuel cells have higher efficiency and a much smaller adverse environmental impact [1]. Solid oxide fuel cells (SOFC) are capable of using a wide range of fuels and energy-carriers (stored energy that can be released through chemical/physical processes) including hydrogen, ethanol, hydrocarbons like gasoline/natural gas and even carbon [1-3]. Besides their efficiency and low environmental impact, SOFCs also have the best volumetric power density and one of the best gravimetric power densities as shown in Figure 1.1 [2, 3].



Figure 1.1 Gravimetric and volumetric power densities for different electricity generation technologies, from [2, 3].

Figure 1.2 [2] shows the schematic of a typical SOFC, which is a three-layer structure consisting of a solid oxygen ion conducting electrolyte sandwiched between two porous electrodes (cathode and anode). Oxygen from air is reduced at the cathode side, producing O^{2-} ions to be transported through the electrolyte to the anode side. Then the O^{2-} ions will react with the fuel/energy carriers (in a gas form) to produce water and carbon dioxide (equation in Figure

1.2), which generates electricity and heat at the same time [1-3]. Because the reaction relies on the transport of O^{2-} ions in a solid state diffusion process, the operation temperature of SOFCs is in the range of 600°C ~ 1000°C to achieve a sufficient rate of diffusion [1, 3]. Also, at such high temperatures, the fuel or energy carrier must be separated from the O₂ in air to prevent energy loss and formation of an explosive gas mixture. Therefore, sealants are required in a SOFC to separate the fuel and O₂ during normal operations.



Figure 1.2 Schematic diagram showing the components and operation of a typical SOFC, from [2].

A schematic of the sealant cross-section of a typical planar SOFC device is shown in Figure 1.3 [4]. The sealant is an Ag-CuO braze in this case. It should be noted that the sealant also needs to serve as a bond between stainless steel and yttria stabilized zirconia (YSZ). During normal operation, the sealant bonds the metal and ceramic together and keeps the dual atmosphere (fuel/energy-carrier on one side and air on the other) separated at ~750°C. Such complex conditions create many concerns for the design of a successful sealant [5-9]:

- Joining condition (e.g. temperature, pressure, atmosphere) of the metal and ceramic parts with such a sealant need to be compatible with other SOFC components during production;
- The sealant needs to provide sufficient wetting and adhesion at the two interfaces that have very different surface chemistries;
- The sealant needs to be compliant to accommodate the coefficient of thermal expansion (CTE) mismatch between the stainless steel and the YSZ (25-750 °C: CTE_{441 steel}=12 ppm/K [10], CTE_{YSZ}=9 ppm/K [8]);
- The sealant needs to be able to provide a hermetic seal over a long period (>40,000 hours) to enable consistent function of the SOFC device.



Figure 1.3 Cross-section of a 97.5Ag-2.5CuO braze joint. Each planar SOFC cell is bonded around its edges to a stainless-steel picture frame with a braze, from [4]. G18 is a glass sealant developed by the Pacific Northwest National Lab (PNNL) to slow air intrusion into the braze seal.

Currently, the most widely used sealing material is a Ag-CuO filler as shown in Figure 1.3 [4]. This 97.5Ag-2.5CuO braze is the state-of-the-art braze composition used by Delphi but it can only achieve normal operation of the SOFC device for ~10,000 hours. The end of life is limited by major problems in the silver-based braze.

As mentioned above, the two parts to be joined in the commercial SOFC device are stainless steel and YSZ. The current sealant is a silver-based reactive air braze (RAB), which is vulnerable to several types of porosities that have been observed after the brazing process or operation of the device. Three types of pores I, II, and III have been identified. Type I pores are usually observed after brazing and is shown in Figure 1.4a and 1.4b. This type of pore is speculated to be caused by insufficient wetting (on both the alumina coating on the steel and the YSZ surface) [11] and vaporization of the binding agent (trapped volatile species) [12] during the brazing process. A type I pore was proved to have little impact on the initial performance of the SOFC device, however, overtime it could contribute to the more damaging effects of the two other types of porosities. Type II and III pores are defined as the micro-pores formed by the reduction of the CuO to Cu within the braze (mostly at the interfaces) and the reaction between the diffused H_2 and O_2 respectively (Figure 1.4c). This porosity is the major damage source in mid/long term applications. Formation of Type II and Type III pores result from the high diffusivity of hydrogen and oxygen in silver [13-16]. These pores lead to swelling of the braze and eventually the hermetic failure as pores coalesce and provide a rapid percolative path for O₂ and H_2 in the silver-based braze during long-term operations, which can terminate the functionality of the SOFC device and potentially lead to explosion. A more detailed discussion of the effects of these porosities is presented in section 1.2.3.2.



Figure 1.4 (a) Cross-section (side view) of a Type I pore, (b) top-view radiograph of a braze with a Type I pore (light area), and (c) cross-section showing Type II (interfacial) and III (internal) pores after long-term operation, from [4].

In the following sections in Chapter 1, background knowledge of the SOFC sealants is introduced and reviewed. Four general types of sealing techniques for SOFC devices are discussed and compared. The reasoning behind the choice to search for an alternative braze is provided.

Chapter 2 presents the effort spent on the approach to design a new silver-free braze for SOFC sealing applications. The designing criteria, materials and candidate alloy system selection, as well as various characterization results are discussed in detail. Several novel designs related to the new braze candidates are also presented.

Chapters 3 and 4 explore the approach to improve the current silver-based brazes and provides details on the newly invented silver nickel brazing method for SOFCs. Chapter 3

focuses on the designing the oxidation tolerance of the new braze, which is also presented in a published document [17]. Chapter 4 investigates the dual-atmosphere stability of the new silver nickel braze by comparing it with the state-of-the-art Ag-3CuO braze provided by Delphi.

Chapter 5 shows the controlled wetting and spreading behavior of molten silver on various substrates inspired by the silver nickel brazing process, providing opportunities in other applications like high temperature/power ceramic circuits, ceramic-ceramic bonding, currently collectors for ceramic electrodes etc.

Chapter 6 concludes this dissertation and provides recommendations for future work related to the present study.

1.2 Background on the Current SOFC Sealing Technologies

A variety of different materials and methods for SOFC sealing methods have been investigated over the last two decades [5-7, 9, 18-20]. These sealing technologies can be divided into four major categories: glass and glass-ceramic seals, compressive seals, braze seals and other sealing techniques. Advantages and disadvantage for each joining method will be discussed in the following sections.

1.2.1 Glass and Glass-Ceramic Sealants

Glass and glass-ceramic sealants are one of the first and most widely used sealing materials employed in planar SOFCs. Stability of these materials seems to be acceptable during high temperature SOFC operations in a dual atmosphere setting (oxidizing/reducing) atmospheres) for short term applications [9]. Also, the low cost of these materials makes them very appealing to industrial applications. Glass and glass-ceramic materials can be engineered to have a good CTE that's compatible with the joined materials (which are usually stainless steel and YSZ). One of the biggest advantages of the glass and glass ceramics is their possibilities in tuning different properties in order to fulfil specific engineering requirements; because the glass and glass-ceramic materials consist of many different oxides that contribute to different aspects of the overall properties of the sealant. Some common compositional modifiers (i.e. Al₂O₃, B₂O₃, BaO, CaO, V₂O₅ etc.) and their functions for silicate-based glass-ceramic sealants are summarized in Ref. [21]. By changing the composition of different modifiers in the sealant, proper CTE, glass transition temperature (T_g) and temperature at which the glass first softens (T_s) can be achieved. With further control of the crystallization process, mechanical properties and wetting behavior at the interfaces can also be modified. An early study done by Ley et. al. [20]

showed that the SrO-La₂O₃-Al₂O₃-B₂O₃-SiO₂ system with modifications in compositions of different oxides resulted in different T_g (560 °C ~ 780 °C) and CTE values (8.04 × 10⁻⁶/°C ~ 13.1 × 10⁻⁶/°C), which are good matches with ceramic components in the SOFC, and they were well bonded to the electrolyte, cathode and anode ceramics. Sohn et. al. [22] studied the interfacial reactions and thermal cycling stabilities of different BaO-Al₂O₃-La₂O₃-B₂O₃-SiO₂ systems on YSZ, where the B₂O₃:SiO₂ ratio greatly affects T_g , T_s and CTE of the glass-ceramic. One particular sample presented good wetting and bonding characteristics as well as good thermal cycling stabilities.

However, when joined to oxidation resistant alloys (e.g. stainless steel), the bonding characteristics can be a problem, especially during the long-term operations of SOFCs. For example, barium chromate (BaCrO₄) can form when the glass-ceramic interacts with chromia-forming alloys, which not only leads to depletion of barium in the glass-ceramic but also causes separation of the glass-ceramic matrix with the alloy matrix due to CTE mismatch [23, 24]. This interaction also generates bubbles or pores at the interface, which is more severe in the case of joining with alumina-forming alloys where both large and small pore were distributed in the seal [23]. Additionally, an increase in crystallinity and phase transformations during high temperature operations can change the mechanical properties of the sealant in the long run. A decrease in shear strength and CTE was observed in barium aluminosilicate glass-ceramic joints after aging at 750°C [21]. Similar observations were also reported by Lin et. al. [25] when BaO-B₂O₃-Al₂O₃-SiO₂ glass-ceramic joints with stainless steel were tested in a reducing atmosphere to identify thermal aging effects.

In conclusion, although glass and glass-ceramic sealant are acceptable in terms of their dual atmosphere stabilities, cost, CTE similarity and versatilities in materials engineering. There

are also major drawbacks for this type of sealants. The biggest challenge is the internal brittleness of the glass/ceramic materials, especially at lower temperatures [6, 9, 25]; another concern is their bonding with oxidation resistant alloys [6, 9, 21, 23-25], where reaction products have high CTE and anisotropy that lead to strength degradation in the thermal aging tests [23-25]. These disadvantages prevent the glass sealants from being widely used in commercial SOFC devices.

1.2.2 Compressive Seals

Instead of actually bonding with the metallic and the YSZ parts, compressive seals employ materials that are deformable under compression to serve as gaskets. With the applied compressive stress on the entire sandwiched window frame/sealant/YSZ structure, small gaps are closed, and gas leakage can be greatly reduced. There are several advantages of the sealing technique [9]. First, the sealant material will be easy to produce and apply since there is no actual bonding needed between the sealant and other components in the SOFC. Secondly, such seals will leave more freedom for the designers with respect to alloys selection. Additionally, it will make mid-term repair possible for the SOFC stacks by removing the compressive load, replacing and reassembling the SOFC components.

The sealant used in this technique must be deformable under compressive load and stable in dual atmospheres at high temperature (600° C ~ 1000° C). Candidate sealant materials including ductile noble metals like silver and gold as well as compressible mica-based materials [9, 26].

Duquette and Petric [26] used silver wire as a metal gasket and tested the performance of the compressive seal. It was shown that the material needs to be ductile enough to provide a

sufficient seal, otherwise either the integrity of the compressed structure will be compromised, or the leakage cannot be reduced to an acceptable level. Long-term stability of the silver sealants is also a problem, as Chou et. al. [27] found that the leak rate will increase due to cracking along the grain boundaries during thermal cycling in a compressed silver seal. Moreover, for silverbased materials, dual atmosphere tolerance with air on the cathode side and hydrogen on the anode side is a big problem. Because the diffusivity of both oxygen and hydrogen in silver is very significant, reaction of hydrogen and oxygen within the silver-based sealant will produce water pockets (voids) that greatly degrade the mechanical properties of the seal [15].

Another material that is commonly used in compressive seals is mica-based sealant. With applied compression, the plate like mica crystals will collapse into each other, creating a gas tight seal within the sealant itself. This type of conventional compressive mica seal is shown in Figure 1.5a, which was reported to have a major leak path along the sealant/metal interface [27]. Simner et. al. [28] suggested that the roughness coming from the mica plates at the interface is the major source of the leak, and a single-crystal mica with a smooth surface finish can greatly reduce the leak rate. Chou et. al. [27] proposed a hybrid compressive seal with the application of compliant interlayer (e.g. glass or silver) at the sealant/ceramic or sealant/metal interface (shown in Figure 1.5b[27]) to reduce the impact of the major leak path. The authors [29-31] proposed an improvement of the hybrid compressive seal by "infiltrating" the mica paper with a wetting or melt-forming agent (H₃BO₃ and bismuth nitrate), which showed better leak performance and decreased leak rate in the first ~15 thermal cycles. Regarding the choice of the compliant interlayer, glass is better than silver in all the cases.



Figure 1.5 Schematic drawing of (a) a conventional compressive mica seal; (b) a hybrid compressive mica seal, from [27].

Mica-based compressive sealants are in many cases superior to metal gaskets. With improvements, the mica-based sealant can achieve good gas-tightness and thermal cycling stability. However, there are still concerns in the real application of compressive seals. First, leak performance of the sealant improves with the increase of the applied stress and sufficient gas-tightness need to be achieved before the compressive stress becomes detrimental; Secondly, the compliant interlayer of glass or silver will still have long-term stability issues arising from its brittleness and interfacial bonding with oxidation resistant alloys; finally, the stress needs to be maintained uniformly over a large area and a high temperature, which would be challenging in designing the SOFC device. This type of sealants is not commonly applied in the industry because of these disadvantages.

1.2.3 Brazing

Brazing is one of the most common techniques to join two dissimilar materials for high temperature applications (similar to soldering but at much higher temperature, >450°C). In the brazing process, a filler material (usually metal) with melting temperature much lower than the joined parts is heated above its melting temperature, so that the filler materials becomes liquid and leads to consequent flow and wetting [11]. After the filler material is cooled, a solid joint will form between the two joined parts. Compared to glass seals and compressive seals, brazing will result in better hermeticity, mechanical properties and long-term stability [9]. However, in ceramic to metal joining applications, wetting of the braze material on the ceramic can be a big problem because of different basic surface chemistry. Several brazing techniques have been explored in the application of SOFCs.

1.2.3.1 Active Brazing

Active brazing uses filler materials that contains active elements like titanium, which will react with the ceramic, facilitating wetting between the filler material and the ceramic [9, 11]. Thus, chemical bonding will form at the braze/ceramic interface to provide good adhesion. However, to apply this technique, an inert or vacuum atmosphere is needed to prevent the active elements from oxidizing before reacting with the ceramic, which could damage SOFC cathode materials [32, 33]. Previous study also shows that the resulting joint is insufficient in oxidation

resistance in air at high temperatures [34, 35], which will be unfavorable in the application of SOFCs, and a recent study by Lin et. al. [36] also found poor interaction between the gold-based active braze/YSZ interface as well as Au segregation in the zirconia grain boundaries and fine cavities. To overcome the disadvantages of active brazing, a new method called reactive air brazing (RAB) was developed [6, 37, 38].

1.2.3.2 Reactive Air Brazing

The RAB technique utilizes the solubility of metal oxides in noble metals to achieve a thin, adherent oxide scale at the joined interfaces upon heating, during which the noble metal base will provide excellent oxidation resistance so that the RAB process can be carried out in air without the need for flux (a chemical cleaning agent to improve flowing and remove oxides) [37-39]. Such soluble metal oxides can be added in the metal form, which will turn into oxides during brazing. There are several candidates for this (noble metal)-(metal-oxide) combination including Ag-CuO, Ag-V₂O₅, and Pt-Nb₂O₅ [37, 39]. By far, the Ag-CuO system is the most popular RAB system and it is also the sealant that's been applied in the commercial SOFC device shown in Figure 1.3.

It was shown that pure silver wets poorly on the stainless steel and most ceramic surfaces [40]. The addition of CuO into the silver-based braze can significantly increase the wetting properties of the material probably due to its lower interfacial energy with silver, its affinity with the ceramic substrates [41], as well as its reaction with Al_2O_3 [6]. Early studies were focused on determination of the optimal amount of CuO in the RAB filler material [6, 37, 38, 42, 43]. The wetting angle of Ag-CuO brazes with different CuO content on different SOFC components are shown in Figure 1.6 [6], where less than 10 mol% of CuO addition into the filler material can

reduce the contact angle on YSZ from ~100° to ~40°, and the contact angle on stainless steel from ~100° to ~50°.



Figure 1.6 Wetting angle for Ag-CuO on YSZ, stainless steel (FeCrAlY) and cathode (lanthanum strontium cobalt ferrite/LSCF) materials with increasing CuO contents, from [6].

More recent efforts have further improved the wetting and adhesion of the Ag-CuO based braze by adding titanium [14, 35, 38, 43-46]. Hardy et. al. [43] studied the wetting of Ag-CuO braze on $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, and as shown in Figure 1.7, 0.5 mol % of TiO₂ can significantly improve the wetting behavior of the Ag-CuO braze; whereas the addition into brazes with 0 and 1 mol % CuO, it can be detrimental to wetting due to the formation of a continuous scale of TiO₂ on the liquid surface. Lin et. al. [44] studied the interfacial reactions and mechanical properties of a stainless steel/braze/YSZ component joined by a Ag-26.7Cu-4.5Ti (in wt.%) braze. It was found at the braze/YSZ interface that Ti reacted with the oxygen from the YSZ and formed a layer of Ti₂O₃, and the Fe from the steel diffused across the interface further reacted with the Ti₂O₃ to form a layer of Fe₂Ti₄O. All the fractures in strength testing occurred at the braze/YSZ interface probably caused by the low plasticity of the Ti₂O₃ and Fe₂Ti₄O layers.



Figure 1.7 Sessile drop measurements of binary Ag-CuO-(0% TiO₂) and ternary Ag-CuO-TiO₂ (0.5 mol% TiO₂) filler metals with 0, 1, and 2 mol% CuO at 1000°C, from [43].

In general, Ag-CuO based RAB sealants have many advantages compared to other methods. For example, the hermeticity over thermal cycling is much superior compared to compressive seals as shown in Figure 1.8a [40]. These silver-based materials also show very good ductility and fracture resistance [47] (Figure 1.8b).



Figure 1.8 (a) The leak rate of different seals at initial condition and after 20 thermal cycles, from [40]; (b) fracture energy of SOFC components and different sealants, from [47].

Unfortunately, conventional Ag-CuO YSZ-SS braze joints suffer from several porosity generation mechanisms that limit their useful 750 °C lifetimes to ~10,000 hours [15], which is well below the ~40,000 hours often cited as necessary for commercially-viable stationary SOFC deployment [13]. The biggest problem regarding the current Ag-CuO RAB braze is the high diffusivity of oxygen and hydrogen within the braze, as shown in Figure 1.9 [48]. First, as shown in Figure 1.3a, RAB braze joints often exhibit manufacturing defects (denoted as Type I pores) resulting from the relatively high ~45° wetting angle of Ag-4CuO on YSZ. Second, as shown in Figure 1.3b, during SOFC operation interface pores caused by anodic gas reduction of CuO (denoted as Type II pores) weaken the braze/SS and braze/YSZ interfaces over time, and provides a fast percolation path for H₂ invasion into the center of the joint [16, 49-51]. Third, as shown in Figure 1.3c, gaseous water pockets (denoted as Type III pores) form from hydrogen and oxygen that has migrated into the braze [13]. The kinetics of Type III pore formation is enabled by the moderately high, 750 °C hydrogen and oxygen ionic conductivity in silver (8×10⁻⁵ and 1.5×10⁻⁵ cm²·s, respectively [48]).



Figure 1.9 Oxygen (solid) and hydrogen (dotted) diffusivities in several common metals (plotted with data from reference [48]).

1.2.3.3 Commercial Self-Passivating Nickel-Based Brazes

Besides reactive air brazing, nickel based brazing materials have also been studied as sealant for SOFC applications[11, 52, 53]. Nickel based materials are ideal basis alloys for high temperature joining applications due to their high-temperature mechanical properties and corrosion resistance [11]. Commercial nickel-based alloys named the BNi series were studied for SOFC applications: Lee et. al [53] used the BNi-3 braze in joining surface coated 316 stainless steel and NiO-YSZ cermet, the filler metal was fully fused and interdiffusion was observed at the stainless steel interface, and little interaction was observed at the YSZ interface. The idea of active brazing was also combined for interfacial studies, Chung et. al. [52] added
different amount of TiH₂ into BNi-2 and BNi-4 brazes, and obtained good wettability on the YSZ surface, and the modified BNi-4 showed good gas-tightness at 750°C for 600 hours. This result shows opportunities for further modification on the commercial BNi brazes with active elements.

In nickel-based brazes, proper addition of other alloying elements like Cr and Al, can help form a continuous scale of protecting oxides that makes the materials oxidation and corrosion resistant at high temperatures [11, 54-59] (self-passivation). It was concluded that the formation of a protective Cr_2O_3 scale requires ~ 20 wt. % of Cr addition and a protective scale of Al₂O₃ requires 3~6 wt. % of Al addition [57-59]. The oxidation resistant surface scale can help the nickel based brazes to survive in the SOFC operation atmosphere and lead to possibilities in air brazing.

The nickel-based braze systems haven't been intensively studied for SOFC sealing application, while there exists great opportunity that they can replace the conventional Ag-CuO brazes. Systematic modifications were carried out to investigate the effect of different elements on melting, wetting, oxidation and mechanical properties. Detailed discussion will be further provided in Chapter 2.

1.2.4 Other Sealing Techniques

Glass and glass-ceramic seals, compressive seals and RAB seals are the major sealing techniques adopted in the SOFC industry, but other methods have also been reported to join ceramics and stainless steels for high-temperature applications. These attempts will also provide insights for the development of the new, self-passivating braze.

Mei and Xiao [19] used a thermite reaction between Ni and Al to join zirconia with metals. Joining was carried out in argon at temperatures from 640°C to 1250°C and the filler metal was successfully bonded to the calcium stabilized zirconia (CSZ) and stainless steel. However, 5 thermal cycles to 900°C resulted in cracks within the CSZ substrate. Gorji et. at. [60] successfully sintered/bonded stainless steel to YSZ using nano-particles of Ag and Ni with diameter of ~80 nm. Although the resulting joint was very porous, the bond was fabricated at 270°C with 72 % solid loading, which provide a new angle for developing new sealants. A more recent study by Si et. al [61] also obtained reasonable joint strength (24 MPa) with 300°C fabrication temperature using silver nano-particles. These studies reveal opportunities in lowering the brazing temperature (other than melting range) requirements.

Diffusion bonding or partial transient liquid phase brazing was also reported. Zhang et. al. [18] used Ni and Ni-Cr as filler metals that sandwiched with Cu and Ti foils to join Al₂O₃ and stainless steel. The Ni and Ni-Cr filler metals are compliant layers to relieve the thermal residual stress induced by CTE mismatch. Indacochea et. al. [62] used a Ni/Ti/Ni tri-layer filler material to join zirconia and stainless steel with different brazing parameters. The resulting joint had a layered structure and reaction with filler materials at both the zirconia and stainless-steel interfaces were observed. Wei and Lin [63] successfully joined YSZ to stainless steels with a Ti/Ni/Ti filler, and a layered structure was also observed with reaction at both ceramic and metal interfaces. There is a lack of information about the long-term (thermal aging and thermal cycling) stabilities of the joined structures. However, these results provide ideas for improving interfacial bonding characteristics.

Bonded compliant seal (BCS) is a new sealing technology designed for SOFC applications. The technique was first proposed by Weil [9] and so far research efforts has been

limited to computational study [9, 64-66]. The structure of the BCS structure is shown in Figure 1.10 [65]. Different parameters like thickness of different parts in this design were tested and optimized computationally, and good creep as well as damage resistance were also achieved by simulation. Realization of this method will still require brazing. Similarly, Ag-based brazes will cause long-term problems but the new brazes proposed later may provide a solution.



Figure 1.10 The cross-section of the Bonded Compliant Seal (BCS) structure, from [65].

1.2.5 Summary of Different Sealing Technologies

Several major sealing techniques for SOFC devices have been discussed above. Each of these methods have their own pros and cons as shown in Table 1.1. It can be concluded that reactive air brazing is relatively better than the other techniques when cost is excluded as a major factor. It has better ductility, hermeticity and moreover, better relatively long-term stability. However, the "long-term" reliability of the RAB brazes is only good for up to ~10,000 hours [15], limiting the lifetime of the entire SOFC device. Either a new, self-passivating braze or a CuO-free braze is needed to overcome the problem with silver and achieve longer SOFC operation.

	Pros	Cons
Glass and glass- ceramic seals	 Good CTE and wetting characteristics; Low cost and easy to apply. 	 Mechanically detrimental reaction with stainless steel; Inherent brittleness; Lack of long-term stability in mechanical and chemical properties.
Compressive seals	 More freedom in alloy selection since no actual bonding is needed; Easy to apply; Possible in mid-term repair; 	 Generally bad hermeticity and long-term stability compared to other seals; Compressive stress needs to be maintained over a long time at high temperature.
RAB	 Relatively easy in application (compared with other brazes); Better long-term stability compared to glass and compressive seals; Better ductility and hermeticity compared to glass and compressive seals. 	 Micro-pore formation prohibits its application for >10,000 hours; CuO and other oxide at the interfaces are mechanically weak.

Table 1.1 Summary of major sealing technologies for SOFCs.

As mentioned above, two approaches were taken to solve the sealing problem for SOFCs in this study. For both approaches, there are many requirements that need to be fulfilled regarding both the general SOFC sealing demands and the specific restrictions from the commercial SOFC design and manufacturing. A list of the requirements is shown in Table 1.2 [4].

For the first approach to develop a new, silver-free braze, a computationally aided materials design method is used. Phase diagram calculation software was used for fast screening through different alloy systems with regard to their melting ranges, and then candidate compositions were physically fabricated to check for physical, chemical and mechanical properties, and further optimization according to Table 1.2. These results are detailed in Chapter 2.

For the second approach to develop a new CuO-free braze, because a silver-based braze will fulfill most of the criteria in Table 1.2, alternatives to CuO with a focus on the improvement of surface wetting properties are investigated. Nickel porous networks were found to be effective in controlling the molten silver wetting and spreading on ceramics so that a novel, two-step, silver nickel brazing method was invented for SOFC sealing applications. The design, fabrication, optimization, oxidation testing, dual-atmosphere reliability testing, as well as other potential applications of the silver nickel brazes are studied (Chapter 3-6).

No.	Design Parameter	Target Values	Justification	97.5Ag-2.5CuO Values				
1	Solidus Temperature (T _s)	$900^{\circ}C \le T_{s} \le 1015^{\circ}C$	So the braze is solid during SOFC operation	912°C				
2	Linear Coefficient of Thermal Expansion (CTE)	7 ppm/K ≤ 25- 750°C CTE ≤ 16ppm/K	To prevent surface oxide spallation. 25-750°C YSZ CTE=9 ppm/k. 25-750°C 441 steel CTE=12 ppm/K.	~21 ppm/K Non-passivating spallation-prone CuO forms on the surface in air.				
3	Wetting Angle (θ)	$0^{\circ} \le \theta \le 30^{\circ}$	To ensure that the braze spreads through the joint during manufacturing	45°, Causes Type I pores to form in the braze				
4	Metallurgical Bonding with Al ₂ O ₃ and YSZ	Interdiffusion or new phase formation	To promote good, active brazing with the both faying surfaces	Bonding with chemical reaction				
5	Braze Joint Strength (σ_B)	$\sigma_B > 120 \text{ MPa}$	So the braze can accommodate YSZ-441 CTE mismatch stress	220 Mpa				
6	Ductility	≥ 3%	So the braze can withstand YSZ-441 thermal expansion mismatch stress	Sufficient, but unknown				
7	Vapor Pressure	750°C Vapor Pressure < 1×10 ⁻⁸ torr	To ensure that volatilization does not degrade the braze or the protective oxide	Ag 750 °C Vapor Pressure in Air = 1×10^{-5} torr				
8	Oxygen and Hydrogen Conductivity (σ ₀₂ ,σ _{H2})	$\sigma_{02} < 1 \times 10-8$ S/cm $\sigma_{H2} < 1 \times 10-8$ S/cm	If no surface oxide forms, the braze should have a low oxygen conductivity to prevent pores formation. If a surface oxide forms, the oxide should have a low oxygen conductivity	Ag stable above 160° C in air. $\sigma_{02} < 2 \times 10^{-4}$ S/cm promoting Type III pores.				
9	Stability over 40,000 hours of SOFC Operation	Retention of all design parameter target values	To ensure reliable SOFC operation	Does not last past 10,000 hours of SOFC operation				

Table 1.2 Braze design criteria for commercial SOFC applications [4].

1.3 Characterization of SOFC Braze Properties

1.3.1 Mechanical Properties

As indicated in Table 1.2, requirements #4-#6, mechanical bonding strengths at both braze interfaces are crucial for the reliability of SOFC braze seals. Various testing methods have been used by different research groups to study the bonding strength, and/or the strength of the braze material its self. Conventional three-point or four-point bending tests were commonly used [38, 67]. However, the tested bending strength is not equivalent to the bonding strength at the braze interfaces, and their values are also dependent on the specific testing conditions and parameters used, making it difficult to compare systematically between different studies. Also, because ceramic substrates (sometimes porous ceramic substrates) are used for the bending test samples, pre-mature failure usually occurs in the ceramic parts of the samples, further affecting the interpretation of the results.

Since the braze seal typically experiences CTE-mismatch induced shear loading in realworld SOFCs during thermal cycles, shear tests should be performed to assess the braze joint mechanical stability. To apply shear loading at the braze regions of the joint samples, several experimental designs have been in the literature. As shown in Figure 1.11, Lin et. al [44], used 'cross-bonded' samples to assess tensile and shear bond strength. This method uses bulk ceramic and stainless steel bars to avoid failure and deformation in the YSZ and stainless steel parts. Other testing fixtures explored in the literature include the method shown in figure 1.12a, which shows the schematic of the testing fixtures used by Wang et. al [68], where tensile loading applies shear deformation on the braze. Figure 1.12b shows the schematic of testing fixtures used by Yang et. al [69] that use compressive loading to test the bonding strength at the braze/Invar alloy interface. Figure 1.12c shows a double shear lap geometry used for fully

reversed fatigue testing of solder joints [70]. Inspired by these testing methods, a new experimental setup was proposed to test the bonding characteristics, which will be discussed in detail in Chapter 3.



Figure 1.11 (a, b) Schematic diagrams of applied load, support and bonded area for the crossbonded samples in the tensile and shear test, respectively; (c) picture of the tensile and shear strength test sample of steel/Ag26.7Cu4.5Ti/YSZ joint, from [44].



Figure 1.12 Schematics of testing fixtures for the shear bonding strength of braze/solder joints using (a) tensile, (b) compressive loading, and (c) double shear laps, from [68], [69], and [70], respectively.

1.3.2 Braze Reliability in Dual Atmosphere

To evaluate the reliability of the SOFC brazes, it is important to use real-life SOFC

operation conditions. In practice, the SOFC will operate at a relatively high temperature

(~750 °C) with its anode compartment exposed to reducing atmospheres like fuel or hydrogen, and its cathode compartment exposed to air (hence, 'dual atmosphere'). Because chemical reactions occur between the braze components and the H_2 and O_2 from the atmosphere at high temperatures, it is crucial to understand the microstructural as well as phase evolutions of the braze joint in dual atmosphere conditions.

Tests are typically performed with specially design sample geometries. Figure 1.13 shows a common type of dual atmosphere testing setup [16]. The Ag-CuO braze portion inside of the alumina tube was exposed to H_2 to mimic the anode atmosphere and the Ag-CuO braze portion exposed to air in the furnace simulate the cathode atmosphere. After testing, the braze joint was cross-sectioned to examine the microstructural difference with respect to the two atmospheres.

Several studies in the literature have investigated the dual atmosphere tolerance on SOFC brazes [13-16, 46, 50, 71], with a focus on silver-based brazes. It was consistently found that the Type II pore formation occurs within the first 100 hours of dual atmosphere exposure, primarily at the reducing side. Also, significant porosity was found at the braze/stainless steel interface [13, 50]. Kim et. al [15] investigated the effect of aluminum addition on the dual atmosphere tolerance of RAB brazes. Their results show that aluminum addition has only limited effect on the RAB dual atmosphere tolerance and it degrades the joint strength.



Figure 1.13 A schematic of the dual atmosphere testing apparatus used in [15].

To further assess the operational reliability of the braze, accelerated thermal cycling tests are needed. Because of the high operating temperature (~750 °C) of SOFC devices, accelerated thermal cycling tests must be able to ramp between 25 °C and 800 °C at relatively high rates (20~40 K/min). Due to the complexity in the test setup and the long periods of time required for testing, only a few studies involving thermal cycling tests were found in the literature [13, 46, 72], and only two dual atmosphere thermal cycling study were reported [13, 73]. Bause et. al [13] analyzed several actual SOFC stacks with an Ag-8CuO after dual atmosphere thermal cycling and found severe porosity formation. Similar results were also reported by Brandenberg et. al [73].

1.4 Summary

Different materials requirements for SOFC sealing applications were introduced and reviewed. Four general types of sealing techniques for SOFC devices were discussed and compared for their feasibility in production, chemical and mechanical stability in operation as well as their reliability during thermal cycling. As shown in Table 1.1, each sealing technique has its own strengths and weaknesses. Among these methods, reactive air brazing stands out as it has better ductility, hermeticity and relatively better "long-term" stability. However, the reactive air brazes are only good for up to ~10,000 hours of SOFC operation due to the formation of several types of porosities either during fabrication or dual-atmosphere exposure.

Thus, a new braze with better mid/long term reliability is needed. This work explores two approaches to solve the problem: one is the attempt to design a new silver-free, Type III pore resistant braze (Chapter 2); the other is to improve upon the current Ag-CuO braze and overcome the drawbacks arising from the CuO additions to achieve longer lifetimes of the braze (Chapter 3). Furthermore, as the literature lacks detailed knowledge on dual-atmosphere stability of SOFC brazes, a new testing setup was designed for both isothermal and accelerated thermal cycling conditions. Materials properties using the newly proposed Ag-Ni method and reactive air brazing are compared in both dual-atmosphere isothermal aging and dual-atmosphere thermal cycling tests (Chapter 4).

CHAPTER 2

Nickel-Based Braze Development

2.1 Introduction

Designing a replacement silver-free braze alloy from scratch requires three major aspects to be considered. First, hundreds of different alloy systems need to be efficiently screened and assessed; secondly, the candidate alloy needs to be oxidation resistant to survive the high temperature operating conditions, so surface passivation needs to be considered during candidate selections; finally, chemical, physical and mechanical properties of the alloy candidate needs to be characterized and optimized to meet all the requirements in Table 1.2. These considerations are discussed in the following sections, respectively. The computational work described in this chapter was done by Dr. Tridip Das, and Mr. Young Kim from Dr. Yue Qi's research group at the department of Chemical Engineering and Materials Science at Michigan State University.

2.1.1 Computation-Aided Materials Design

In order to quickly screen through various alloy systems, a computationally aided approach to design a new, self-passivation braze was proposed, especially to meet the requirements #1 and #2 in Table 1.2. Identifying the melting point/range of new alloy systems would be very costly and time-consuming using experiments because all the different metal basis materials need to be purchased and samples with various compositions need to be experimentally fabricated and characterized. However, using the CALPHAD (CALculation of the PHAse Diagrams) approach embedded in Thermo-Calc^{® TM} [74], liquidus information can be estimated

for alloy systems with two, three or even more elements. The CALPHAD method analyzes and models information from a vast amount of experimental data using thermodynamic properties and phase boundaries, so that phase diagrams outside the experimentally known range can be extrapolated using thermodynamic models [75]. Furthermore, the computational search can be improved by limiting the candidate elements through considerations of cost, toxicity, compatibility with other SOFC components, effects on existing brazes, and the feedback from experiments. In addition, through the automation of the entire search process, time-efficiency will be significantly improved to allow more focus on the promising alloy systems.

2.1.2 Surface Passivation on Candidate Alloys

To further reduce the scope of the computational search, and to solve the biggest problem regarding the current Ag-CuO braze, which is the high diffusivity of oxygen and hydrogen within the braze (requirement #8, Table 1.2), two approaches can be used: One is to use a base material that has very low diffusivity for hydrogen and oxygen. Another is to develop a passivating layer on the braze surface to serve as a diffusion barrier for hydrogen and/or oxygen. These two approaches could also be combined in the same candidate system.

It is obvious that an alloy with low diffusivity for oxygen and hydrogen will not be vulnerable to formation of Type II and Type III pores. As shown previously in Figure 1.9 [48], some metals have much lower diffusivity for hydrogen and/or oxygen than Ag, like Co, Ni, Ti and Zr. Utilizing these metals as a braze base will suppress the formation of micro-pores within the joint. In fact, nickel based brazes are ideal to join materials for high temperature applications due to their good mechanical properties and corrosion resistance at such temperatures [11]. With addition of other elements, the melting point/range can be adjusted for different application

requirements, which can be assessed efficiently through computations. Also, preliminary studies have demonstrated the possibilities in joining YSZ to stainless steel with modified commercial BNi brazes [52, 53].

The other approach to form a passivating layer on the alloy surface is most commonly accomplished in stainless steels with chromium additions. With a proper chromium addition, a uniform scale of protective Cr_2O_3 will form on the surface of the steel, which protects the metal from oxidation and corrosion to achieve a "stainless" protected surface. A similar mechanism is also present in other alloy systems like nickel/chromium and cobalt/chromium [11, 76-78]. The oxidation resistance of these alloys is superior compared to stainless steels because nickel and cobalt are more noble than iron. Prior work indicates that ~20 wt. % of Cr or 3~6 wt. % of Al is needed to form protective scales of Cr_2O_3 or Al_2O_3 on the surface of nickel-based alloys [11, 54-59]. It should be noted that this approach must applied regardless of the H_2/O_2 diffusivity of the base metal, because (1) the commercial brazing process is carried out in air and (2) the braze exposed to the air side in the SOFC device cannot be continuously oxidizing, which would cause the integrity of the joint to be compromised.

Essentially, the two approaches can be combined for alloys based on Ni and Co. One extra benefit with these systems is that the low diffusivity for O_2 (in either Ni or Co) will lead to less formation of internal oxides of Cr_2O_3 or Al_2O_3 , which will facilitate the formation of the protective Cr_2O_3 or Al_2O_3 scale at the surface [58, 59]. This knowledge was incorporated in to the computational search by starting with low H_2/O_2 diffusivity element basis and/or addition of passivating-layer-forming elements like Cr and Al to broaden the search for promising brazing systems.

2.1.3 Materials Properties of Candidate Alloys

The major concern with the current Ag-CuO braze is the mechanical failure in the longterm (>10,000 hours) caused by H₂O micro-pores. With a new braze that has a passivating surface oxide scale, this problem can be solved. However, this is not the only requirement for the new braze design. According to Table 1.2, there are more requirements for the braze application in commercial SOFC devices (requirement No. 3, 4, 5, 6).

For brazing applications, the filler alloy (the braze) needs to melt and wet both of the faying surfaces (YSZ and Al₂O₃-coated stainless steel in this case) in order to bond with both of the surfaces. Good bonding/adhesion is also needed at the braze/substrate interface so that the interface will not crack after brazing. Good bonding between metals and ceramics can be hard to achieve because of the different bonding characteristics of these two materials, but with chemical reaction or diffusion at the interface, adequate strength can be obtained in brazed joints [6, 7, 9, 55, 79]. Active elements or metal oxides can be added to the braze to improve the wetting on both faying surfaces as well as to introduce chemical reaction at the interface, which will be discussed in section 2.3.

Besides the mechanical properties at the joint interfaces, the mechanical properties of the braze materials themselves is also crucial for long-term SOFC applications. There are very different CTE values in stainless steel and YSZ (25-750 °C: CTE_{441 steel}=12 ppm/K [10], CTE_{YSZ}=9 ppm/K [8]) in the commercial SOFC design. The braze needs to either have (1) a compatible CTE with both substrates so that the CTE mismatch doesn't cause too much stress in the joint during thermal cycling; or (2) very good ductility in the temperature range (25-750 °C), so that the stress generated by the CTE mismatch can be compensated by plastic deformation of the braze metal (as with the Ag-CuO braze).

2.1.4 General Strategy for New Braze Design

As discussed above, all the three aspects need to be considered for the design of the new, silver-free braze alloy. The general strategy used is shown in a design and validation flow chart in Figure 2.1. First, computational efforts were made to identify candidate alloy systems with acceptable melting ranges, together with the considerations of alloying effects of different elements. Then, these candidate alloys were physically fabricated and characterized using various techniques. Chemical, mechanical properties, as well as wetting and bonding on different substrates were evaluated and further modified according to the industrial requirements. Furthermore, the candidate alloys were engineered such that a passivating surface oxide scale will form during either brazing or operation, which will prevent the formation of micro-pores during SOFC operation. Eventually, this process should provide a design and development of a new braze that can wet and bond both surfaces with considerable strength as well as ductility, and most importantly, passivate during the SOFC operation to ensure the long-term operation of the commercial SOFC devices. To fulfill the different requirements in Table 1.2, Figure 2.1 also shows the several adjustments that could be applied to either the candidate alloy or the brazing system. These techniques include addition of melting point depressants for melting ranges adjustments; addition of surface passivation layers formers for enhanced surface passivation; addition of active elements for improved wetting and bonding characteristics; and other pretreatments of the brazing substrates or other brazing techniques. A multilayer approach was also investigated to improve the wetting and bonding at different interfaces.



Figure 2.1 Flow chart showing the design, development, and testing process for the new braze candidate alloys (DSC: Differential Scanning Calorimetry; TLPB: Transient Liquid Phase Bonding).

2.2 Materials and Experiments

2.2.1 Candidate Alloy Sample Fabrication and Preparation

Braze samples were fabricated by arc-melting pure materials in a controlled atmosphere. Figure 2.2 shows the general procedures taken to fabricate candidate alloys. Typically, raw materials with ~99.99% purity were weighed according to the target composition. Then the combination of different raw material pieces was transferred into the arc-melting container. The combined weight of the materials was usually ~2-6 g. The chamber was evacuated and refilled with purged with Ar gas 3 times and then maintained at a pressure of 1×10^{-3} torr before the final braze sample was taken out. Then, arc-melting of getter materials was done to lower the partial pressure of oxygen within the chamber and protect the target materials from oxidizing. Typically, pure Al was used as the oxygen getter to further reduce the oxygen partial pressure. After solidification of the liquid sample mixture, the sample in the chamber was flipped and remelted at least 5 times (up to 20 times in some cases) to promote a homogeneous composition distribution. After sample fabrication, high-speed diamond saw machining was used to section each sample for microstructural evaluation.

In some cases, raw metal powders were used for sample fabrication. The metal powders were weighed according to the candidate alloy composition and then mixed in a glass jar by a powder shaker for ~20 minutes. A total weight of 2.5 g was typically used. The powder mixture was then compressed into a pellet with a diameter of 0.5". Candidate alloy samples were fabricated through arc-melting the compressed pellet in a similar way as previously described.

Raw Materials (Cut, Clean, Weighed)



Select the right getter material to secure the partial pressure of O_2 during melting.



Arc-Melt in controlled atmosphere (Ar/lower PO₂)





The as-fabricated samples in this chapter were arc-melted metal lumps (2~6 g each), placed in position to fabricate stainless-steel|braze|ceramic lap joints, or more simply, ceramics with metal brazed on the surface. The metal samples with high hardness levels like nickel-based alloys were initially sectioned to make smaller pieces with a high-speed diamond saw in order to prepare samples; then a low speed diamond saw was used for all the other sectioning processes to prevent the ceramic parts from chipping and breaking, as well as to improve accuracy in sectioned sample geometry. Different diamond embedded copper wafer blades were used for different types of samples handled, i.e. high concentration blades for soft metals and low concentration blades for hard ceramics.

The samples are sometimes mounted for the ease of handling. Prior to mounting, all the samples were cleaned in acetone with an ultrasonic cleaner for 10 minutes. The cross-sectioned samples from the low-speed diamond sectioning process were ultrasonically cleaned in acetone for at least one hour to remove the machine oil residue. An epoxy mounting kit (Epofix, Buehler Inc.) was used and the samples were cured at room temperature for at least 24 hours. For grounding and polishing, the samples were mechanically grounded with 60, 240, 320, 400, 600, 800 and up to 1200 grit sandpapers (Allied High Tech. Products). Further polishing was done on samples for scanning electron microscopy (SEM) analysis, by polishing with 5 μ m, 1 μ m, 0.3 μ m Al₂O₃ (AP-302, Mager Scientific, Inc.) and then 0.04 μ m colloidal silica (OP-S NonDry, Struers Inc.) was applied.

Smaller samples ($\sim 3 \times 3 \times 0.5$ mm) were sometimes glued to a metal block for polishing on all the sides for thermogravimetric analysis (TGA). These samples can be detached by heating the sample and the metal block together with a hot plate to ~ 200 °C, and the glue residue on the sample was cleaned by ultrasonic cleaning in acetone. The samples were glued to the metal

block multiple times on different sides in order to grind and polish the entire surface of the samples to achieve a uniform surface roughness. These small samples for the TGA analysis were all polished to 1200 grit sandpaper to achieve a consistent sample surface roughness.

2.2.2 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was also performed with a Jupiter 449 F5 DSC-TGA analyzer (Netzsch) on the as-fabricated samples to measure the solidus and liquidus temperatures. Because measurements up to 5 days were done, the instrument was placed in a dedicated basement room with the ventilation system disabled to provide a very uniform temperature. Also, the water circulation for the balance chamber (within the TGA-DSC) temperature stabilization was set to a temperature slightly higher than the room temperature, to ensure stability in the balance readings (i.e. 27 °C water temperature when room temperature is 25 °C). Periodically, or after any conditions were changed, a new correction run with no sample would be performed to provide a basis for correcting data runs, and to ensure reliability in the TGA data. All results discussed in the following sections are corrected with their corresponding baseline files.

Before any measurements were made, temperature calibration was performed. An example of the calibration is shown in Figure 2.3, where the measured melting point for pure aluminum (99.999 wt.% purity) is 660.2 °C (melting point of Al is 660.3 °C). For the DSC test, a small piece (~5 mg) from the as-fabricated sample was placed in an Al₂O₃ crucible; it was then heated up to 1200-1300 °C at a ramp rate of 5K/min in order to observe the melting event; the sample was then held isothermally at 1300 °C for 10 minutes and finally cooled to 800 °C at the

same ramp rate of 5K/min to observe the solidification event. The test was performed in flowing Argon at 60 sccm (standard cubic centimeters per minute).



Figure 2.3 Example DSC calibration data from a piece of pure aluminum.

2.2.3 Thermogravimetric Analysis

Small pieces of samples with dimensions of ~3mm×3mm×0.5mm were extracted from candidate alloys and polished as described above for the TGA analysis. This was done because the oxidation of the samples is a surface reaction, so that the thermogravimetric data needs to be normalized by each of their surface areas for comparison. To measure the total surface area of

each TGA sample, optical microscopy was used. Prior to TGA tests, the area of each side of the TGA samples were measured and then summed to calculate the total surface area of each sample.

A Jupiter 449 F5 DSC-TGA analyzer (Netzsch) was used for the TGA analysis. Samples were placed in an Al₂O₃ crucible and then held at the current temperature for at least 2 hours to stabilize the balance reading of the sample weight. Then the sample was heated to 750 °C at a rate of 5K/min. The temperature of 750 °C was chosen to mimic the operating temperature of Delphi SOFC cells. The sample was then isothermally held at 750 °C for typically 120 hours (5 days) and then cooled at 20K/min back to room temperature. This entire process was carried out in 60 sccm of flowing air (20%O₂/80%N₂).

To reduce the background noise as well as the buoyancy effect of the TGA data, a correction run for the base line information was performed periodically with the exact same parameters but an empty crucible. All the results presented in this work are corrected based on these correction files.

Since the TGA test is a very costly measurement, especially in time, measurement on all the candidate samples would not be realistic given the relatively short amount of time on this project. A simplified, semi-quantitative thermogravimetric analysis was performed on the candidate samples before the 5 day TGA assessments. This test was done by placing a piece of the candidate alloy sample in a static air furnace at 750 °C for 2 days (48 hours). The sample weight before and after the 2 day oxidation test provided a rough estimate on the amount of oxidation. Samples with good surface passivation properties usually shows minimal change in the weight gain after 2 days of oxidation in air, and such "good" candidates were selected for further analysis using the DSC-TGA

2.2.4 Characterization of Wetting Properties

As shown by the schematic diagram in Figure 2.4, an existing tube furnace was adapted to perform in-situ wetting experiments on different substrates in a controlled atmosphere. Typically, the candidate alloy sample was placed onto the center of the testing substrate (i.e. a YSZ substrate); this assembly was then placed onto a supporting Al₂O₃ plate and set in the center of the tube. The tube was sealed at both ends and one end had a quartz window for optical observations. The entire tube was rotated along the longitudinal axis to ensure that wetting substrate is horizontal. Prior to the test, the tube was vacuumed with a roughing pump three times with three purges of pure Ar gas (99.999% purity) to establish a controlled atmosphere inside.

For the wetting measurements, the samples were heated at 5K/min to a maximum of 1100 °C and hold for ~10 minutes before cooling back to room temperature at 20K/min. During the process, an Ar gas flow at 20 sccm was maintained throughout the experiments. During heating of the sample, a camera was placed in front of the quartz window to record the sample-substrate wetting interaction. Images were recorded every 10~20s as the sample approached the solidus temperature. Wetting angles of different candidate alloys on various substrates were extracted from the recorded images.

Various substrates were tested including YSZ|NiO-YSZ, Al₂O₃-SS441, Pure Cu, Pure Ni and Al₂O₃ substrates. The YSZ|NiO-YSZ substrate was provided by Delphi, and it is used as the anode-supported electrolyte part in their SOFC device. This YSZ|NiO-YSZ substrate is a tri-layer substrate consisting of a dense, ~15 μ m thick YSZ electrolyte, a ~15 μ m thick NiO-YSZ function layer and a ~500 μ m thick porous NiO-YSZ layer. The Al₂O₃-SS441 substrate

(provided by Delphi) was a 441 stainless steel (AK Steel) piece coated with \sim 5 µm of Al₂O₃ through PVD.

For some wetting experiments, pre-treated substrates were used. Some of the substrates were coated with 15 nm or 500 nm of titanium or copper through physical vapor deposition (PVD) by an Axiss PVD system (Kurt Lesker) in the Electrical and Computer Engineering Research Cleanroom at Michigan State University.



Figure 2.4 Schematic of the wetting furnace set-up.

2.2.5 Multilayer Brazing Experiments

Figure 2.5 shows a schematic diagram of different materials used in the multilayer braze. The two substrates to be joined were Al₂O₃-SS441 and YSZ|NiO-YSZ. The braze material used in this figure was a home-made Ni10Si1B piece (~50 mg), and droplets of a commercial flux (HANDY FLUX HI-TEMP® Boron modified, Lucas-Milhaupt, Inc.) were applied on the top and bottom sides of the alloy piece to enhance wetting and bonding characteristics. Nickel foils with a thickness of 0.25 mm was used as the middle layer. Copper foils with a thickness of both 0.13 mm and 0.025 mm were used to wetting and bond to the YSZ|NiO-YSZ substrate. In some cases, only the nickel foil, copper foil, and the YSZ|NiO-YSZ substrate assembly were tested to optimize the thickness of the copper foil to be used.

The brazing process was performed in the same tube furnace used in wetting experiments. The multilayer assembly was placed onto an Al₂O₃ supporting plate and set in the center of the tube furnace. Prior to heating, the tube was vacuumed with a roughing pump three times with three purges of pure Ar gas (99.999% purity) to set a controlled atmosphere inside. Then the assembly was heated to 1100 °C at 5K/min to hold for 30 minutes up to 4 hours before cooling back to room temperature also at 5K/min.

Oxidation tests were also performed on some of the samples by placing the joined samples in a static air furnace at 750 °C for up to 2 days.



Figure 2.5 Schematic showing the multilayer brazing assembly before joining.

2.2.6 Scanning Electron Microscopy

To reduce the charging effects during SEM imaging, two methods were used for the nonconductive samples, including all of the epoxy mounted samples, and samples (especially brazed joint samples) with ceramic components. In most of the cases, these samples were covered by conducting copper tapes on all the sides other than the top surface containing the area of interest. Then this top surface was platinum sputter coated at 30 mA for 30 seconds using a Desk II Sputter Coater (Denton Vacuum, LLC) to obtain electronic conductivity on the surface. In other cases, the samples were platinum coated with the same process repeated multiple times on all the sides to ensure conductivity on the sample surface.

Two SEMs equipped with energy dispersive X-ray spectroscopy (EDS) analysis systems were used. Most of the work in this dissertation was performed using a MIRA3 field emission SEM (Tescan, Inc.) in the Composite Materials and Structures Center (CMSC) at Michigan State University. Both secondary and backscatter electron imaging were available with this microscope and output images with 1024×1024 and 2048×2048 resolutions were obtained for analysis. For most analyses, the accelerating voltage was set to either 20kV or 30kV, and the working distance was ~16mm for energy dispersive x-ray spectroscopy (EDS) analysis and ~8-10 for imaging. For the EDS analysis, point, line, and sometimes mapping scans were performed to identify compositional characteristics on the samples. Some SEM and EDS analysis were performed with an EVO LS25 SEM (Zeiss, GmbH) located in the same laboratory at CMSC. This SEM is equipped with the same EDS detector and software, and similar imaging/EDS conditions were used.

2.3 Computational Search for Candidate Alloys

The computational work was done in Dr. Yu Qi's research group by Dr. Tridip Das and Mr. Young Kim. This section summarizes their work to facilitate the discussion on other results in this chapter.

2.3.1 Element Selection for Computational Search

Element selection is the first consideration for alloy design, because the number of candidate elements needs to be reduced to limit the required calculations. Obviously, all the elements in the periodic table could be used, so the next step was to reduce the selection with other considerations like radioactivity, toxicity, material cost etc.

Table 2.1 summaries the elements eliminated from the computational search and their respective reasoning. Initially, 25 elements were selected based on these criteria (B, C, Mg, Al, Si, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Y, Zr, Nb, Mo, Ag, In, Sn, Hf, Ta, W). Then, additional elements were added to search for binary base alloys that could later be dope with minor additions (such as B, C, etc.) to fine tune their melting ranges, wetting and bonding characteristics, etc. Thus, the list of allowed base elements were further expanded to 37 (Mg, Al, Si, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Y, Zr, Nb, Mo, Ag, In, Sn, Sb, I, La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, Yb, Hf, Ta, W, Bi). Again, this new list is still based on avoiding radioactivity, high cost, toxicity and the ability of the element to make-up a significant portion of the braze.

The above element selection is intended for the braze base, minor addition of other elements is not limited to these 13 elements. Minor addition of Si and B can suppress the melting point of nickel/cobalt based braze filler metals [11]. Cu and Ti can be added to improve

the wetting and bonding between the filler material and the YSZ substrate [6, 14, 35, 37, 38, 42-

46]. There are also surface oxide scale considerations when a passivating layer is needed, which

will require proper amounts of Cr and Al additions.

Elements Eliminated	Considerations
Noble gases (He, Ne, Ar etc.)	Hardly any bonding with metals to form alloys. Also, the gaseous materials are not practical in alloy fabrication.
Pm (Z:61), Po and higher atomic number elements (Z>83)	Braze should not be radioactive.
Alkali metals, Halogens and Chalcogens	Reactive with air and water, hard to mix with metal, form brittle phases.
Bi and Lanthanide group	Braze should not have good conductivity for oxygen and hydrogen ions.
Alkaline earth metals and semiconducting elements	Braze should not have high vapor pressure (≥ 0.1 Torr) at 750 °C.
Cd, Pb, Tl	Elements should not be toxic.
e, Pd, Ru, Pt, Au, Os, Ir, Sc and Rh	Elements should not to too expensive.

Table 2.1 Elements dropped from the periodic table for the computational search and considerations.

2.3.2 Phase Diagram Calculation and Candidate Selection

Once candidate elements were determined, an automated phase diagram calculation using

Thermo-Calc^{® TM} was performed to seek compositions ranges of interest among the binary or

ternary systems. Using the Solidus requirement from Table 1.2, phase diagrams of 900 °C and 1000 °C isothermal sections were generated to search for target composition regions.

One example of the Ni-Ta-Mn system is shown in Figure 2.6. The blue region in both isothermal sections is the liquid zone at 1000 °C (top) and 900 °C (bottom); white regions with irregular shapes are solid solution phases; regions with green "tie lines" are two phase regions, which have the two phases at the two ends of the green tie line at the calculated temperature; white triangular regions contain the three phases defined by the three corners of the triangles. The blue outline in the 900 °C isothermal section (bottom) is the overlaid liquid zone from the 1000 °C isothermal section (top). A target composition can be found within the blue outline where no liquid is present. The black cross in Figure 2.6 represents a possible candidate composition, which is liquid at 1000 °C and solidifies into a solid solution phase as it cools down to 900 °C.



Figure 2.6 Isothermal sections of calculated Ni-Ta-Mn ternary phase diagram at 1000 $^{\circ}$ C (top and 900 $^{\circ}$ C (bottom), generated by Thermo-Calc[®].

Using this approach, a search was performed within the different ternary combinations of the selected elements. Alloys systems with possible braze candidates were calculated and selected. Due to the vast amount of data generated in this search, only the promising systems of the nickel-based, cobalt-based, and copper-based ternary alloy systems are show here in Figure 2.7, 2.8, and 2.9, respectively.

In these figures, a white background means there is insufficient data for such element combination in the system; a blue background means the compositions of a liquid phase at 1000 °C remains as a liquid or solid+liquid phase below 900 °C in the alloy system; a red background indicates no liquid phase is present in the alloy system below 1000 °C; and a green background means that there exists some specific composition zone that mostly solidifies from a liquid phase when cooling from 1000 °C down to 900 °C (like the possible candidate shown in Figure 2.6).



Figure 2.7 Nickel-based ternary alloy systems of potential interest for SOFC braze applications.

Co	В	С	Mg	Al	Si	V	Cr	Mn	Fe	Ni	Cu	Zn	Ga	Nb	Mo	In	Sn	Та	W	Ti	Y	Zr	Hf	Ag
В																								
С	Co-B-C																							
Mg	Co-B-Mg	g Co-C-Mg		-																				
Al	Co-B-Al	Co-C-Al	Co-Mg-Al																					
Si	Co-B-Si	Co-C-Si	Co-Mg-Si	Co-Al-Si		\sim																		
V	Co-B-V	Co-C-V	Co-Mg-V	Co-Al-V	Co-Si-V																			
Cr	Co-B-Cr	Co-C-Cr	Co-Mg-Cr	Co-Al-Cr	Co-Si-Cr	Co-V-Cr																		
Mn	Co-B-Mn	Co-C-Mn	Co-Mg-Mi	Co-Al-Mn	Co-Si-Mn	Co-V-Mn	Co-Cr-Mn																	
Fe	Co-B-Fe	Co-C-Fe	Co-Mg-Fe	Co-Al-Fe	Co-Si-Fe	Co-V-Fe	Co-Cr-Fe	Co-Mn-Fe																
Ni	Co-B-Ni	Co-C-Ni	Co-Mg-Ni	Co-Al-Ni	Co-Si-Ni	Co-V-Ni	Co-Cr-Ni	Co-Mn-Ni	Co-Fe-Ni															
Cu	Co-B-Cu	Co-C-Cu	Co-Mg-Cu	Co-Al-Cu	Co-Si-Cu	Co-V-Cu	Co-Cr-Cu	Co-Mn-Cu	Co-Fe-Cu	Co-Ni-Cu		~												
Zn	Co-B-Zn	Co-C-Zn	Co-Mg-Zn	Co-Al-Zn	Co-Si-Zn	Co-V-Zn	Co-Cr-Zn	Co-Mn-Zn	Co-Fe-Zn	Co-Ni-Zn	Co-Cu-Zn													
Ga	Co-B-Ga	Co-C-Ga	Co-Mg-Ga	Co-Al-Ga	Co-Si-Ga	Co-V-Ga	Co-Cr-Ga	Co-Mn-Ga	Co-Fe-Ga	ı Co-Ni-Ga	Co-Cu-Ga	Co-Zn-Ga												
Nb	Co-B-Nb	Co-C-Nb	Co-Mg-Nb	Co-Al-Nb	Co-Si-Nb	Co-V-Nb	Co-Cr-Nb	Co-Mn-Nb	Co-Fe-Nt	Co-Ni-Nb	Co-Cu-Ni	Co-Zn-Nb	Co-Ga-Nb		~									
Mo	Co-B-Mo	Co-C-Mo	Co-Mg-Me	Co-Al-Mo	Co-Si-Mo	Co-V-Mo	Co-Cr-Mo	Co-Mn-Mo	Co-Fe-Mo	Co-Ni-Mo	Co-Cu-M	Co-Zn-Mo	Co-Ga-Mo	Co-Nb-Mo										
In	Co-B-In	Co-C-In	Co-Mg-In	Co-Al-In	Co-Si-In	Co-V-In	Co-Cr-In	Co-Mn-In	Co-Fe-In	Co-Ni-In	Co-Cu-In	Co-Zn-In	Co-Ga-In	Co-Nb-In	Co-Mo-In									
Sn	Co-B-Sn	Co-C-Sn	Co-Mg-Sn	Co-Al-Sn	Co-Si-Sn	Co-V-Sn	Co-Cr-Sn	Co-Mn-Sn	Co-Fe-Sn	Co-Ni-Sn	Co-Cu-Sn	Co-Zn-Sn	Co-Ga-Sn	Co-Nb-Sn	Co-Mo-Sn	Co-In-Sn								
Та	Со-В-Та	Co-C-Ta	Co-Mg-Ta	Co-Al-Ta	Co-Si-Ta	Co-V-Ta	Co-Cr-Ta	Co-Mn-Ta	Co-Fe-Ta	Co-Ni-Ta	Co-Cu-Ta	Co-Zn-Ta	Co-Ga-Ta	Co-Nb-Ta	Co-Mo-Ta	Co-In-Ta	Co-Sn-Ta		-					
W	Co-B-W	Co-C-W	Co-Mg-W	Co-Al-W	Co-Si-W	Co-V-W	Co-Cr-W	Co-Mn-W	Co-Fe-W	Co-Ni-W	Co-Cu-W	Co-Zn-W	Co-Ga-W	Co-Nb-W	Co-Mo-W	Co-In-W	Co-Sn-W	Co-Ta-W						
Ti	Co-B-Ti	Co-C-Ti	Co-Mg-Ti	Co-Al-Ti	Co-Si-Ti	Co-V-Ti	Co-Cr-Ti	Co-Mn-Ti	Co-Fe-Ti	Co-Ni-Ti	Co-Cu-Ti	Co-Zn-Ti	Co-Ga-Ti	Co-Nb-Ti	Co-Mo-Ti	Co-In-Ti	Co-Sn-Ti	Co-Ta-Ti	Co-W-Ti	\geq				
Y	Co-B-Y	Co-C-Y	Co-Mg-Y	Co-Al-Y	Co-Si-Y	Co-V-Y	Co-Cr-Y	Co-Mn-Y	Co-Fe-Y	Co-Ni-Y	Co-Cu-Y	Co-Zn-Y	Co-Ga-Y	Co-Nb-Y	Co-Mo-Y	Co-In-Y	Co-Sn-Y	Co-Ta-Y	Co-W-Y	Co-Ti-Y		-		
Zr	Co-B-Zr	Co-C-Zr	Co-Mg-Zr	Co-Al-Zr	Co-Si-Zr	Co-V-Zr	Co-Cr-Zr	Co-Mn-Zr	Co-Fe-Zr	Co-Ni-Zr	Co-Cu-Zr	Co-Zn-Zr	Co-Ga-Zr	Co-Nb-Zr	Co-Mo-Zr	Co-In-Zr	Co-Sn-Zr	Co-Ta-Zr	Co-W-Zr	Co-Ti-Zr	Co-Y-Zr	\geq	_	
Hf	Co-B-Hf	Co-C-Hf	Co-Mg-Hf	Co-Al-Hf	Co-Si-Hf	Co-V-Hf	Co-Cr-Hf	Co-Mn-Hf	Co-Fe-Hf	Co-Ni-Hf	Co-Cu-Hf	Co-Zn-Hf	Co-Ga-Hf	Co-Nb-Hf	Co-Mo-Hf	Co-In-Hf	Co-Sn-Hf	Co-Ta-Hf	Co-W-Hf	Co-Ti-Hf	Co-Y-Hf	Co-Zr-Hf		
Ag	Co-B-Ag	Co-C-Ag	Co-Mg-Ag	Co-Al-Ag	Co-Si-Ag	Co-V-Ag	Co-Cr-Ag	Co-Mn-Ag	Co-Fe-Ag	g <mark>Co-Ni-Ag</mark>	Co-Cu-Ag	Co-Zn-Ag	Co-Ga-Ag	Co-Nb-Ag	Co-Mo-Ag	Co-In-Ag	Co-Sn-Ag	Co-Ta-Ag	Co-W-Ag	Co-Ti-Ag	Co-Y-Ag	Co-Zr-Ag	Co-Hf-Ag	
	No liquid	l phase pres	ent in the pl	ase diagra	m below 1	000 °C																		
	There exi	ists some sp	ecific comp	osition zor	ne, which c	ompletely s	olidifies fro	m liquid pl	hase, betwe	een tempera	ature windo	w of 900 ar	nd 1000 °C											
	The comp	position of l	liquid zone a	t 1000 °C,	, remains li	quid or sol	id+liquid be	low 900 °C	2															
	Not avail	lable in data	ibase																					

Figure 2.8 Cobalt-based ternary alloy systems of potential interest for SOFC braze applications.

Cu	В	С	Mg	Al	Si	V	Cr	Mn	Fe	Co	Ni	Zn	Nb	Mo	In	Sn	Та	Ti	Zr	Ag
В																				
С	Cu-B-C																			
Mg	Cu-B-Mg	Cu-C-Mg																		
Al	Cu-B-Al	Cu-C-Al	Cu-Mg-Al																	
Si	Cu-B-Si	Cu-C-Si	Cu-Mg-Si	Cu-Al-Si																
V	Cu-B-V	Cu-C-V	Cu-Mg-V	Cu-Al-V	Cu-Si-V															
Cr	Cu-B-Cr	Cu-C-Cr	Cu-Mg-Cr	Cu-Al-Cr	Cu-Si-Cr	Cu-V-Cr														
Mn	Cu-B-Mn	Cu-C-Mn	Cu-Mg-Mn	Cu-Al-Mn	Cu-Si-Mn	Cu-V-Mn	Cu-Cr-Mn													
Fe	Cu-B-Fe	Cu-C-Fe	Cu-Mg-Fe	Cu-Al-Fe	Cu-Si-Fe	Cu-V-Fe	Cu-Cr-Fe	Cu-Mn-Fe												
Co	Cu-B-Co	Cu-C-Co	Cu-Mg-Co	Cu-Al-Co	Cu-Si-Co	Cu-V-Co	Cu-Cr-Co	Cu-Mn-Co	Cu-Fe-Co		_									
Ni	Cu-B-Ni	Cu-C-Ni	Cu-Mg-Ni	Cu-Al-Ni	Cu-Si-Ni	Cu-V-Ni	Cu-Cr-Ni	Cu-Mn-Ni	Cu-Fe-Ni	Cu-Co-Ni	\sim	_								
Zn	Cu-B-Zn	Cu-C-Zn	Cu-Mg-Zn	Cu-Al-Zn	Cu-Si-Zn	Cu-V-Zn	Cu-Cr-Zn	Cu-Mn-Zn	Cu-Fe-Zn	Cu-Co-Zn	Cu-Ni-Zn		_							
Nb	Cu-B-Nb	Cu-C-Nb	Cu-Mg-Nb	Cu-Al-Nb	Cu-Si-Nb	Cu-V-Nb	Cu-Cr-Nb	Cu-Mn-Nb	Cu-Fe-Nb	Cu-Co-Nb	Cu-Ni-Nb	Cu-Zn-Nb								
Mo	Cu-B-Mo	Cu-C-Mo	Cu-Mg-Mo	Cu-Al-Mo	Cu-Si-Mo	Cu-V-Mo	Cu-Cr-Mo	Cu-Mn-Mo	Cu-Fe-Mo	Cu-Co-Mo	Cu-Ni-Mo	Cu-Zn-Mo	Cu-Nb-Mo							
In	Cu-B-In	Cu-C-In	Cu-Mg-In	Cu-Al-In	Cu-Si-In	Cu-V-In	Cu-Cr-In	Cu-Mn-In	Cu-Fe-In	Cu-Co-In	Cu-Ni-In	Cu-Zn-In	Cu-Nb-In	Cu-Mo-In		_				
Sn	Cu-B-Sn	Cu-C-Sn	Cu-Mg-Sn	Cu-Al-Sn	Cu-Si-Sn	Cu-V-Sn	Cu-Cr-Sn	Cu-Mn-Sn	Cu-Fe-Sn	Cu-Co-Sn	Cu-Ni-Sn	Cu-Zn-Sn	Cu-Nb-Sn	Cu-Mo-Sn	Cu-In-Sn		_			
Та	Cu-B-Ta	Cu-C-Ta	Cu-Mg-Ta	Cu-Al-Ta	Cu-Si-Ta	Cu-V-Ta	Cu-Cr-Ta	Cu-Mn-Ta	Cu-Fe-Ta	Cu-Co-Ta	Cu-Ni-Ta	Cu-Zn-Ta	Cu-Nb-Ta	Cu-Mo-Ta	Cu-In-Ta	Cu-Sn-Ta		-		
Ti	Cu-B-Ti	Cu-C-Ti	Cu-Mg-Ti	Cu-Al-Ti	Cu-Si-Ti	Cu-V-Ti	Cu-Cr-Ti	Cu-Mn-Ti	Cu-Fe-Ti	Cu-Co-Ti	Cu-Ni-Ti	Cu-Zn-Ti	Cu-Nb-Ti	Cu-Mo-Ti	Cu-In-Ti	Cu-Sn-Ti	Cu-Ta-Ti		_	
Zr	Cu-B-Zr	Cu-C-Zr	Cu-Mg-Zr	Cu-Al-Zr	Cu-Si-Zr	Cu-V-Zr	Cu-Cr-Zr	Cu-Mn-Zr	Cu-Fe-Zr	Cu-Co-Zr	Cu-Ni-Zr	Cu-Zn-Zr	Cu-Nb-Zr	Cu-Mo-Zr	Cu-In-Zr	Cu-Sn-Zr	Cu-Ta-Zr	Cu-Ti-Zr		
Ag	Cu-B-Ag	Cu-C-Ag	Cu-Mg-Ag	Cu-Al-Ag	Cu-Si-Ag	Cu-V-Ag	Cu-Cr-Ag	Cu-Mn-Ag	Cu-Fe-Ag	Cu-Co-Ag	Cu-Ni-Ag	Cu-Zn-Ag	Cu-Nb-Ag	Cu-Mo-Ag	Cu-In-Ag	Cu-Sn-Ag	Cu-Ta-Ag	Cu-Ti-Ag	Cu-Zr-Ag	
	No liquid	phase prese	ent in the pha	ase diagram	below 100	00 °C														
	There exis	ts some spe	ecific compo	osition zone	, which cor	npletely so	lidifies fro	m liquid pha	ase, betwee	n temperatu	are window	of 900 and	l 1000 °C							
	The compo	osition of li	quid zone at	t 1000 °C, r	emains liqu	uid or solic	l+liquid be	low 900 °C												
	Not availa	ble in datab	base																	

Figure 2.9 Copper-based ternary alloy systems of potential interest for SOFC braze applications.
2.4 Candidate Braze Alloys

Candidate braze compositions were selected from the "green" boxes from Figures 2.7-2.9, and physical samples were made for further analysis according to section 2.2.1. During physical sample fabrications, some of the candidate alloys were excluded based on their experimental observations. In most cases, samples with high volatility, low oxidation-resistance, and low ductility would be excluded from the candidate list.

Table 2.2 shows preliminary ductility, oxidation resistance, and melting ranges of some selected candidate alloys, with a green color indicating favorable properties, an orange color indicating properties that need to be further adjusted, and a red color indicating unfavorable properties. The names of the samples were made according to their compositions, i.e. alloy Ni43.5Mn14.8Nb means the base metal is nickel and the alloy contains 43.5 wt.% of manganese and 14.8 wt.% of niobium. Preliminary oxidation resistance was semi-qualitatively determined by the method describe in section 2.2.3. Details on the TGA and DSC analysis will be discussed in the next two sections.

Alloy Composition	Ductility	48 hr 750 °C Oxidation Resistance in Air	Solidus Temperat ure @ 5k/min, °C	Liquidus Temperat ure,°C	Comments
Ni43.5Mn14.8Nb	Sufficient	Poor			
Ni48.5Mn14.6Mo	Sufficient	Poor	Poor		
Ni50Mn5Si	Insufficient	Poor			
Ni36.9Mn11Si	Insufficient				
Ni52.2Mn10.9Ta	Sufficient	Poor			
Ni26.0Mn22.4Si	Insufficient				
Ni4.5Si7.0Cr3.1B 3.0Fe (Commercial BNi2 Containing Iron)	Sufficient	Excellent	Excellent (970.0)	Excellent (1000.0)	Promising Braze if Cr Volatilization Can be Managed
Ni5Si2Cr60Al	Insufficient				
Ni5Si20Ta	Sufficient	Poor	Too High (1132.0)	Too High (1138.0)	
Ni7Si20Ta	Sufficient	Good	Too High (1124.8)	Too High (1139.1)	
Ni7Si20Ta1B	Sufficient	Good	Good (1035.9)	Good (1068.0)	Solidus/Liquid us may be workable.
Ni7Si20Ta3B	Insufficient	Good	Good (1051.0)	Good (1086.8)	Needs improvement in ductility
Ni10Si20Ta	Insufficient	Excellent	Too High (1144.0)	Too High (1162.9)	

Table 2.2 Ductility, oxidation resistance, and melting temperatures for a variety of nickel-based, cobalt-based and copper-based candidate braze alloys.

Table 2.2 (cont'd)

Ni7Si32Ta1B	Sufficient	Good	Good (1041.2)	Good (1070.1)	Wetting on alumina and zirconia is inherently poor
Ni7Si32Ta	Sufficient	Marginal	Too High (1122.7)	Too High (1146.1)	
Ni7Si25Ta	Sufficient		Too High (1127.4)	Too High (1137.9)	
Ni7Si10Ta	Sufficient		Too High (1124.6)	Too High (1140.3)	Solid solution
Ni71.5Ti	Sufficient	Extremely Poor	· · · · · · · · · · · · · · · · · · ·	· · · · · · · · ·	
Ni41Ti17Nb2Al	Marginal	Fair			
Ni41Ti17Nb3Al	Marginal	Poor			
Ni41Ti17Nb5Al	Sufficient	Fair			
Ni42.5Zr2Al3.5Si	Sufficient	Poor			
Ni9Zr11Nb4Si	Sufficient	Poor			
Ni35Zr13.3Y	Sufficient	Extremely Poor			
Ti15Ni15Fe	Marginal	Poor	Good (1020.4)	Good (1037.7)	Excellent Wetting on Pure Al ₂ O ₃
Ti32Ni8Cr	Marginal	Poor	Good (1013.3)	Good (1025.1)	Excellent Wetting on Pure Al ₂ O ₃
Ni17Zr5.5Al	Marginal	Poor	Too High (1187.4)	Too High (1221.4.4)	

Table 2.2 (cont'd)

Ni15Zr3.5Si2Al	Marginal	Poor	Good (1060.4)	Good (1066.2)	Sample reacted with crucible during DSC measurement
Ni30In5Zn	Sufficient	Good	Good (917.1)	Good (923.1)	Zn/In will vaporize at high temperature
Ni41.4In (eutectic)	Insufficient	Good	Good (916.0)	Good (926.2)	In vaporize at high temperature. Does not wet pure Al ₂ O ₃
Al15Ni15Ti6Si4C r	Poor				
Ti41Ni18Nb	Sufficient	Poor			
Ag10Cr					Ag and Cr are hard to mix
Ag20Cr					during arc melting
Ni10Ta7Si1B	Sufficient	Excellent	Good (1037.6)	Good (1074.3)	-
Ni10Si	Sufficient	Excellent	Too High (1214.7)	Too High (1222.5)	
Ni10Si1B	Sufficient	Excellent	Good (1001.4)	Good (1032.8)	
Ni7Ta2Si	Sufficient	Poor			
Ni20Cu10Si		Excellent			
Cu1.5Cr	Excellent		Good (1073.3)	Good (1085.9)	
Cu5Si	Excellent		Good (956.3)	Good (974.0)	
Cu9A1	Excellent	Good	Good (1034.1)	Good (1047.5)	
Ni6Co5Si	Excellent	Good	Too High (>1300)	Too High (>1300)	

The suitable oxidation, mechanical, and melting temperatures of the Ni-Si and Cu-Al brazes shown in Table 2.2 comes as little surprise because Ni-Si and Cu-Al serve as the basis, respectively, of the BNi and Cu-ABA families of commercially available brazes. In fact, commercially available BNi and Cu-ABA brazes have been used to successfully braze yttria stabilized zirconia and stainless steel [80, 81]. Unfortunately, literature studies have shown that brazing with these alloys must be performed in oxygen partial pressures less than $\sim 10^{-11}$ (achieved through vacuum brazing, brazing in hydrogen gas mixtures, etc) to ensure that either active elements (such as Ti in the case of Cu-ABA) [80] or the brazes themselves (in the case of the BNi brazes) [81] do not prematurely oxidize and hence are able to bond to/react with the yttria-stabilized zirconia (YSZ) at brazing temperatures. This low pO₂ is problematic because pO₂ levels less than $\sim 10^{-6}$ cause the decomposition and mechano-chemically induced break-up of high performance SOFC cathode materials such as lanthanum strontium cobalt iron oxide (LSCF) [32, 33]. Approaches to prevent the premature oxidation of active elements (such as Ti and Zr) so that active element brazing to YSZ in air can be achieved have included using expensive physical vapor deposition (PVD) techniques to bury them under protective layers at room temperature [82] and presumably using flux to locally lower the oxygen partial pressure at the brazing location. These approaches will be further discussed in section 3.7.

2.5 Melting Ranges of Candidate Alloys

Figure 2.10 shows an example set of DSC data from a Ni20Ta7Si sample for determining its solidus and liquidus temperature at a heating rate of 5K/min in Ar atmosphere. The sample temperature profile is indicated by the red dotted line associated with the right vertical axis. The blue curve shows the corrected DSC signal from the sample associated with the left axis. A peak (pointing up, endothermic) in the DSC data was observed at around 280 minutes during heating of the sample. This is correlated with a melting event of the tested sample and the onset of this peak indicates the 1122.9 °C solidus temperature of the sample. During cooling, another DSC peak (pointing down, exothermic) was observed at around 350 minutes. This peak is showing the solidification process of the tested sample and the onset of the peak indicates that the liquidus temperature of the Ni20Ta7Si sample is 1163.1 °C. It should be noted that a cooling rate of 5K/min was used for the DSC measurements, so that the measured liquidus temperature would contain some undercooling of the samples for this cooling rate in Ar atmosphere.



Figure 2.10 Example DSC data of a Ni20Ta7Si sample.

Melting ranges of the candidate samples were measured in the same way and the obtained solidus and liquidus temperatures are presented in Table 3.2. Interestingly, it was a surprise that tantalum, with a melting point of 3020 °C, could be used as a Ni-Si alloy melting point depressant (lowering the 1214 °C liquidus of Ni10Si by ~60 °C).

2.5.1 Discrepancies between Predicted and Experimental Melting Ranges

The DSC measurements also provide an opportunity to validate the computational predictions of the candidate melting ranges. Table 2.3 shows a comparison of DSC measured melting ranges of some nickel-based braze candidates with the Thermo-Calc[®] predictions. In

general, computational predictions can be off for either the solidus temperature or the liquidus temperature by up to ~150 °C. However, even though the computational values are not highly accurate, they still lead to possible candidates among all the element combinations. The predicted values also correctly indicated the effect of tantalum in some of the nickel-based systems.

To better utilize the computational power of efficiently screening though hundreds of element combinations, while still taking the accuracy of predictions into consideration, searching criteria were "loosened" to avoid missing potential candidates, i.e. the upper bound and lower bond for the melting range was adjusted to 1100 °C and 800 °C, respectively, in some cases.

Sampla	DSC Mea	sured (°C)	Thermo-Calc [®] Predicted (°C)		
Sample —	Solidus	Liquidus	Solidus	Liquidus	
BNi2* (commercial)	970**	1000**	1019	1290	
Ni20Ta5Si	1134.8	1134.7	1028	1190	
Ni20Ta7Si	1122.9	1163.1	1027	1067	
Ni20Ta10Si	1124.1	1144	883	1132	
Ni17Zr5.5Al	1207.4	1187.4	1137	1187	
Ni42.5Zr3.5Si2Al	1060.6	NA	916	1144	
Ni32Ta7Si1B	1059.3	1070.1	NA	NA	
* Composition of BNi2: Ni-7Cr-4.5Si-3.1B-3Fe					
** Data provided by supplier					

Table 2.3 Comparison of the DSC measured and Thermo-Calc predicted melting ranges of some selected nickel-based alloys.

2.6 Oxidation Behavior of Top Candidate Alloys

The 5 day TGA tests to characterize oxidation properties were quite costly, so only the most promising candidates from Table 2.2 were tested. Figure 2.11 shows the TGA data on the selected samples. It should be noted that the gravimetric data of all the samples only shows changes during the 750 °C holding for 5 days, the weight changes of the samples during heating are not shown on the plots in Figure 2.11. The data were also processed such that the vertical axis indicates the weight changes per sample surface area, which made the data from different samples comparable to each other. These results show that a variety of Ni-Si based brazes (Ni20Cu10Si, Ni20Ta7Si1B, Ni10Si1B, etc.) possess oxidation resistances similar to commercially available BNi2, but do not contain the Cr known to poison LSM, LSCF and other SOFC cathode materials [83]. In particular, the Ni10Si and Ni10Si1B sample showed even superior oxidation resistance compare to that of the commercial BNi2 sample. Also, when the Ni10Si1B sample was pre-oxidized in air at 750 °C for 800 minutes prior to the TGA measurements, and it still showed good oxidation resistance.



Figure 2.11 Sample surface area normalized TGA data for different sample tested at 750 °C in flowing air. Note that the Ni10Si1B sample was pre-oxidized in air at 750 °C for 800 minutes prior to the TGA assessment.

Using the data from Figure 2.11, the TGA curves can also be fitted using the parabolic oxidation model, from which the parabolic oxidation rate constant can be determined for the specific testing temperature. Figure 2.12 plots the parabolic oxidation rate constants from the Ni20Ta7Si1B samples together other common metals and alloys from the literature [84-86]. It is apparent that the samples showed good oxidation resistance also have extremely low parabolic oxidation rate constants in the first few days of high temperature exposure in air.



Figure 2.12 The parabolic oxidation rate constants of various metals and alloys. Plotted with data from references [84-86].

2.7 Wetting Properties of Top Candidate Alloys

Figure 2.13a shows an example image recorded during the wetting measurements, and the testing set-up can be observed as well. Figure 2.13b shows how the wetting angles were measured. Basically, the molten sample contour in the images were fitted with a part of a circle. Then its tangent line at the liquid-solid-gas tri-phase contact region is determined, which was later digitized to calculate the wetting angle θ as previously defined in Figure 2.4.



Figure 2.13 (a) An example image showing a recorded image of the wetting measurements; (b) a zoomed-in view of the sample|substrate interface, as well as the determination if the wetting angles.

Using this method wetting angles of three selected samples on various substrates were measured. Figure 2.14 shows the wetting angle measured from the commercial BNi2 sample, the Ni20Ta7Si1B sample, and the Ni20Ta7Si3B sample on different substrates. It should be noted that sometimes the sample formed a 'crust' layer of SiO₂ (or maybe some boron oxide as well) on the molten metal surface. This layer was not considered in the wetting angle measurements.

The wetting angle for commercial BNi2 on YSZ measured here, 129°, matched with the literature reported value of ~126° [87]. Unfortunately, none of the tested alloys wetted or bonded to Al₂O₃-SS441 or YSZ. As evidenced by the Figure 2.14 wetting shapes and post-measurement SEM-EDS analysis, SiO₂ leeched out and affected the wetting of the BNi2, Na20Ta7Si1B, and Na20Ta7Si3B on many bare and metalized substrates. Also, some compositions either did not melt, or retained their shape due to surface oxides that formed a mechanically supporting structure. It can be concluded that the tested alloys had difficulty wetting and bonding to various metals and metallized ceramic substrates.



Figure 2.14 Alloy wetting on various bare and metal PVD coated substrates at ~1080 $^{\circ}$ C in air. Solidified alloys that could not be pried off the substrate after the wetting tests are indicated by green dots.

To improve the wetting properties, other metallization schemes, fluxing agents, brazing atmospheres, and brazing temperatures were explored. Figure 2.15 shows another set of wetting experiments conducted with nickel-based alloys and flux on the Al₂O₃-SS441 substrate and pure copper with and without flux additions on the YSZ|NiO-YSZ substrates. Compare to the results in Figure 2.14, it can be concluded that the addition of flux can significantly improve the wetting behavior of Ni20Ta7Si3B and Ni10Si1B on the alumina coated SS441 substrate. The flux composition is confidential; however, it is very likely that the boron containing flux lowered the local partial pressure of oxygen and/or dissolved some of the surface oxides form the alloy (such as SiO₂) during the wetting and spreading process. Unfortunately, the flux was shown to embrittle the YSZ|NiO-YSZ substrate, so that its application at the YSZ interface is unacceptable

As shown in Figure 2.15, pure copper was found to have a relatively good wetting characteristics on the YSZ|NiO-YSZ substrates. The wetting sample also survived cross-sectioning and showed a dense, pore-free interface with YSZ.

These improvements on the Al₂O₃-SS441 and YSZ|NiO-YSZ substrate lead to the design of a multi-layer brazing process, which can separate the wetting problems on the two substrates into two parts.

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Figure 2.15 Before and after images of different wetting experiments done with flux on the Al_2O_3 -SS441 substrates, as well as wetting of pure copper on the YSZ|NiO-YSZ substrate with and without flux. The bottom two optical images show the surface after the Ni10Si1B+Flux wetting on the Al2O3-SS441 and the cross-sectioned copper on YSZ|NiO-YSZ wetting samples, respectively.

2.8 Multilayer Braze Design

A transient multilayer braze approach allowing the brazing of alumina coated 441 to YSZ|NiO-YSZ was investigated. As shown in Figure 2.5, this multilayer structure of aluminacoated 441 stainless steel, braze, with a foil that remains solid during the brazing process (currently Ni), a YSZ wetting/bonding layer that is molten at fabrication temperatures (presently copper), and YSZ|NiO-YSZ, separates the brazing problem into two separate parts: (1) bonding the copper foil to the YSZ NiO-YSZ, and (2) bonding the nickel foil to the Al_2O_3 -SS441). This allows different chemistries to be used to bond to the two substrates. Furthermore, this architecture allows YSZ brazing to occur in one atmosphere and Al₂O₃-SS441 brazing to occur in another atmosphere. For instance, brazing of the Ni foil to the alumina coated stainless steel could be conducted under low local pO₂ environments (since the YSZ-supported SOFC cathode materials will not be involved) and then the Al₂O₃-SS441|braze|Ni-foil could be bonded to YSZ in an inert atmosphere. Alternatively, as shown in Figure 2.15, the application of a commercial flux (HANDY FLUX HI-TEMP® Boron modified, Lucas-Milhaupt, Inc.) can also be used to braze Ni foil (and by extension most nickel-based super alloys) to the Al₂O₃-SS441substrate in Argon.

Figure 2.16 shows the backscattered electron (BSE) image of a cross-section from the multilayer brazed joint. The different layers of materials can still be observed from the EDS line scan results, and the braze region contains a Ni10Si-rich layer, a nickel-rich layer, and a copper-rich layer from the SS441 side to the YSZ side with interdiffusion occurred in-between.



Figure 2.16 (left) A BSE images showing the cross-section of a multilayer brazed joint and (right) EDS line scan data showing the atomic percentage of different elements along the red dotted line on the left.

Molten copper was used as the YSZ bonding agent that produces strong, reliable braze joints due to its suitable melting range and ability to wet/react with YSZ (as shown in Figure 2.15 and 2.16 as indicated in the literature [88, 89]). However, once heated in air, the volume changes associated with copper oxidation cause failure at the copper-YSZ interface.

Hence, an approach to use a transient YSZ wetting layer (copper foil) was explored so that after reacting and bonding with the YSZ, the copper would inter-diffuse with the nickel layer and produces a Ni-Si-Cu alloy with a higher oxidation resistance. In theory, any metal which (i) remains a molten metal (i.e. does not oxidize) at the braze temperatures and pO₂ combinations that will not harm the cathode materials and (ii) bonds with YSZ (such as Ag, Bi, etc.), could be used as a YSZ bond layer.

Figure 2.17 demonstrates that extended braze times produced partially homogenized Ni-Cu braze joints using thin copper foils with 25 μ m thickness, but due to the different diffusivities of Ni and Cu, Kirkendall voids developed which detached the braze joint from the YSZ [90].



Figure 2.17 (left) BSE images and (right) EDS line scan results of the 1/3/5 day homogenized Ni-Cu-YSZ|NiO-YSZ.

2.9 Summary

In this chapter, a combined simulation and experimental approach was used to design and test new, silver-free brazes for SOFC applications.

First, binary and ternary alloys with solidus temperatures equal to or greater than ~900 °C and liquidus temperatures equal to or less than ~1000 °C were identified through Thermo-Calc phase diagram calculations. All 828 of the ternary Ni-based, Co-based, and Cu-based alloy systems containing B, C, Mg, Al, Si, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Y, Zr, Nb, Mo, Ag, In, Sn, Hf, Ta, and/or W were analyzed by Thermo-Calc and 114 ternary alloy systems with the desired melting point characteristics were identified.

Selected candidate compositions were then physically fabricated and various material properties were characterized. Melting point measurements with DSC, oxidation resistance evaluation with TGA and mechanical property tests on alloys in 43 of these systems found Ni-Si, Cu-Cr, and Cu-Al alloys worthy of additional study. However, further in-situ wetting studies indicated that these alloys exhibited poor wetting on both bare and also surface pre-treated YSZ|NiO-YSZ and Al₂O₃-SS441 substrates in inert gas atmospheres.

In response to these wetting challenges, a novel multilayer braze architecture was developed and the production of a high strength Al₂O₃-SS441/braze/Ni-foil/Cu-foil/YSZ|NiO-YSZ braze joint was produced in inert atmosphere. Unfortunately, this braze joint did not survive service in air due to oxidation of the copper layer. Continued efforts were spent on (1) alterative multilayer braze joint layer compositions, and (2) through the use of YSZ bonding layers that bond with the YSZ and then become protected from subsequent oxidation in air by homogenizing with other braze layers. Copper fits both of these requirements in that it can bond to the YSZ surface and also can be homogenized into the nickel layer through inter-diffusion. However, due to the different diffusivity of copper and nickel, extensive Kirkendall voids formation was observed after prolonged homogenization, which led to easy detachment at the YSZ interface.

As a result, the search for a new, replacement, silver-free SOFC braze was not successful. The complexity of the requirements in Table 1.2 led to conflicting desired material properties. For example, for non-noble metal-based alloys, the integrity of the braze seal as well as criterion #8 requires an oxidation resistant alloy; but the surface passivation layer (an oxide scale that easily forms in inert atmospheres) will prevent the braze alloy from wetting and spreading on the YSZ|NiO-YSZ and Al₂O₃-SS441 substrates, which is criterion #3 and #4. To avoid this conflict, noble metal based brazing systems should be explored.

The most affordable noble metal brazing base material is silver. Currently the industry uses the state-of-the-art RAB (Ag-CuO) braze as SOFC sealants. However, the wetting of silver on the YSZ substrate needs to be improved, and also the addition of CuO causes problems like Type II pores that significantly shortens the lifetime of the RAB brazes.

Chapters 3-5 explore the possibilities of a CuO-free, silver-based braze with a newly invented silver nickel brazing method.

CHAPTER 3

Silver Nickel Brazing

3.1 Introduction

Successful SOFC operation requires separation of the fuel and oxidant. For SOFC designs with metal supports and/or sealing manifolds, this necessary hermetic seal can be made by brazing SS to the SOFC electrolyte, as shown schematically in Figure 1.3. Compared to competing technologies such as glass or mica seals, brazes offer higher joint strengths and lower joint permeabilities [6]. Unfortunately, brazes often have difficulty wetting ceramics such as YSZ [79]. To overcome this problem, the SOFC community has utilized flux-free, RAB where oxidizable metals are added into silver for improved ceramic wettability [39, 91, 92]. For instance, the addition of 4 wt.% Cu (which oxidizes to CuO during flux-free brazing in air) lowers the wetting angle of Ag on yttria-stabilized-zirconia (YSZ) from ~85° to 40° +/-5° in air [6, 45, 50, 93-99]. One of the benefits of the RAB technique, which has been used by various SOFC manufacturers such as Delphi [100] and General Electric [101], is that brazing can be performed in air so that the mechanical and electrochemical integrity of the mechano-chemically active oxygen exchange materials used in the cathode is maintained [102-104].

Unfortunately, conventional 96% Ag-4 wt.% Cu (denoted as Ag-4CuO) YSZ-SS braze joints suffer from several porosity generation mechanisms that limit their useful 750 °C lifetimes to ~10,000 hours [15], which is well below the ~40,000 hours often cited as necessary for commercially-viable stationary SOFC deployment [13]. First, as shown in Figure 1.4b, RAB braze joints often exhibit manufacturing defects (Type I pores) resulting from the relatively high ~45° wetting angle of Ag-4CuO on YSZ. Second, as shown in Figure 1.4a, during SOFC operation interface pores caused by anodic gas reduction of CuO (Type II pores) weaken the braze/SS and braze/YSZ interfaces over time, and provides a fast percolation path for H₂ invasion into the center of the joint [16, 49-51]. Third, as shown in Figure 1.4c, gaseous water pockets (Type III pores) form from hydrogen and oxygen that has migrated into the braze [13]. The kinetics of Type III pore formation is enabled by the moderately high, 750 °C hydrogen and oxygen ionic conductivity in silver (8×10⁻⁵ and 1.5×10⁻⁵ cm²·s, respectively [48]).

The hypothesis of the work reported in this chapter is that porous nickel interlayers, instead of reactive element additions, could be used to 1) promote Ag wetting on YSZ and 2) produce high-quality YSZ-stainless steel braze joints in inert atmospheres. This seemed possible for several reasons. First, although silver has a high ~1000 °C wetting angle of ~90° [105] on nickel in air (because NiO forms on the surface in air), this drops to $< 30^{\circ}$ for pO₂ $< 10^{-9}$ atm [106]. This reduced wetting angle should make Type I pores much less likely. Second, because spontaneous liquid infiltration into porous solid media occurs for wetting angles below 51° [107], brazing with a porous nickel interlayer should bring the Ag into intimate contact with the YSZ, lowering the likelihood of Type I pore formation. Third, the high 1455 °C melting point of Ni [108], the low 962 °C melting point of Ag [108], and the low, ~1 % 1000 °C solubility of Ni in Ag [108] should ensure that a solid, porous nickel network remains present long enough to bring silver into contact with the YSZ. Fourth, because commonly used SOFC cathode materials, such as La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-x} (LSCF) and La_{0.6}Sr_{0.4}MnO_{3-x} (LSM), are thermodynamically stable down to a pO₂ $\sim 10^{-12}$ atm at ~ 1000 °C and kinetically stabilized for a few hours at even lower oxygen partial pressures [102, 109], it should be possible to braze cathode-containing SOFCs for short times in inert atmospheres without decomposing them

[110]. Lastly, and perhaps most importantly, the nickel will be protected from oxidation during inert atmosphere brazing by 1) the decomposition of carbon-containing nickel paste organic additives during porous nickel interlayer production (carbon sets the local 850 °C pO₂ at ~10⁻¹⁷ atm [110] even though the incoming inert atmosphere will have a pO₂ ~10⁻⁶ atm), and 2) stainless steel chromium oxidation (which sets the local pO₂ even lower [110]) during brazing as molten silver infiltrates the porous nickel interlayer. Hence, since NiO will not form at 1000 °C in pO₂ < 10⁻¹¹ atm brazing atmospheres [110], so joints with porous nickel interlayers produced in inert atmospheres should be free of Type II pores.

Conversely, several factors could prevent porous nickel interlayers from enabling the production of high-quality YSZ-stainless steel braze joints. For instance, Ni additions could degrade the braze interface strengths because the stress induced by swelling resulting from nickel oxidation on the cathode side of the braze joint (enabled by oxygen diffusion through silver) could nucleate cracks in the joint. Hence, the objective of the present work was to investigate (1) the feasibility of producing high quality porous-nickel-interlayer-enabled YSZ-SS SOFC braze joints, and (2) characterize the microstructure, chemistry, and mechanical strength of these braze joints both before and after 500 hours of 750 °C oxidation in air.

3.2 Experimental Methods

3.2.1 Sample Fabrication

Porous nickel interlayers were produced on YSZ supports in three steps. First, nickel paste was produced by hand-mixing 99.9% pure nickel powder that had an average particle size of 3-7 µm (Alfa Aesar Inc.) with a V-737 organic vehicle (Hereaus, Inc.) in a 2:1 ratio by weight. The nickel paste was then screen printed onto 25 mm \times 25 mm trilayer substrates consisting of a dense, ~15 µm thick YSZ electrolyte, a ~15 µm thick NiO-YSZ function layer and a \sim 500 µm thick porous NiO-YSZ layer. Two passes were used to print each layer, and 10 minutes of 80 °C drying was used between prints. A 400-mesh screen containing 17.78 µm diameter stainless steel wires at 22° and a 9 μ m thick E80 emulsion (Sefar Inc.) was used for screen printing. Second, in 20 sccm of Ar, the samples were ramped at 5 °C/min, held at ~850 °C for 2 hours, and cooled to room temperature with a 5 °C /min nominal cooling rate to produce partially sintered nickel layers. Third, a 75 μ m thick, ~6.3 mm × 6.3 mm piece of 99.95% pure silver foil (Alfa Aesar Inc.) was sandwiched between the Ni|YSZ|NiO-YSZ substrate and a bare 441 stainless steel sheet (AK Steel Corp.) with a ~20 g weight on top, and the joint assemblies were ramped at 5 °C/min, held at ~1000 °C for either 15 or 30 minutes, and cooled to room temperature with a 5 °C /min nominal ramp rate in 20 sccm of Ar.

3.2.2 Oxidation Testing

For oxidation testing, joints brazed for 30 minutes were placed in a static air furnace and ramped at 5 °C/min, isothermally held at 750 °C for 120 or 500 hours, and cooled to room temperature with a 5 °C /min nominal ramp rate.

3.2.3 Mechanical Testing

As shown in Figures 3.1a and 3.1b, a symmetric double shear lap geometry was used to test the shear strength of the as-produced and oxidation-tested braze joints using a mechanical tensile test machine (SFM-20, United Testing Systems, Inc.). Each double shear lap sample contained four 0.635 cm \times 0.635 cm square brazed joints (two on each side). As shown in Figure 3.1c, an extensioneter was fixed on both stainless steel plates to measure the real extension in the braze regions, and all samples were tested to failure at room temperature with displacement rate of 0.009 mm/min. The shear stress σ_{shear} and strain ε_{shear} were estimated using the equations:

$$\sigma_{\text{shear}} = F/2[a \times (a - \delta)] \tag{1}$$

$$\varepsilon_{\text{shear}} = (\delta/2)/t \tag{2}$$

where F is the load; a is the lateral length of the joints (here 0.635 cm); δ is the extension; and t is the joint thickness (here ~100 µm) [51]. A double shear lap geometry, which restricts rotational loading on each braze joint through its symmetrical design, places each braze joint in a simple shear loading geometry that resembles the coefficient-of-thermal-expansion-mismatch induced loading conditions present in a planar SOFC braze joint such as that shown in Figure 1.3.



Figure 3.1 (a) A front-view schematic, (b) a side-view schematic, and (c) picture of the symmetric double shear lap samples used here for mechanical testing.

3.2.4 Scanning Electron Microscopy

Samples for Scanning Electron Microscopy (SEM) were prepared using a low-speed diamond saw to section the sintered nickel layers, as-brazed joints, or oxidation-tested joints, which were then mounted in epoxy (Epofix, Buehler Inc.). The epoxy-mounted samples were mechanically ground the with 240 to P4000 grit sand paper (Allied High Tech. Products), and finally polished with 0.3μ m Al₂O₃ (AP-302, Mager Scientific, Inc.) and 0.04μ m colloidal silica (OP-S NonDry, Struers Inc.). Prior to SEM characterization, the epoxy mounted samples were platinum sputter coated at 30 mA for 30 seconds using a Desk II Sputter Coater (Denton Vacuum, LLC) to obtain electronic conductivity on the surface. Back-scattered electron images were taken with a MIRA3 SEM (Tescan, Inc.) at 1.2 kX, 2 kX and 10 kX magnification to examine the sample microstructure. Energy Dispersive X-ray (EDS) Spectroscopy point and line scans were performed with an EVO LS25 SEM (Zeiss, GmbH) to analyze the local sample composition.

3.3 Results and Discussion

3.3.1 As-Produced Microstructure

Figure 3.2 shows back-scattered electron images of the partially sintered nickel interlayers, indicating that laterally uniform, porous layers $\sim 20 \,\mu m$ (2-6 Ni particles in thickness) were produced by the procedure described in Section 4.2.1.



Figure 3.2 Representative backscattered electron images showing lateral uniformity of a partially sintered porous Ni interlayer (left) and a magnified image (right) showing the region indicated by the red box.

Figure 3.2 shows that both 15 and 30 minutes of brazing at ~1000 °C in Ar were sufficient to produce pore-free, laterally-uniform braze joints. Specifically, Figures 3.3a and 3.3b indicate that both firing conditions were sufficiently long to allow Ag to spontaneously infiltrate the porous nickel interlayers, in the process drawing the Ag against the YSZ (i.e. circumventing the poor wetting of Ag on YSZ). As shown in the higher magnification images in Figures 3.3c-e, the porous nickel interlayer layer originally located at the braze-YSZ interface largely disappeared during 15 minutes of brazing (some remnants of this layer can be seen in the middle of the silver braze joint in Figures 3.3f-h, 30 minutes of brazing resulted in the complete

elimination of the porous nickel interlayer from the braze-YSZ interface and a correspondingly thicker reaction layer. In both cases, the silver remained well-bonded to the YSZ even after the porous nickel layer disappeared (which, as discussed in Section 3.3.4 is likely the result of Ni and Cr from the stainless steel diffusing to the YSZ-Ag interface and preventing Ag de-wetting). Figures 3.3c-g also show that the residual SS surface oxides present along the SS-reaction layer interface (black dots) did not adversely affect brazing. In fact, the change in SS contrast above the line of residual surface oxides denoting the original SS-Ag boundary suggests significant intermixing and a strong metallurgical bond between the SS and the reaction layer. Joints brazed upside down achieved the same microstructure as those in Figure 3.3 indicating that chemical potential differences, and not density differences, drove reaction layer formation. (Note, joints produced with identical procedures but brazed in air showed inadequate wetting of silver wetting due to nickel oxidation.)



Figure 3.3 Representative backscattered electron images of (a) an entire 15 minutes brazed joint cross-section, (b) an entire 30 minute brazed joint cross-section, (c-e) zoomed-in, representative portions of the 15 minutes brazed joint, and (f-h) zoomed-in, representative portions of the 30 minutes brazed joint. The red dotted lines indicate the paths of Energy Dispersive X-ray Spectroscopy line scans in Figure 3.4.

3.3.2 As-Produced Braze Joint Compositional Analysis

Figures 3.4a-c shows the results of 30 minute brazed joint EDS compositional analyses collected along the red dotted lines in Figures 3.3f-h, respectively. As shown in Figures 3.4a and 3.3f, most of the as-produced braze joint consisted of "pure" silver, consistent with the low solubility of nickel, iron, and chromium in silver [108, 111]. Hence, the present braze joints are expected to benefit from the conveniently large ductility of silver. This high ductility provides a stress-relief mechanism that allows YSZ-SS braze joints made with Ag-Cu brazes to survive for extended thermal cycling [13, 49] despite the fact that YSZ, 441 SS, and Silver have 25-1000°C coefficients of thermal expansion of ~8.9-10.6 [8], ~9.3-13.5 [10], and ~15-25 [112] ppm/K, respectively).

Figure 3.4b shows that the braze-SS reaction layer consisted of relocated nickel from the porous interlayer and diffused Fe and Cr from the SS. Figures 3.4a-b also show good nickel, iron, and chromium inter-diffusion across the SS-reaction layer interface, suggesting a strong metallurgical bond between these layers. The good bond was enabled by (1) The lack of discrete nickel particles within the silver matrix in the reaction layer, (2) the fact that samples were brazed upside down (i.e. the lower pairs of double shear lap sample joints), (3) the microstructure is the same as that shown in Figure 3.3, and (4) the presence of the nickel interlayer remnants in the Figures 3.3a and 3.3c braze interiors. These outcomes all suggest that both atomic diffusion and convective transport assist in the disintegration or dissolution of the porous nickel interlayer and the formation of the reaction layer.

Figure 3.4c shows that a compositionally "sharp" Ag-YSZ interface results after removal of the porous nickel interlayer. It is important to note that the "diffusion distance" implied by the apparent gradual transitions of the Ag, Y, Zr, and O content across the transition is equal to the

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~3 micron estimated EDS electron beam interaction volume diameter and therefore cannot be interpreted as intermixing of Ag and YSZ (the intermixing distances in Figure 3.4b are much larger than 3 microns, which implies that true intermixing took place between the SS and the reaction layer). Similarly "sharp" Ag-YSZ compositional interfaces have been observed in other silver-YSZ brazing systems [113].



Figure 3.4 Representative Energy Dispersive X-ray Spectroscopy line scan results from the 30 minute as-brazed sample (a) across the joint center, (b) across the SS-braze interface, and (c) across the YSZ-braze interface at the locations indicated in Figure 3.3. The x-axis is in microns.

3.3.3 Post-Oxidation Braze Joint Microstructure

Figures 3.5a and 3.5b show the 30 minute brazed joint microstructure after 120 and 500 hours of 750°C oxidation in air, respectively. Zoomed-in images of these joints are also presented in Figure 3.6. In both cases, the braze joints remained solid and dense after oxidation

and the braze remained bonded to both the SS and the YSZ. Further, the majority of the braze joint, which consisted of pure silver, was microstructurally unaffected by the 750 °C exposure to air. The dense, pore-free braze joint microstructures in Figure 3.5 and 3.6, and the similarities between the 120 and 500 hour oxidized braze joint microstructures suggests that 120 hours was plenty of time for oxygen to diffuse into all portions of the braze joint.



Figure 3.5 Representative backscattered electron images of (a) an entire 120 hour 750 °C and (b) an entire 500 hour 750 °C oxidized braze joint cross-section.

Figures 3.5b, 3.6a-b, d-e show that the Ni-rich portion of the reaction layer oxidized and formed two distinct layers, each with reduced porosity with increasing oxidation time. This is consistent with (1) the fact that pure Ni oxidizes quickly in 750 °C air [85, 110], (2) the fact that Ag has a high oxygen ion conductivity of 1.5×10^{-5} cm²·s at 750 °C, and (3) the fact that the Ni-rich portion of the reaction layer was adjacent to the thick silver layer at the interior of the braze joint. These figures also show that the Fe and Cr rich portion of the reaction layer (which extends past the line of residual surface oxide particles and up into the SS) did not oxidize, and that a thin silver layer (denoted Ag*) often separated the oxidized and unoxidized portion of the reaction layer. Given the high ductility of pure Ag [114], it is likely that this Ag* layer formed from the volume expansion associated with oxidation of the nickel-rich portion of the reaction layer (the atomic volumes of iron oxide, nickel oxide, and chromium oxide are greater than that of their constituent cations [85]).
Figures 3.6c and 3.6f show that except for a thin dark phase forming at the interface, the oxidized braze-YSZ interface microstructure did not change with long-term 750 °C oxidation.



Figure 3.6 Representative backscattered electron images of (a-c) higher magnification representative portions of the 120 hour 750 °C oxidized braze joint in Figure 3.5a, and (d-f) zoomed-in, representative portions of the 500 hour 750 °C oxidized braze joint in Figure 3.5b. The red dotted lines indicate the paths of Energy Dispersive X-ray Spectroscopy line scans in Figure 3.7. Both samples were brazed for 30 minutes.

3.3.4 Post-Oxidation Braze Joint Compositional Analysis

Figures 3.7a-f shows results of 30 minute brazed joint EDS compositional analyses collected along the red dotted lines shown in Figures 3.6a-f, respectively.

Consistent with the SEM contrast in Figure 3.5 and 3.6, Figures 3.7a and 3.7d show that the center of the braze joint remained nominally pure after 120 and 500 hours of 750 °C oxidation. Figures 3.7b and 3.7e clearly show the Ag* layer, the unoxidized reaction layer, and (especially in Figure 3.7e) two different phases within the oxidized portion of the reaction layer. These figures also show that a chromia-rich layer (denoted by the green highlighting) formed between the Ag* and oxidized reaction layer. Given the excellent surface passivation of at 750 °C in other systems [59, 115], this chromia layer probably helped protect the unoxidized portion of the reaction layer from the oxygen conducted through the silver in the center of the braze joint, providing a diffusion barrier that at least partially protected the SS from oxidation.



Figure 3.7 Representative Energy Dispersive X-ray Spectroscopy line scan results from a 30 minute brazed sample (a) across the 120 hour 750 °C oxidized joint center, (b) across the 120 hour 750 °C oxidized SS-braze interface (c) across the 120 hour 750 °C oxidized YSZ-braze interface, (d) across the 500 hour 750 °C oxidized joint center, (e) across the 500 hour 750 °C oxidized SS-braze interface (f) across the 500 hour 750 °C oxidized YSZ-braze interface. The x-axis is in microns.

Like the as-produced braze joint EDS analysis of Figure 3.4c, the 120 hour oxidized sample EDS analysis of Figure 3.7c shows a "sharp" interface between the braze and the YSZ. However, as shown in Figure 3.7e, longer oxidation times resulted in detectable amounts of nickel oxide and chromium oxide at the braze-YSZ interface. These phases likely correspond to the dark phase seen along the braze-YSZ interface in Figure 3.6f (and to a lesser extent Figure 3.6c). In light of the poor wetting characteristics of Ag on YSZ [47] and the low predicted work of adhesion for Ag on YSZ [41], the higher work of adhesion predicted between Ag and nickel, nickel oxide, or chromium oxide on the surface on YSZ [41], it is likely that small amounts of residual nickel from the porous nickel layer and chromium that diffused through the Ag may have oxidized in the interface to the braze-YSZ interface and also helped prevent Ag dewetting after dissolution of the porous nickel interlayer.

Figure 3.8 displays EDS composition maps showing the lateral continuity of the various braze joint layers with the same trends as the Figure 3.7 line-scans.



Figure 3.8 Braze-SS interface element distribution maps for a representative 30 minutes brazed sample after 500 hours of 750°C oxidation. The top left picture is the backscattered electron image of the mapped area.

3.3.5 Braze Joint Stress-Strain Curves

Figure 3.9 shows room temperature stress-strain curves for the SS|Ni-Ag|YSZ braze joints after 1000 °C fabrication in Ar, 120 hours of 750 °C oxidation, and 500 hours of 750 °C oxidation. In all cases the braze joints exhibited large amounts of deformation (>30% shear strain) before failure, and when failure did occur it always occurred with the brittle fracture of the underlying YSZ|NiO-YSZ supports and not through braze or braze interface. This is shown in Figure 3.10 where no delamination of either the braze/SS or the braze/YSZ interface was observed in as-brazed, 120 hour oxidized, or 500 hour oxidized samples. Kuhn *et al.* observed similar cracking within the YSZ supports in their SS|Ag|YSZ brazes [47].



Figure 3.9 Shear stress and strain curves from symmetric double shear lap samples after no, 120 hours, and 500 hours of 750 °C oxidation. "×" indicates failure in the YSZ substrate.

In addition, other studies have shown similar SS-Ag-YSZ failure mechanisms to those reported here [51, 67]. Despite the variations in the shape of the curves, which is probably due to lateral braze joint thickness variations (such as those in Figures 3.3a, 3.3b, and 3.5a) caused by the lack of precision in the experimental setup, both sets of samples showed good reproducibility. The decreasing failure strain with increasing oxidation shown in Figure 3.9 is indicative of a loss of ductility, or a reduction in the effective braze joint thickness, with oxidation (and hence earlier load transfer to the YSZ|NiO-YSZ substrate). However, the fact that (1) much of the joint will remain unoxidized in a real SOFC application (due to the pO_2) gradient extending laterally across the Figure 1.3 joint and the low oxygen partial pressure set on the fuel side of the joint), and (2) the large > 30% failure strains observed here for the heavily oxidized portion of the joint after 500 hours, suggest that these SS|Ni-Ag|YSZ braze joints will likely remain mechanically robust over SOFC lifetimes. In addition, shorter brazing times closer to the 1-5 minutes reported in the literature [97] may be able to increase joint longevity by keeping the remnants of the porous nickel interlayer within the middle of the joint so that Ni can oxidize "freely" in "all" directions into a ductile silver matrix. The viability of this braze still needs to be examined in the context of oxygen and hydrogen gradients expected in fuel cell operation, but the present analysis suggests that problems observed with the conventional braze are at least partially mitigated with this braze design.



Figure 3.10 Representative images of post shear test samples with different amount of oxidation. Fracture only occurred in the YSZ|NiO-YSZ supports for all the samples tested in this study.

3.4 Summary

This study presents a new transient porous-nickel enabled silver-based braze for improved YSZ-to-stainless steel joining, and it may also serve as a design paradigm to enable silver (or other braze) metal to ceramic sealing in automotive, aerospace, and other joining applications. Like reactive air brazing, the current brazing technique can be performed in atmospheres (i.e. inert atmospheres) that do not degrade the mechanical and electrochemical performance of pO₂ sensitive SOFC electrode (such as LSCF) or electrolyte (such as ceria) materials. As summarized in Table 3.1, this technique reduces the porosity commonly found in the conventional YSZ-stainless steel braze joints produced using reactive air brazing (Ag-CuO), and the likelihood of enhanced lifetimes and operational robustness in SOFC braze joints appears to be likely.

The operational reliability of this silver nickel braze remains to be tested. In the next Chapter, dual atmosphere isothermal tests as well as dual atmosphere accelerated thermal cycling tests assessed the practical robustness of this novel braze.

Pore Type	Reactive Air Brazing		Ag-Ni Brazing
Type I (wetting) Pore Formation	$\theta \approx 45^{\circ}$ (for Ag-4CuO) occasionally leads to pores during manufacturing [93, 94] Organics in the braze paste can also lead to pores during manufacturing [12]	•	$\theta = 30^{\circ}$ leading to a fully infiltrated porous Ni network [105-107] Since no organics are used during brazing (these are removed by heating the nickel paste in Ar to obtain the porous nickel network) binder burnout cannot cause pores during brazing
Type II (interfacial) Pore Formation	With the reduction of CuO along the braze/YSZ and braze/SS interface, micro- pores will form during SOFC operation near the H ₂ side of the joint [13, 49].	•	Even after 500 hours of oxidation no oxides are present at the SS- braze interface on the anode side of the joint (the oxides forming from the reaction layer are within ductile silver, and only form on the air side of the joint), hence they cannot be reduced by anode gases to produce pores.
Type III (H ₂ +O ₂) Pore Formation	H_2 and O_2 diffuse through Ag and form water pockets (Type III pores) that mechanically compromise the braze joint after ~10,000 hours of SOFC operation [15].	•	Since Type II pores form much faster than Type III pores [16, 49] and thereby provide a short-circuit path for H_2 invasion into the center of the braze, the elimination of Type II pores should increase joint reliability by delaying the onset of Type III pores.

Table 3.1 Comparison of Conventional Reactive Air vs. Porous-Nickel-Enabled Ag Brazing.

CHAPTER 4

Reliability of Silver Nickel Brazes

4.1 Introduction

To operate safely and efficiently, SOFCs require hermetic sealing between the anode compartment (which contains fuel-rich gases) and the cathode compartment (which contains air). Compared to competing sealing technologies such as glass seals [116], and compressive mica seals [28], brazes provide higher joint strengths, lower joint permeabilities and better long-term stabilities [6]. Unfortunately, molten braze alloys often have difficulty wetting ceramic substrates like yttria-stabilized-zirconia (YSZ) [79]. For instance, the wetting angle of pure silver on YSZ is 85° [96]. To circumvent this problem, the SOFC community has developed several strategies to facilitate silver wetting on ceramics.

Historically, reactive elements that oxide during brazing in air have been added to promote silver wetting on various ceramic substrates including zirconia [44, 94], lanthanum strontium cobalt ferrite (LSCF) [39, 43] and gadolinium-doped ceria (GDC) [117]. Critically, the oxides of these Reactive Air Braze (RAB) additions, most commonly CuO [6], are soluble in molten silver [39, 91, 92], ensuring that flux-free brazing can be conducted in air [6, 45, 50, 93-99]. Unfortunately, addition of these oxides should be controlled (typically ~4 mol %) to avoid decrease in interfacial strength, which limits the reduction in silver wetting angle (4 mol % of CuO for ~40° +/-5° on YSZ [6, 45, 50, 93-99]). Also, CuO is easily reduced in the low oxygen partial pressure environments encountered in the SOFC anode compartment [12-16, 46, 49-51, 71], resulting in significant amounts of porosity which reduce braze lifetime and mechanical stability. In fact, significant porosity was found in Ag-CuO brazes even after 100 hours of 800°C dual-atmosphere exposure [12-16, 46, 49-51, 71].

In Chapter 3, it was demonstrated that using a porous interlayer of nickel (denoted as the Ag-Ni method hereafter), instead of reactive air additions (i.e. Cu \rightarrow CuO), the joining of YSZ to stainless steel (SS) can be improved with better controlled wetting and spreading of silver, due to the low wetting angle of silver on nickel in inert atmospheres (< 30° for pO₂ < 10⁻⁹ atm [106]) [17]. This atmosphere should still be applicable for SOFC brazing because commonly used cathode materials, such as La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-x} (LSCF) and La_{0.6}Sr_{0.4}MnO_{3-x} (LSM), are thermodynamically stable down to a pO₂ ~10⁻¹² atm at ~1000 °C and are kinetically stabilized for a couple hours at even lower oxygen partial pressures [102, 109]. With much less initial porosity (with improved wetting), the Ag-Ni braze joints are expected to have longer lifetime compare to the RAB braze joints. On the other hand, real-world SOFCs involves dual-atmosphere operations, and it was theorized that the Type II porosity (porosity due to the reduction of CuO in RAB joints [17]) should not occur in dual atmosphere conditions for Ag-Ni braze joints (with no reducible oxides after brazing). But it is yet to be tested in dual atmosphere conditions since different microstructural evolution and damage nucleation mechanisms might be present.

In this work, dual atmosphere isothermal aging (DAI) tests and dual atmosphere accelerated thermal cycling tests (DAATC) on both Ag-CuO and Ag-Ni SS to YSZ braze joints were conducted. A testing geometry was developed for both DAI and DAATC tests using samples with the novel Ag-Ni method as well as the of conventional RAB (Ag3CuO, mol.%) braze joints for comparison. The DAI tests were designed to evaluate the interfacial damage caused by Type II porosity formation. Considering the large differences in the 25-1000 °C coefficients of thermal expansion in YSZ, 441 SS, and silver (~8.9-10.6 [8], ~9.3-13.5 [10], and

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~15-25 [112] ppm/K, respectively), high levels of shear stress will be imposed on the braze interfaces during thermal cycling. The DAATC tests were designed to assess the combined effects from thermal-mechanical loadings and chemical reactions from the dual atmosphere temperature cycles.

4.2 Materials and Experiments

4.2.1 Sample Fabrication

Ag-Ni braze samples were prepared using similar methods described in Chapter 3, but with a different geometry. Instead of square braze patterns, Figure 1a shows that ring shaped braze seals with inner diameters (ID) of 18.4 mm and outer diameters (OD) of 25.4 mm were produced. The paste preparation, screen specification, screen-printing procedure, silver foil preparation, as well as the brazing set-up (30 minutes) were the same as those in Chapter 3, except for the geometry and dimensions of the materials used. As shown in Figure 4.1a, the Ag-Ni braze is applied in a 'ring' shape between a 441 SS (ID 18.0 \pm 0.5 mm, OD 25.4 \pm 0.1 mm) and a YSZ|NiO-YSZ substrate (ID 18.0 \pm 0.5 mm, OD 38.1 \pm 0.1 mm).

The RAB (Ag3CuO, mol%) material was applied in the form of pastes obtained by mixing the Ag3CuO powder and the Hereaus V-101 organic vehicle in an 8:1 ratio by weight. To make sure the RAB paste were properly disposed in 'ring' shapes, a layer of the Hereaus V-101 organic vehicle was printed onto the YSZ|NiO-YSZ substrates using the same screen for the Ag-Ni samples. This allowed the later carefully hand-dispensed RAB paste to distribute accordingly to the printed 'ring' shapes after drying at 80 °C for 10 minutes. Then the SS and the YSZ|NiO-YSZ (with dried paste) substrate were assembled according to the schematic in Figure 4.1a and brazed in an air furnace. For brazing, the RAB samples were initially ramped at 5 °C /min to soak at 900 °C for 10 minutes, then ramped at 10 °C /min to 960 °C for 10 minutes of brazing, and finally cooled back to room temperature with a nominal rate of 10 °C /min. It should be noted that the SS441 and YSZ|NiO-YSZ substrates for both Ag-Ni and RAB samples were the same.

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Figure 4.1 (a) Schematic diagrams of sample geometry and stack arrangement in the test set-up (note that the thicknesses of the components are exaggerated); (b) Picture of the test set-up where the sample is cycled in and out of the three-zone furnace; (c) Recorded inlet and external temperature of the test stack during dual atmosphere thermal cycling.

4.2.2 Dual Atmosphere Isothermal Tests

The as-fabricated 3-layer (SS, braze, YSZ|NiO-YSZ) ring samples (typically four samples) were then stacked up with a mica ring between each sample; then the whole stack was screwed tight between two thick SS plates (Fig 4.1a bottom). As shown in Figure 4.1b, the assembly was placed on top of the gas inlet tube with a block of SS cylinder piece on top. To achieve dual atmosphere conditions, a 300 sccm flow 4% H₂ 96% N₂ through a distill water bubbler was sent through the gas inlet at the bottom of the stack, creating a reducing atmosphere near the center of the ring samples (denoted as the 'RE' side); whereas the outer rim of the braze region was exposed to an oxidizing atmosphere (denoted as the 'OX' side) by exposing the entire stack to air. After passing through the center of the stack, the gas stream went directly into the exterior atmosphere. A SS piece marked as the "stopper" was placed on top the stack to decrease the size of the gas stream outlet and maintain a slight positive pressure in the center gas stream. Also, there is an 'exterior thermocouple' ('External Temperature') attached to the top SS plate (Figure 4.1b) as well as an interior thermocouple ('Inlet Temperature') at the gas inlet next to the bottom SS plate. These thermocouples monitored the sample temperatures throughout the tests. For the DAI test, the entire assembly was sent up into a three-zone furnace to keep both the inlet temperature and external temperature at 755±5 °C for 310 hours.

4.2.3 Dual Atmosphere Accelerated Thermal Cycling Tests

For the DAATC tests, the dual atmosphere was achieved with the same set-up for the DAI tests, while accelerated thermal cycling of the samples were performed by sending the assembly in Figure 1b in and out of the three-zone furnace with controlled speeds. Figure 1c shows the recorded 'External Temperature' at the exterior of the top SS plate and the 'Inlet

Temperature' at the gas inlet during the tests. Throughout the DAATC test, the samples were cycled between \sim 35°C and \sim 830 °C at a ramping rate of \sim 25 °C/min for 300 cycles.

4.2.4 Sample Characterization

As-brazed, DAI tested and DAATC tested braze samples for Scanning Electron Microscopy (SEM) were prepared by first sectioning with a low-speed diamond joints, and then mounted in epoxy (PELCO[®] 24-hour Epoxy, Ted Pella Inc.). The epoxy-mounted samples were mechanically grounded with 240 to 1200 grit sand papers (MetLab Corp.), and polished with 5µm, 0.3µm Al₂O₃ (Mager Scientific, Inc.) and finally up to 0.04 µm colloidal silica (OP-S NonDry, Struers Inc.). Prior to SEM characterization, the epoxy mounted samples were platinum sputter coated at 30 mA for 30 seconds with a Desk II Sputter Coater (Denton Vacuum, LLC) to provide electronic conductivity on the sample surface. Back-scattered electron (BSE) images were taken with a MIRA3 SEM (Tescan, Inc.) at different magnifications to examine the sample microstructure at different locations. Energy Dispersive X-ray (EDS) Spectroscopy point and line scans were performed to analyze the local sample composition.

4.3 Results and Discussion

All the experimental results in this section are presented in two tracks, with the first being conventional Ag-3CuO RAB samples as the control group and the other being the novel Ag-Ni braze samples. Test results from both DAI and DAATC conditions are compared for reliability assessment.

4.3.1 As-brazed Microstructure

4.3.1.1 Ag-3CuO Samples

Figure 4.2 shows that a relatively dense joint was obtained with Ag-3CuO RAB material. There is a big pore reaching both the SS and YSZ interface at the middle of the joint, which is a common characteristic of RAB brazing related to its mildly high wetting angle on YSZ and/or organics within the RAB paste [6, 12, 45, 50, 93-99]. The labels 'OX' and 'RE' in Figure 4.2 indicate the two sides at the outer rim and inner rim within the sample that would subject to oxidizing (air) and reducing (4% H₂ 96% N₂) environments in the following tests, respectively. During conventional RAB brazing, the molten filler material filled the gap between the two faying surfaces through capillary reaction. So, the brazed region in Figure 4.2 extends all the way between the SS and YSZ|NiO-YSZ substrates, reaching a width of 4.32 mm, which is $\sim 23.4\%$ wider compared to the original 'ring' width from design (3.50 mm).



Figure 4.2 Representative BSE images of an entire as-brazed Ag-3CuO joint cross-section.

Figure 4.3a shows the through-thickness microstructure of the Ag-3CuO braze joint between 441 SS and YSZ|NiO-YSZ, which is representative of the microstructure between the OX and RE sides in Figure 4.2. The EDS line scan results from the red dotted lines in Figure 4.3 are presented in Figure 4.4. It is obvious from Figure 4.3a and Figure 4.4a that the bulk of the braze joint is consisted of pure silver with the lightest contrast, and that the phase within the bulk silver in the middle (vertical) of the joint is a Cu-Cr-O oxide (also confirmed at dot 'A' by EDS point scan). There is also a reaction layer (denoted as the "reaction' layer" or "rxn' layer" hereafter) at the SS interface that is typical to RAB joints made between SS and ceramic substrates [37, 47, 50].



Figure 4.3 Representative BSE images of zoomed-in, representative portions of the joint microstructure in Figure 4.2, (a) through thickness, (b) at the SS interface, and (c) at the YSZ interface. The red dotted lines indicate the paths of EDS line scans in Figure 4.4.



Figure 4.4 Representative BSE images of zoomed-in, representative portions of the joint microstructure in Figure 4.2, (a) through thickness, (b) at the SS interface, and (c) at the YSZ interface. The red dotted lines indicate the paths of EDS line scans in Figure 4.4.

Figure 4.3b shows a zoomed-in view of the reaction' layer at the SS interface. The contrast difference within the reaction' layer indicates consists of two parts. Figure 4.4b shows the EDS line scan results, and it is obvious that the layer with the darker contrast closer to the SS is a high-Cr containing oxide layer, probably chromia; and the layer with the lighter contrast

closer to the bulk silver portion is a Cu-Cr-Fe-O layer. This phase distribution is very similar to other studies where a reaction' layer consisting of Cr-O and Cu-Fe-Cr-Mn-O layers is observed in Crofer/RAB/ceramic joints [37, 47, 50, 118].

Figure 4.3c shows the typical as-brazed RAB microstructure at the YSZ interface. A thin layer (<300 nm) can be observed between silver and YSZ at the interface. This layer is probably CuO that decorates the YSZ surface for improved silver wetting [37, 93]. However, the CuO layer is not detected by the EDS line scan in Figure 4.4c, probably due to its low thickness.

4.3.1.2 Ag-Ni Samples

Figure 4.5 and 4.6 shows the typical as-braze joint microstructure with the novel Ag-Ni method. The microstructural details are very similar to that in the previous chapter. The brazed region in Figure 4.5 is very dense and mainly consisted of pure silver. It is noted that the braze region is thicker at the OX side and there are some non-uniform features at the RE side. This is due to the crude alignment and materials set-up during sample preparation. However, the width of the braze region is ~3.48 mm that is almost the same as designed (3.50 mm), indicating excellent control of wetting and spreading of molten silver during brazing, in contrast to conventional brazing methods.



Figure 4.5 Representative BSE images of an entire 30 minute as-brazed Ag-Ni joint cross-section.

Figure 4.6a and 4.7a show the typical through thickness joint microstructure and elemental distribution, respectively. The majority of the Ag-Ni braze joint is pure silver, and there is a 'reaction layer' at the SS interface formed by inter-diffusion between nickel and SS elements (mainly Fe, Cr). Although the nickel was applied as a porous interlayer at the YSZ interface before brazing, the nickel became transient during brazing and migrated toward the SS side and then formed the reaction layer. Figure 4.6b and 4.7b show more detailed information at the SS interface. It is obvious that inter-diffusion occurred, and that the reaction layer is richer in Fe and Cr toward the SS side; and is richer in Ni toward the pure silver region. The black phase that appears as a dotted line/layer between the SS and the reaction layer is the oxide scale formed on the original SS faying surface during brazing (containing Ti, Si, etc.), which showed no apparent effect on brazing. Figure 4.6c and 4.7c show the YSZ braze interface. An Fe-Ni-Cr-O layer with dark contrast can be observed, which didn't show a damaging effect on the wetting of the YSZ. This layer is sometimes observed during silver brazing with SS substrates (especially with longer brazing times and higher brazing temperatures), and it is probably formed by the diffused Fe and/or Cr from the SS and/or residual Ni [17, 50].

Compared to the Ag-3CuO joints, the Ag-Ni as-brazed joints exhibits better control of the wetting and spreading process during brazing and usually lead to less porosity.



Figure 4.6 Representative BSE images of zoomed-in, representative portions of the joint microstructure in Figure 4.5: (a) through thickness, (b) at the SS interface, and (c) at the YSZ interface. The red dotted lines indicate the paths of the Figure 4.7 EDS line scans.



Figure 4.7 Representative EDS line scan results from the 30 minute as-brazed Ag-Ni sample (a) across the joint thickness, (b) the SS-braze interface, and (c) the YSZ-braze interface at the locations indicated in Figure 4b-d, respectively. Note, the x-axis is in microns.

4.3.2 Dual Atmosphere Isothermal Tests

4.3.2.1 Ag-3CuO Braze Joints

Figure 4.8a shows the BSE image of the entire cross-section of a 300 hour DAI tested Ag-3CuO braze joint. Compared to the as-brazed Ag-3CuO microstructure in Figure 4.5a, there is a bigger portion of material with a dark gray contrast at the SS interface. Figure 4.8b shows zoomed-in images at the areas indicated by the blue arrows in Figure 4.8a, respectively. It is obvious that a significant amount of porosity developed along the SS interface within the dark gray reaction layer. From the middle of the joint toward the RE side, observed pores are larger in size and appear to be more percolated, whereas the pores developed toward the OX side are much smaller in both size and quantity. This is consistent with the fact that the major pore formation mechanism is the reduction of CuO by absorbed hydrogen from the RE side [16, 49-51] (Type II reduction pores). H₂ from the RE side attacks the Cu-rich portions within the reaction' layer, and after the reduction of CuO and pore formation start at the RE side, H₂ percolation into the braze joint is further enhanced with faster diffusion paths [16, 49]. This pore formation and propagation mechanism accounts for the difference in pore morphology as well as distribution between the OX and RE sides. Another feature of these Type II pores is that the porosity is mostly concentrated within the reaction layer and closer to the silver portion (vertically) of the braze joint. This is because the Cu-rich oxides in the reaction' layer are mainly distributed toward the silver phase, as discussed previously in section 4.3.1.1 (Figure 4.3b). Other studies [13, 50] also reported the same observations with dual atmosphere experiments.

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Figure 4.8 Representative BSE images of (a) an entire 300 hour DAI tested Ag-3CuO braze joint cross-section; (b) a series of zoomedin images of the areas marked by the blue arrows (pointing down in top row, pointing up in bottom row). The red dotted circles highlight the porous structures at the SS interface.

Figure 4.9a-c shows the typical Ag-3CuO braze microstructure after 300 hour DAI testing. Except for the porosity developed, the braze microstructure after the DAI test in Figure 4.9a is very similar to that in the as-brazed condition (Figure 4.3a). This is reasonable since the 441 SS, the reaction' layer, the silver phase, as well as the YSZ|NiO-YSZ substrate are almost immune to oxidation, and that only Cu-rich oxides within the reaction' layer will react with H₂ from the RE side. Similar observations at both the SS interface (Figure 4.9b) and the YSZ interface (Figure 4.9c) have confirmed this finding.

Figure 4.10a-c show the EDS line scan results from the red dotted lines in Figure 4.9a-c, respectively. Compared to similar measurements made on as-brazed Ag-3CuO samples (Figure 4.4), the compositional distributions in the 300 hour DAI tested samples are almost the same through the joint thickness direction and also at the SS and YSZ interfaces, which is consistent with previous discussion on the microstructural features.



Figure 4.9 Representative BSE images of zoomed-in, representative portions the joint microstructure in Figure 4.8a: (a) through thickness, (b) at the SS interface, and (c) at the YSZ. The red dotted lines indicate the paths of EDS line scans in Figure 4.10.



Figure 4.10 Representative EDS line scan results from the 300 hour DAI tested Ag-3CuO sample (a) across the joint thickness, (b) the SS interface, and (c) the YSZ interface at the locations indicated in Figure 4.9a-c, respectively. Note, the x-axis is in microns.

4.3.2.2 Ag-Ni Braze Joints

Figure 4.11 shows the BSE image of the entire cross-section of a 300 hour DAI tested Ag-Ni braze joint. The majority of the joint is still silver as indicated by the white contrast. Compared to the as-brazed Ag-Ni braze microstructure in Figure 4.5, there seems to be some features showing up as a layer with black contrast at the SS interface (note the dark dots within the bulk silver is some oxidized nickel particles similar to the 15 minute brazed case [17]; the nickel particles were probably left within the Ag due to insufficient heating due to thermal gradients in the brazing process). Figure 4.12b and 4.12c provide zoomed-in views of this layer at the OX side. This microstructure is very similar to the results from the air-oxidized Ag-Ni samples (Figure 3.5 in section 3.3.3). The OX side was exposed to air at the same temperature (~750 °C) for 300 hours during the DAI test, so that it shows features with intermediate level of oxidation between the 120 hour and 500 hour oxidized microstructures in [17]. The original Ag-Ni braze reaction layer was partially oxidized, became micro-/nano-porous, and separated from the unoxidized reaction layer, creating a layer of silver in between (denoted as the Ag* layer). The formation of the Ag* layer has been previously discussed in [17].



Figure 4.11 Representative BSE images of an entire 300 hour DAI tested Ag-Ni braze joint cross-section.

Figure 4.13a shows the EDS line scan results from Figure 4.12a. Compared to the asbrazed condition in Figure 4.7a, there is no change to the bulk silver whereas most of the changes occurred within the reaction layer. Figure 4.12b further shows that layered features can be observed both below the Ag* layer (with a continuous dark contrast) and within the oxidized reaction layer. EDS line scan results in Figure 4.13b shows that a protective chromia layer (green shade) has formed within the Ag* layer next to the oxidized reaction layer; and that the compositional distribution within the oxidized reaction layer shows a layer of Ni, Fe oxides with irregular Ag in between. It should be noted that the black phase layer between the SS and the unoxidized reaction layer is the same surface oxide scale from the SS as previously mentioned in section 4.3.1.2.

Figure 4.12d shows the through thickness microstructure of the 300 hour DAI test Ag-Ni sample at the RE side. Compared to Figure 4.12a at the OX side, the Ag* layer is not continuous, and the oxidized reaction layer is much thicker but less uniform. Compositional distribution in Figure 4.13d is consistent with the phase contrast in Figure 4.12d and showed minimal change in the bulk silver compared to that in the as-brazed condition or the OX side (Figure 4.7a and Figure 4.13a, respectively). A zoomed-in view of the SS interface is shown in Figure 4.12e, and much less unoxidized reaction layers can be observed. Compared to the OX side in Figure 4.12b, the Ag* phase and the chromium oxides appear to be interlaced and no longer continuous. These observations are confirmed with the EDS line scan results in Figure 4.13e, in which interpenetrating Ag* phase and chromia can be observed. The dense oxidized reaction layer resembles that in the 500 hour air-oxidized Ag-Ni sample in [17].



Figure 4.12 Representative BSE zoomed-in images showing the microstructure near the OX side (a-c) and near the RE side (d-f) in Figure 4.11: (a, c) through thickness, (b, e) at the SS interface, and (c, f) at the YSZ interface. The red dashed lines indicate the paths of EDS line scans in Figure 4.13.



Figure 4.13 Representative EDS line scan results near the OX side (a-c) and near the RE side (d-f) from the 300 hour DAI tested Ag-Ni sample (a, d) across the joint thickness, (b, e) across the SS-braze interface, and (c, f) across the YSZ-braze interface at the OX side. These corresponds to the red dotted lines at the locations indicated in Figure 4.12a-f, respectively. The x-axis is in microns.

It is surprising that oxidized reaction layer is still present at the RE side and furthermore, it is similar to that in the 500 hour oxidized case. Three proposed hypotheses may have independently or collaboratively contributed to this surprise: Firstly, as discussed in the previous work on Ag-Ni braze oxidation, the initial formation of the oxidized reaction layer tends to be micro-porous [17]. Thus, there would be a faster O_2 migration path along with the formation of the oxidized reaction layer from the OX side toward the RE side, leading to higher oxygen partial pressure (pO2) within the initial oxidized reaction layer even at the RE side. Secondly, the initial chromia layer was probably not protective (i.e. dense and continuous) at the RE side, caused by interrupted initial chromia layer formation due to the H_2 presence from the RE side. Some locations near the RE side will have higher H_2 content, leading to a low enough pO₂ atmosphere to prevent chromia formation. Hence, without the protective chromia 'layer' more oxidation is possible, resulting in a non-uniform oxidized reaction layer at the RE side. A similar phenomenon has been observed in dual atmosphere high-temperature exposed SS samples, where surface oxidation leads to a more porous and thicker oxide scale due to diffused H_2 [119-121]. Furthermore, it was found that the diffused H₂ may promote Fe diffusion out of the SS to form oxides in both SS430 [120] and SS441 [121]; and a H_2O rich atmosphere will lead to thick surface oxide scale on SS [122]. This hypothesis will also be further discussed in section 4.3.3.2. Thirdly, since only 4% H₂ is used in this study, it is possible that the pO₂ is low enough reduce Cu oxides but not quite enough to reduce Ni or Fe oxides, since Ni and Fe oxides are much more stable than Cu oxides.

The microstructural features at the YSZ interface in Figure 4.12f as well as its corresponding EDS line scan results in Figure 4.13f shows no reaction products when compared

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to the as-brazed condition (Figure 4.6c, 4.7c) in both the RE and OX sides in the same sample (Figure 4.12c, 4.13c).

4.3.2.3 Comparison of the DAI Tested Ag-CuO and Ag-Ni Samples

For Ag-3CuO braze joints, it is obvious that 300 hours of DAI test has already led to serious porosity formation at the SS interface, and pores can be even observed at near the OX side. The Type II porosity would certainly be accelerated by the presence of occasional wetting pores (Type I pores) from brazing, leading to a very short SOFC operating life-span.

With the Ag-Ni braze, there was nearly no porosity after 300 hours of DAI test, and the overall microstructure was similar to the oxidized case. As previously tested mechanically [17], the interfacial bonding strength after 500 hours of air oxidation is still stronger than the YSZ|NiO-YSZ subtrate itself. Consequently, the DAI tested Ag-Ni samples should perform similarly and have good DAI stability. Since the 'worst case scenario' of the Ag-Ni braze under DAI conditions is total oxidation of the reaction layer, which has been shown to have adequate mechanical stability, it is suggested that the Ag-Ni braze seal would lead to significantly longer SOFC operation life-span.

4.3.3 Dual Atmosphere Accelerated Thermal Cycling Tests

Different from DAI tests that mimic the SOFC operating conditions, DAATC tests take a step further to simulate not only the steady SOFC operation condition, but also the switch on and off processes of the SOFC devices due to thermal cycling. Thermal cycles impose shear stress (most likely concentrated along the SS or the YSZ interfaces) according to the CTE difference between the SS, silver, and the YSZ. However, it should be noted that although dual atmosphere

is applied during the 300 thermal cycles, the samples were exposed to dual atmosphere condition at >700 °C for only ~75 hours. Thus, the effect of H_2 should be less than that in the case of 300 hours of DAI exposure.

4.3.3.1 Ag-3CuO Braze Joints

Figure 4.14a-b shows BSE images of the entire cross-section of a 300 DAATC tested Ag-3CuO braze joint and the corresponding zoomed-in images at the areas marked by the blue arrows. Surprisingly, although this sample has less exposure to high-temperature dual atmosphere condition, it showed similar or even worse interfacial porosity formation at the SS interface compared to the 300 hour DAI tested sample (Figure 4.8a-b). In the middle picture of the bottom row in Figure 4.14b, stripes with a dark contrast radiating from interfacial pores can be observed. These features are from residual cutting oil that came out from percolated pores deep within the sample. Although a more vigorous cleaning procedure was performed (2 hours of ultrasonic cleaning in acetone), the persistent presence of the residual machine oil is indicative of how extensive the pore percolation is.



Figure 4.14 Representative BSE images of (a) an entire 300 DAATC tested Ag-3CuO braze joint cross-section; (b) a series of zoomed-in images of the areas marked by the blue arrows (pointing down in top row, pointing up in bottom row). The red dotted circles highlight the porous structures at the SS interface.

Figure 4.15a-c shows the typical Ag-3CuO braze microstructure after 300 DAATC testing. These images are very similar to the previous observations from the 300 hour DAI tested sample (Figure 4.9a and 4.9b). The microstructural evolution as well as pore formation mechanisms are almost the same, despite the fact that this sample had much less high-temperature dual atmosphere exposure. This implies that the cyclic shear loading at the SS interface has a significant detrimental effect on pore and/or crack developments.

Figure 4.16a-c shows the EDS line scan results from the red dotted line in Figure 4.15a-c, respectively. Compositionally, the 300 DAATC tested sample shows no difference from the 300 hour DAI tested sample, which are also similar to that in the as-braze condition (Figure 4.4).



Figure 4.15 Representative BSE images zoomed-in, representative portions the joint microstructure in Figure 4.14a: (a) through thickness, (b) at the SS interface, and (c) at the YSZ interface. The red dotted lines indicate the paths of EDS line scans in Figure 4.16.



Figure 4.16 Representative EDS line scan results from the 300 DAATC tested Ag-3CuO sample (a) across the joint thickness, (b) the SS interface, and (c) the YSZ interface at the locations indicated in Figure 4.15a-c, respectively. The x-axis is in microns.

4.3.3.2 Ag-Ni Braze Joints

Figure 4.17 shows the BSE image of the entire cross-section of a 300 DAATC tested Ag-Ni braze joint. Similar to the 300 hour DAI tests, the majority of the joint is still silver as indicated by the white contrast, but some features related to oxidization can be observed in Figure 4.18 a, b, d, and e. A more uniform oxidized reaction layer was formed at the OX side (Figure 4.18a) as compared to the as-brazed Ag-Ni braze microstructure in Figure 4.5, whereas a non-uniform oxidized reaction layer was formed at the RE side (Figure 4.18d). Figure 4.18 b, e shows zoomed-in views of the SS interface at the OX side and RE side, respectively. Compared to the microstructure in Figure 4.12b and 4.12e on the 300 hour DAI sample, the amount of oxidation appears to be less in the 300 DAATC case, with a semi-continuous chromia layer next to the oxidized reaction layer (within the Ag* layer) in Figure 4.18b, and the dotted chromium oxide formation between the unoxidized and oxidized reaction layer in Figure 4.19b and 4.19e.



0.5 mm

Figure 4.17 Representative BSE images of an entire 300 DAATC tested Ag-Ni braze joint cross-section.



Figure 4.18 Representative BSE zoomed-in images of the microstructure near the OX side (a-c) and near the RE side (d-f) in Figure 4.17: (a, d) through thickness, (b, e) at the SS interface, and (c, f) at the YSZ interface. The red dashed lines indicate the paths of EDS line scans in Figure 4.19.



Figure 4.19 Representative EDS line scan results near the OX side (a-c) and near the RE side (d-f) from the 300 hour DAI tested Ag-Ni sample (a, d) across the joint thickness, (b, e) across the SS-braze interface, and (c, f) across the YSZ-braze interface. These correspond to the red dotted lines at the locations indicated in Figure 4.18a-f, respectively. The x-axis is in microns.

The comparison of chromia formation at both OX and RE sides between the DAI and DAATC tests supports the second hypothesis in section 4.3.2.2. With only ~75 hours of dual atmosphere exposure at >700 °C, the DAATC tested Ag-Ni sample shows a microstructure representative of the initial chromia formation. For the RE side, the initial chromia formation is interrupted by the H₂ presence in Figure 4.18e, so that a continuous protective chromia layer couldn't be formed, which finally led to interlaced chromia and Ag* formation when the reaction layer was almost totally oxidized. On the OX side, a semi-continuous chromia layer started to form (such as the layer in Figure 4.18b), then a continuous protective chromia layer formed (like the one in Figure 4.12b), preventing further oxidation of the top reaction layer.

Silver chromate has been reported to be volatile at low temperature ranges around ~650 °C [123-125] and it might be problematic for SS braze joints made with Ag-based materials. However, in an Ag-Ni braze joint, it would be difficult for such chromate to form in the braze joint since the reaction requires hydrated chromium oxides [123-125]. Moreover, even with silver chromate formation, due to the passivation of the chromia layer that limits the oxygen supply, as well as the presence of surrounding solid materials like the Ag* and the oxidized reaction layer, the growth and volatilization of the silver chromate will be low. Hence, whether or not silver chromate formation occurs will not be a big concern for the reliability of the Ag-Ni braze joints.

Figure 4.18a also shows a thin layer with dark contrast within the silver portion but close to the YSZ side. This layer is also enlarged in Figure 4.18c with the EDS line scan results presented in Figure 4.18c. The layer was determined to be a Cr-Ni-O phase, which was also observed in the as-brazed condition in Figure 4.6c. It is interesting that the layer seems to be "spalling off" from the YSZ interface, while during the DAATC test, the entire braze joint was

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still in solid state. This may be caused by the cyclic loading of shear stress at the YSZ interface between thermal cycles. However, no detrimental effects of this layer has been found in either the current work nor previous study [17]. On the RE side, Figure 4.18f as well as its corresponding EDS line scan results in Figure 4.19f shows no evidence of reactions when compared to the as-brazed condition (Figure 4.6c, 4.7c) or the OX side in the same sample (Figure 4.12c, 4.13c). However, one interesting difference is that the oxide layer at the YSZ interface remained between silver and YSZ at the RE side (Figure 4.12d, f), whereas at the OX side, 'spallation' of such layer into the solid silver phase was observed.

4.3.3.3 Comparison of DAATC Tested Ag-CuO and Ag-Ni Samples

Similar to DAI test results, the Ag-3CuO braze joint also shows signification porosity formation at the SS interface after 300 DAATC tests. In contrast, the Ag-Ni braze shows almost no porosity formation, and the overall microstructure was similar to that in the case of oxidation, again suggesting good mechanical stability for SOFC applications with power cycles.

4.3.4 Effect of Thermal Cycling in Dual Atmosphere

Although both the 300 hour DAI and 300 DAATC tests led to extensive pore formation at the SS interface in the Ag-3CuO braze joints, the fewer hours of high temperature dualatmosphere exposure in the DAATC test (<75 hours vs. 300 hours) implies that the cyclic shear loading at the SS interface during thermal cycling also contributed to the pore formation or localized delamination.

For the Ag-Ni braze joints, the DAI and DAATC tests showed similar effects on the joint microstructure with more oxidation within the reaction layer in the case of 300 hour DAI test.

This difference is probably caused by the total time of high temperature exposure by comparing with post-oxidation results in [17], suggesting a limited thermal cycling effect on the Ag-Ni braze joints. However, it is interesting that the oxidized reaction layer in the DAATC tested sample (Figure 4.18b, e) is denser than that in the DAI tested sample (Figure 4.12b, e) with much shorter time at high temperature. This contradicts the previous findings in [17], and is probably caused by a 'densification' process imposed by friction within the initial oxidized reaction layer during thermal cycling. Such a mechanism would be favorable to the reliability of the Ag-Ni joints.

The YSZ interface in both Ag-3CuO and Ag-Ni braze joint is relatively inert to either DAI or DAATC conditions on both the OX and RE sides. The most significant feature that developed was the oxide layer at the YSZ interface in the Ag-Ni joints that 'spalled off' into the solid silver phase during DAATC test, but no detrimental effects of this process have been identified.

4.4 Summary

To evaluate the performance of the Ag-Ni transient brazing method in real-world SOFC operating conditions, a thorough comparison of DAI and DAATC tests on both the conventional Ag-3CuO RAB braze joints and the novel Ag-Ni braze joints was performed:

1. The conventional Ag-3CuO RAB braze showed significant porosity at the SS interface after both 300 hour DAI and 300 DAATC tests. The porosity is primarily caused by CuO reduction by H_2 from the reducing atmosphere, and such extensive porosity would lead to early stage hermetical failure in SOFCs.

2. Braze joints with the novel Ag-Ni method showed no porosity formation after the same DAI and DAATC tests. The resulting microstructure most resembles the post-oxidation case in the previous study [17], in which the total oxidation 'worst case scenario' was shown to be mechanically stable for SOFCs.

3. The combined effect of dual atmosphere and thermal cycling lead to similar or worse porosity formation in the Ag-3CuO braze joint even with much less time at high-temperature dual-atmosphere exposure, suggesting that the RAB braze joint is more susceptible to interfacial damage when a SOFC device is given frequent power cycles.

4. Ag-Ni braze joints out-performs the conventional Ag-3CuO braze in both DAI and DAATC tests, showing much improved robustness and life-times for SOFC applications.

CHAPTER 5

Controlled Wetting and Spreading of Silver on Various Ceramic Substrates

5.1 Introduction

Ceramic materials are of growing interest to multiple industries for their superior mechanical, thermal, electrical properties etc., especially for more demanding environments like high-temperature applications. Ceramic materials are widely used in devices such as solid oxide fuel cells, high-power electronics, and for more basic functions like cutting tools and ceramic circuit boards [2, 3, 126-129]. However, practical applications of these ceramic materials often requires them to be joined with another material, like a metal [79], i.e. in ceramic circuit boards to utilize their high thermal conductivity and low thermal expansion[127]; in current collectors to help extract the electrons they generate [129]; and in various cases for their thermal insulation and/or structural properties. There are several ways to join metals to ceramics, such as mechanical joining, solid-state diffusion bonding, and liquid phase bonding [79]. The most common technique for joining ceramics is achieved through the introduction of a liquid phase [79], and liquid metals are widely used to join ceramics. However, metallic materials tend to have poor wetting properties on ceramics [79, 130-132].

Historically, several approaches have been developed to facilitate the wetting of molten metal on ceramic substrates.. One common way to improve the wetting and spreading behavior of liquid metal on ceramic substrates is through reactive wetting, with the addition of reactive elements[79, 132, 133]. Reactive wetting is accomplished by a wetting process with chemical reactions. The addition of the reactive elements such as Si, Ti, Zr, Ge into the liquid metal

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usually contribute to the dissolution of the solid (ceramic substrate elements) and/or formation of a new reaction compound(s) at the solid-liquid interface [132]. However, this process will usually require at least a protective atmosphere, and in many cases, a high vacuum to enable chemical stability of these added reactive elements, making this method costlier and sometimes not viable for industrial applications. An exception is "reactive-air wetting", where wetting is improved in air by formation of interfacial oxidizes that are soluble in the liquid metal [38, 93, 94, 134]). This alternative route for reactive wetting is to achieve a reactive surface layer on the solid instead of using reactive elements in to the liquid metal [113, 135]. This process is usually done by various surface coating methods and thus adds higher cost toward applications.

This work presents a novel, low-cost, non-reactive, surface micro-patterning method to improve and control the wetting of liquid silver on ceramics, which is inspired by surface nano-/micro-patterning methods [136, 137], and some of the wetting/infiltration phenomenon observed in literature [17, 132, 138], as well as the silver-nickel brazing work described in the previous chapters. The surface patterning method is a non-reactive wetting process, in which the wetting/spreading of liquid on the solid surface is controlled by the "hydrophilic" and "hydrophobic" conditions created by different patterns of micropillars on the solid surface. This method has been mostly adopted in water/polymer systems where applications at low/room temperatures are considered, whereas in the case of liquid metal and ceramic substrates, temperatures close to 1000°C are required. In the present work, a micro-porous layer of nickel interlayer on the ceramic substrates is designed to create "silver-philic" regions so that molten silver can readily wet and spread accordingly on the naturally "silver-phobic" ceramic substrates.

The designed silver-nickel wetting system is supported by the following characteristics: (i) Silver has a low wetting angle of $<30^{\circ}$ on nickel when pO₂ $< 10^{-9}$ atm [105, 106], i.e. in

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protective Ar; (ii) spontaneous liquid infiltration into porous solid media occurs for wetting angles below 50.4° [107], so that molten silver can infiltrate the porous nickel layer without any applied pressure; (iii) the 1455 °C melting point of nickel is much higher than the 962 °C melting point of silver [108], and combined with the low, <0.5 wt.% 1000°C solubility of nickel in silver, the porous nickel network should maintain its structure without excess sintering and densification, allowing controlled wetting and spreading of the molten silver.

This novel method poses several benefits. First, only an inert atmosphere is required to prevent the surface oxidation of the nickel particles that increases the silver wetting angle, which is feasible in many production conditions. Secondly, the process doesn't require costly surface deposition techniques, making it more viable for industrial applications. In fact, with the rapid developments in additive manufacturing, the nickel and silver paste can be easily applied with 3D printing. Finally, with the "silver-philic" property of the patterned porous nickel layer and the "silver-phobic" nature of the ceramic surfaces, wetting and spreading of the silver can be easily designed and controlled.

5.2 Materials and Experiments

Figure 5.1 shows schematics diagrams of experimental routes A and B for the proposed method. The nickel and silver pastes were produced by hand-mixing 99.9% pure, -400 mesh sized nickel powder (Alfa Aesar Inc.) or 99.9 % pure, -325 mesh sized silver powder (Alfa Aesar Inc.) with a V-737 organic vehicle (Hereaus, Inc.) in a 2:1 ratio by weight. For both Route A and B, the nickel paste was screen-printed onto different ceramic substrates with designed patterns (i.e. grid, circuit-like lines) and different amounts of passes (for desired thickness of the nickel layer; two and three passes of nickel paste are used for Route A and B in this work, respectively). Samples were dried at 120°C for 10 minutes after each print. Then for Route A, the similar screen-printing and drying process was repeated with the silver paste for desired layer thickness (six passes) on top of the nickel paste printed substrates; whereas for Route B, simply a piece of 99.95% pure silver (Alfa Aesar Inc.) with a mass of ~5 mg was placed atop the nickel paste printed substrates. Finally, the assemblies in both Route A and B were heated to 820°C for 2 hours to remove the organics as well as to partially sinter the nickel powders, and then heated to 1000°C for 30 minutes to allow the silver to melt and spontaneously infiltrate the partiallysintered, porous nickel layer. A ramp rate of 5°C/min was used for both heating and cooling. The entire process was performed in 20 sccm of flowing Ar to prevent nickel oxidation.



Figure 5.1 Schematic diagrams showing Route A and B for the production of silver patterns on ceramic substrates. The 2 hour hold at 820°C partially sintered the nickel particles into a porous network; the 0.5 hour hold at 1000°C allowed the silver to melt, infiltrate, and spread.

5.3 Results and Discussion

Both Routes can be used to place liquid silver in controlled shapes and at designated location on various ceramic substrates, which leads to many different potential applications.

One of the applications was demonstrated previously in Chapter 3 as the silver-nickel brazing method [17], which introduced porous nickel interlayers to improve wetting of silver on YSZ, and eliminated the wetting pores commonly observed with Ag-4CuO brazes (the state-of-the-art braze), and facilitated the joining of stainless steel to YSZ surfaces. It was shown that the square-shaped braze joints were successfully fabricated according to the intended square shape of the screen-printed nickel layer.

5.3.1 Samples with Experimental Route A

Figure 5.2 shows three top-view optical images of a prototype silver circuit with a complicated design on an Al₂O₃ substrate at different manufacturing stages (using Route A in Figure 1). This example showcases another application for high power and/or high temperature circuits and electronics that use ceramic boards. As shown in Figure 5.2a, the silver and nickel material were deposited onto the Al₂O₃ substrate with a predesigned "Spartan head" circuit. The typical line width and height in the as printed condition is ~540 μ m and ~80 μ m, respectively. This circuit design is only for a proof-of-concept study, as smaller line widths could be achieved with further optimization of the screen-printing process. After heating above the melting point of silver, Figure 5.2b shows that the nickel powder had partially sintered into a porous layer and stayed attached to the ceramic substrate, and the silver remained only within the surface region with porous nickel coverage (the "silver-philic" region). The overall line width and height remained the same as compared to Figure 5.2a. In the cross-sectional back-scattered electron

(BSE) images, some individual nickel particles can be observed floating at the top. These are probably some isolated particles that were not attached to the porous nickel layer and could be eliminated in the future by better materials selection and process optimization. Also, similar experiments with only six silver screen-print passes and no nickel passes were also performed, and due to the poor wetting characteristics [139] the silver powder melted and balled-up into individual spheres that did not bond to the Al₂O₃ substrate at all.

Figure 5.2c shows the circuit after 5 hours holding at 850°C in air. Since the electronics using ceramic substrates are usually used for high-power or high temperature applications [126-128], it is important to see if the silver-nickel microstructure is stable with exposure to air at high temperatures. Optically, the circuit showed no apparent difference in the silver portion, no delamination was observed, and the line width remained unchanged. There was only a contrast change in the appearance, which is probably due to the surface oxidation of the silver (the black tip at the bottom right corner is probably caused by insufficient silver deposition during screenprinting, not an effect of the oxidation). The cross-section shows similar width and height of the lines, and it is obvious that the nickel network has undergone some oxidation. The darker grey contrast shows that oxidized parts of the nickel network (NiO), and the cores of some nickel particles are still not oxidized (lighter grey contrast). It is noted that the total silver foot-print (area of silver- Al_2O_3 direct contact) on the Al_2O_3 substrate decreased. However, the majority of the silver is still similar to that in Figure 5.2b, indicating good electrical conduction through the line. In general, the prototype circuit remained dense up to 850°C in air, which should enable some of the most extreme high-temperature conditions.



Figure 5.2 Top-view optical images (top) and cross-sectional back-scattered electron images (bottom) of the silver-nickel circuit on an Al_2O_3 substrate (through Route A) in the (a) as-screen-printed condition, and (b) as-fabricated condition (after silver melt and infiltrated the nickel network); as well as (c) after exposure to air at 850°C for 5 hours.

5.3.2 Samples with Experimental Route B

Figure 5.3 shows the creation of a silver "grid" pattern on Al₂O₃, AlN and YSZ substrates (using Route B in Figure 5.1). When the desired pattern is interconnected and continuous such as that required for current collectors [129], the silver source material can be a bulk piece of the silver metal placed within a part of the nickel printed pattern. Upon melting, the liquid silver only occupies the "silver-philic" regions with porous nickel coverage and did not flow on to the "silver-phobic" regions where the bare ceramics was exposed. Comparing the second and the third row, it is clear that the molten silver infiltrated only in the "grid" pattern even at the sharp edges; and the holes at the center of the pattern that were originally right under the silver pieces (second row) are not covered by silver after infiltration (third row). The bottom row in Figure 5.3 shows the cross-sectional BSE images of the silver-nickel on different substrates. The microstructure shows a partially sintered nickel network (grey contrast) with fully infiltrated silver (light grey contrast) and is very similar to that in Figure 5.2. This method can be used to produce dense current collectors on various ceramic electrodes with well-defined geometries.



Figure 5.3 Optical top-view images of as-printed nickel paste in "grid" patterns on different substrates (first row); with ~5 mg of silver piece on top (second row); after silver melt and infiltrated the nickel interlayer (third row); and cross-sectional back-scattered images of the samples after infiltration. (bottom row). * The scattered white speckles within the AlN substrates are embedded YSZ particles that occurred during polishing.

5.3.3 Preliminary Results on Ni Particle Sizes

As shown in Table 5.1, several nickel powders with different particle sizes were investigated for wetting and spreading characteristics of silver on YSZ|NiO-YSZ substrates. For all the experiments, the porous nickel network was obtained by sintering at ~800°C for 2 hours, and then a piece of silver was placed on top of the nickel network to melt at ~1000°C. "Topdown infiltration" means the molten silver infiltrates the portion of the nickel network right underneath the silver piece; "Spreading within the nickel network" means the molten silver infiltrates and spreads across the entire nickel network.

For the APS (average particle size) 3-7 µm nickel powders, Ag-Ni brazing was successfully performed using square silver foils and square nickel porous interlayers, thanks to their matching pattern size for top-down infiltration. However, during experiments like that with the grid pattern (with a relatively small piece of Ag on a big square Ni pattern), the molten silver breaks the nickel network by pulling in nickel particles and then balls-up. Similar results were also found with APS 2.2-3 µm nickel powders. These results suggest that the integrity of the nickel network (bonding strength between the sintered nickel particles, and the mass of the nickel particles) need to be strong enough to fight back against the surface tension at the infiltration front of the molten silver to allow continuing infiltration within the nickel network.

Nickel powders with particles sizes between $7 \sim 40 \,\mu\text{m}$ are worth investigating for future studies. Sintering temperature and time, material-to-organics ratio within the nickel paste, amount of nickel paste dispensed are also important parameters to consider for improving the structural integrity of the porous nickel network.

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Ni Powder	Top-down Infiltration	Spreading within the Ni Network	Comments
Average Particle Size 2.2 - 3 µm	NO	NO	• Surface tension on the molten Ag breaks the Ni network and lead to balled up Ag beads on YSZ substrates.
Average Particle Size 3-7 µm	YES	NO	 Surface tension on the molten Ag breaks the Ni network sintered at 800°C for 2 hours. Can be used in Ag-Ni brazing when Ag foil in the shape of the Ni pattern is used.
-400 mesh (<37µm)	YES	YES	• Ag spreads according to the Ni pattern.
-325 mesh (<44µm)	YES	YES	• Ag spreads according to the Ni pattern.

Table 5.1 Wetting and Spreading Characteristics on Nickel Networks Fabricated with Different Sized Nickel Particles.

5.3.4 Potential Issues with the Ag-Ni Wetting Method

It should be noted that because the wetting process in this work is non-reactive in nature, and the nickel layer exhibits no reaction with the ceramic substrates, the bonding between the solid silver-nickel structure and the ceramic substrate is solely dependent on the physical adhesion between the two materials. Hence, the interfacial bonding strength will vary depending on the ceramic substrate and care must be taken to ensure sufficient mechanical stability. 5.4 Summary

Control of wetting and spreading of liquid silver on various ceramic substrate has been achieved through a novel method by constructing porous nickel patterns on the ceramic substrates. Dense silver layers were obtained in different shapes/designs on alumina, aluminum nitride and YSZ substrates. With further optimization, many more applications can be realized through this controlled wetting/spreading process, such as ceramic-to-ceramic/metal joining, current collectors for ceramic electrodes, and high-temperature electronics for LEDs, downhole drilling operations, sensors etc. [127].

CHAPTER 6

Conclusions and Future Work

6.1 Conclusions

In this dissertation, two approaches were investigated to find a replacement braze for the current Ag-CuO RAB brazing system used for SOFC sealing applications. One approach was to design a new silver-free, self-passivating braze from scratch using an integrated computational-experimental method. The other was to improve the wetting mechanism of the current RAB brazing system though the development of a CuO-free, silver-based braze.

In the first approach for a silver-free braze, binary and ternary alloys with solidus temperatures equal to or greater than ~900°C and liquidus temperatures equal to or less than ~1000°C were identified through Thermo-Calc phase diagram modeling. All 828 of the ternary Ni-based, Co-based, and Cu-based alloy systems containing B, C, Mg, Al, Si, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Y, Zr, Nb, Mo, Ag, In, Sn, Hf, Ta, and/or W were analyzed and 114 ternary alloy systems with the desired melting point characteristics were identified. Experimental wetting, oxidation resistance and mechanical property tests on alloys in 43 of these systems identified Ni-Si, Cu-Cr, and Cu-Al alloys worthy of additional study. In-situ wetting studies indicated that these alloys exhibited poor wetting on bare and surface-treated YSZ a and alumina-coated stainless steel in inert gas atmospheres. In response to these wetting challenges, a novel multilayer braze architecture was developed and the production of a high strength Al₂O₃-SS441/braze/Ni-foil/Cu-foil/YSZ braze joint was produced in inert atmosphere. Unfortunately, this braze joint did not survive service in air due to oxidation of the copper layer. Further research efforts were spent on (1) alterative multilayer braze joint layer compositions and (2) through the use of YSZ bonding layers that could be transient during or after brazing. However, the copper layer used as the YSZ bonding layer showed significant Kirkendall void formation after homogenizing with the nickel-based layer. As a result, the search for a new, replacement, silver-free SOFC braze was not successful. For future studies, better understanding of the interfacial properties at the braze/YSZ interface during melting and wetting in different local atmospheres is needed.

In the other approach to improve the wetting characteristics of silver-based brazes without CuO additions, a transient porous nickel interlayer, instead of reactive element additions or CuO, was used to promote Ag wetting on YSZ and produce high-quality YSZ-stainless steel braze joints. Mechanical tests on these reactive-element-free, silver-based SOFC braze joints, both before and after 500 hours of 750°C oxidation in air, show that the braze and braze interface strength are higher than the underlying YSZ|NiO-YSZ substrate. The elimination of Type I and Type II porosity enabled by this new technique should improve braze lifetimes for SOFC and other ceramic-to-metal sealing applications. Further, the microstructural and compositional evolution of SS|Ag-Ni|YSZ and SS|Ag-3CuO|YSZ braze joints exposed to air on one side and 4%H₂-96%N₂ on the other side for 300 hours of isothermal 750°C aging or 300 25°C/min 35-830°C rapid thermal cycles were compared. While both brazes displayed considerable microstructural and compositional evolution during both tests, only the Ag-Ni brazes remained pore free and well bonded, suggesting that Ag-Ni brazes may be more suitable for long term SOFC operation than Ag-CuO brazes. These results on the novel silver-nickel method indicate good operational robustness for SOFC devices and should lead to improved SOFC life-times.

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Additionally, the wetting improvements of silver on ceramic substrates in the second approach also inspired some other applications. The wetting and spreading of liquid silver (at ~1000°C) was enabled by the deposition of a micro-patterned nickel layer. The porous nickel interlayer directed the flow of molten silver, resulting in dense silver layers with designed shapes. Different silver patterns can be achieved on various substrates, which could be used for many applications such as ceramic circuits, current collectors for ceramic electrodes, ceramic to ceramic/metal joining etc.

6.2 Recommendations for Future Work

Although oxidation tests and dual atmosphere aging as well as thermal cycling tests were performed on the Ag-Ni brazes and analyzed. The details of the mechanical properties of the Ag-Ni braze under these test conditions are not fully understood. To better simulate the operational conditions of the braze joints, SS and YSZ|NiO-YSZ substrates in SOFC manufacturing were used. But these substrates are not ideal for mechanical testing, i.e. the YSZ|NiO-YSZ substrate is porous and has a very low strength, which lead to early fracture during testing before the Ag-Ni braze is fully deformed. Better sample design should be proposed to investigate the ductility, bonding strength of the Ag-Ni braze under various conditions.

Also, it is necessary to perform a reliability test in a commercial SOFC stack with realistic operating conditions. This test would be time consuming, but it would provide valuable insights into the long-term stability of the Ag-Ni braze.

Several parameters in the Ag-Ni wetting process should be further studied and optimized for different applications. These parameters include but are not limited to the nickel particle size, silver particle size/foil thickness, the materials-organic vehicle ratio in pastes, the nickelsilver materials ratio, the pre-sintering temperature of nickel particles, the brazing/wetting time and temperature. This is especially important for the wetting control of molten silver on ceramic substrates. More ceramic substrates need to be investigated for the Ag-Ni wetting process. Furthermore, depending on the application, there are different requirements of the silver pattern, such as the silver line width, the silver layer thickness, the silver-substrate contact area etc. Stability and reliability of the Ag-Ni patterns in operational conditions should be assessed.

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In the present work, only the Ag-Ni system using pure silver and nickel was investigated. This also imposed some limitations such as substrate selection, fabrication temperature and atmosphere, interfacial bonding strength etc. Similar immiscible systems and/or minor element additions could be explored to expand the materials selection. REFERENCES

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