Full length article

Transient porous nickel interlayers for improved silver-based Solid Oxide Fuel Cell brazes

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A B S T R A C T

Silver-copper oxide reactive air brazes are the most widely used Solid Oxide Fuel Cell (SOFC) brazes. However, the conventional Ag-4 wt.% Cu composition has a high wetting angle of ~40° in air on yttria-stabilized-zirconia (YSZ) that leads to manufacturing defects (denoted as Type I pores). Also, many elements that oxidize during brazing to promote braze wetting (such as Cu) are easily reduced by SOFC fuels. This results in Type II pores that decrease the braze interfacial strength and provide a quick path for hydrogen permeation into the braze (where the hydrogen reacts with diffused oxygen to form gaseous water pockets, denoted as Type III pores). The present work demonstrates 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 reactive-element-free, silver-based SOFC braze joints, both before and after 500 h of 750 °C oxidation in air, show that the braze and braze interface strengths are higher than the underlying YSZ|NiO-YSZ substrate. The elimination of Type I and Type II porosity enabled by this new technique should result in improved braze lifetimes for SOFC and other ceramic-to-metal sealing applications.

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1. Introduction

Solid oxide fuel cells (SOFCs) are electricity generation devices that convert chemical energy directly into electrical energy with higher efficiency and less environmental impact than traditional power generation methods [1,2]. Moreover, SOFCs have the highest volumetric and gravimetric power densities of any electricity generation technology [2,3]. They are also capable of utilizing a wide range of fuels/energy-carriers such as hydrogen, natural gas, etc. [1–3]. 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 stainless steel (SS) to the SOFC electrolyte, as shown schematically in Fig. 1a. Compared to competing technologies such as glass or mica seals, brazes offer higher joint strengths and lower joint permeabilities [4]. Unfortunately, most brazes have difficulty wetting ceramics such as YSZ [5]. To overcome this problem, the SOFC community has utilized flux-free, reactive air brazes (RABs) where oxidizable metals are added into silver for improved ceramic

wettability [6–8]. 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 [4,9–17]. One of the benefits of the RAB technique, which has been used by various SOFC manufacturers such as Delphi [18] and General Electric [19], 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 [20–22].

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 h [23], which is well below the ~40,000 h often cited as necessary for commercially-viable stationary SOFC deployment [24]. First, as shown in Fig. 1b, RAB joints often exhibit manufacturing defects (denoted as Type I pores) resulting from the relatively high ~40° wetting angle of Ag-4CuO on YSZ. Second, as shown in Fig. 1c, 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; providing a fast percolation path for hydrogen permeation into the center of the joint [14,25–27]. Third, as shown in Fig. 1d, gaseous water pockets

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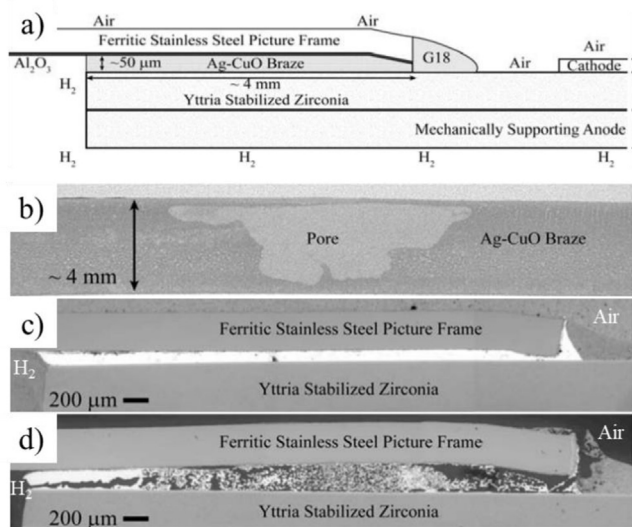
Fig. 1. a) Schematic of a typical planar, stainless-steel-picture-frame supported SOFC, b) an X-ray radiograph top-view showing a wetting pore (i.e. a Type I pore, light central region) incurred in a conventional Ag-CuO RAB joint (i.e. not the Ni-Ag joints presented in this paper) used to join SS and YSZ c) a scanning electron microscopy side-view showing interfacial pores from the reduction of CuO (i.e. Type II pores, black dot) near the H_2 side of an Ag-CuO RAB joint, and d) a scanning electron microscopy side-view showing water pockets (i.e. Type III pores, black dots) in an Ag-CuO RAB after long term SOFC operation.

(denoted as Type III pores) form from hydrogen and oxygen that has migrated into the braze [24]. The kinetics of Type III pore formation is enabled by the moderately high, 750 °C hydrogen and oxygen diffusivity in silver of 8×10^{-5} and 1.5×10^{-5} cm^2 s, respectively [28].

The hypothesis of the present work was 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° [29] on nickel in air (because NiO forms on the surface of Ni), this drops to < 30° for $pO_2 < 10^{-9}$ atm [30]. This low wetting angle should make Type I pores less likely to form (compared to Ni-CuO joints) in Ni-Ag joints made with local pO_2's < 10^{-9} atm. Second, since spontaneous liquid infiltration into porous solid media occurs for wetting angles below 51° [31], 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 [32], the low 962 °C melting point of Ag [32], and the low, <0.5 wt% 1000 °C solubility of Ni in Ag [32] 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 pO_2 ~10^{-12} atm at ~1000 °C and kinetically stabilized for a few hours at even lower oxygen partial pressures [20,33], it should be possible to braze cathode-containing SOFCs for short times in inert or locally mildly reducing atmospheres without decomposing them [34]. Lastly, and perhaps most importantly, nickel can be protected from oxidation during brazing in an inert atmosphere cover gas by either 1) the decomposition of carbon-containing nickel paste organic additives during porous nickel interlayer production (carbon sets the local 850 °C pO_2 at ~10^{-17} atm [34] even though the incoming inert atmosphere will have a pO_2 ~10^{-6} atm), or 2) stainless steel chromium oxidation (which sets the local pO_2 even lower [34]) during

brazing. Hence, since NiO will not form at 1000 °C in $pO_2 < 10^{-11}$ atm [34], joints with porous nickel interlayers produced in inert atmospheres should be free of Type II pores.

Conversely, several considerations suggested that it might not be possible to use porous nickel interlayers to produce high-quality YSZ-stainless steel braze joints. For instance, Ni additions could degrade braze interface strengths because the stress induced by 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 1) investigate 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 h of 750 °C oxidation in air.

2. Experimental methods

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 × 25 mm trilayer substrates consisting of a dense, ~15 μm thick YSZ electrolyte, a ~15 μm thick NiO-YSZ function anode layer and a ~500 μm thick porous NiO-YSZ anode layer. Two passes were used to print each layer, and 10 min 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 μm thick E80 emulsion (Sefar Inc.) was used for screen printing. Second, in 20 sccm of flowing Ar, the samples were ramped at 5 °C/min, held at ~810 °C for 2 h, and cooled to room temperature with a 5 °C/min nominal cooling rate to produce partially sintered nickel layers. Third, a 75 μm 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 ~970 °C for either 15 or 30 min, and cooled to room temperature with a 5 °C/min nominal ramp rate in 20 sccm of Ar.

2.2. Oxidation testing

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

2.3. Mechanical testing

As shown in Fig. 2a and b, 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 × 0.635 cm square brazed joints (two on each side). As shown in Fig. 2c, an extensometer was affixed to both stainless steel plates to measure the real extension in the braze regions, and all samples were tested to failure at room temperature with a displacement rate of 0.009 mm/min. The shear stress σ_{shear} and strain ε_{shear} were estimated using the equations:

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

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