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# An Ag based brazing system with a tunable thermal expansion for the use as sealant for solid oxide cells

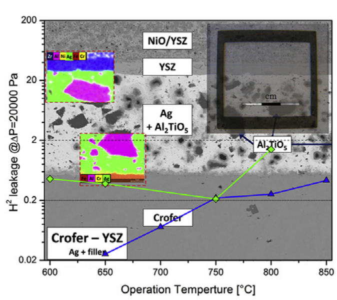
Ragnar Kiebach [a, *], Kurt Engelbrecht [a], Laila Grahl-Madsen [b], Bertil Sieborg [b], Ming Chen [a], Johan Hjelm [a], Kion Norrman [a], Christodoulos Chatzichristodoulou [a], Peter Vang Hendriksen [a]

[a] *Department of Energy Conversion and Storage, Technical University of Denmark, Risø Campus, Frederiksborgvej 399, DK-4000 Roskilde, Denmark*
[b] *IRD Fuel Cell A/S, Kullinggade 31, DK-5700 Svenborg, Denmark*

## HIGHLIGHTS

- Ag-$Al_2TiO_5$ was successfully tested as sealant for SOFC/SOEC applications.
- The thermal expansion coefficient of the Ag-$Al_2TiO_5$ composite braze can be tailored.
- Sufficient low leak rates were obtained.
- Successful operation in air and reducing atmosphere.
- Ag-$Al_2TiO_5$ braze system is applicable for the use in SOFC/SOEC stacks.

## GRAPHICAL ABSTRACT

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## ABSTRACT

An Ag-$Al_2TiO_5$ composite braze was developed and successfully tested as seal for solid oxide cells. The thermo-mechanical properties of the Ag-$Al_2TiO_5$ system and the chemical compatibility between this composite braze and relevant materials used in stacks were characterized and the leak rates as a function of the operation temperature were measured. The thermal expansion coefficient in the Ag-$Al_2TiO_5$ system can be tailored by varying the amount of the ceramic filler. The brazing process can be carried out in air, the joining partners showed a good chemical stability and sufficient low leak rates were demonstrated. Furthermore, the long-term stability of the Ag-$Al_2TiO_5$ composite braze was studied under relevant SOFC and SOEC conditions. The stability of brazed Crofer/Ag-$Al_2TiO_5$/NiO-YSZ assemblies in reducing atmosphere and in pure oxygen was investigated over 500 h at 850 °C. Additionally, a cell component test was performed to investigate the durability of the Ag-$Al_2TiO_5$ seal when exposed to dual atmosphere. The seals performed well over 900 h under electrolysis operation conditions (−0.5 A $cm^2$, 850 °C), and no cell degradation related to the Ag-$Al_2TiO_5$ sealing was found, indicating that the developed braze system is applicable for the use in SOFC/SOEC stacks.



## 1. Introduction

Research on solid oxide fuel cells (SOFC) as well as on hydrogen/syngas production using solid oxide electrolysis cells (SOEC) has increased in the last years [1–6]. The development and testing of sealing materials is a concern for stack developers, and several

* Corresponding author.
*E-mail address:* woki@dtu.dk (R. Kiebach).

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concepts using different materials are currently tested for gas seal applications. Glass and glass-ceramics have been the object of several studies in the last years [7–12], but problems like low thermal expansion coefficients (TEC) compared to other stack components [13–15] and the tendency to react with materials, have not yet been solved completely. Also crystallization during operation leads to changes in microstructure and mechanical properties, which may result in cracking and loss of gas tightness over time [16–18]. Seals in SOFC/SOEC stacks must also be tolerant to a high steam content and should have a low tendency to emit Si to avoid Si poising of the electrodes [19,20]. Especially the last point challenges the use of glass or glass ceramic seals.

Therefore, a number of alternative sealing techniques like compressive mica seals [15,21,22] or brazing are under consideration. Especially brazing is particularly attractive for stack concepts requiring strong interfaces and good sealing also in the absence of a loading force on the seal. In this method a matrix material, with a melting point significantly below that of the materials to be joined, is heated until it melts or becomes sufficiently soft to fill out the gaps between the components to be joined.

Active metal brazing (AMB) and reactive air brazing (RAB) [15,17,23–38] are the two most studied brazing techniques for SOC (solid oxide cell) applications. In AMB, the used matrix contains an active metal addition like Ti, Zr or Hf, which reacts with the ceramic, e.g. YSZ (yttria stabilized zirconia, forming a layer at the interface, which lowers the interfacial energy and promotes wetting [28,29,39]. The disadvantage of AMB is, that an inert atmosphere (Ar, He), a relatively strong vacuum ($<10^{-5}$ mbar) or a reducing atmosphere is required during the sealing process to avoid an uncontrolled oxidation of the sealing material. Compared to simple air fired processes this entails a higher production cost. Also the low $pO_2$ required during the brazing process could be problematic for the oxide materials used as SOC oxygen electrodes, if it lies below the decomposition $pO_2$ of the applied compounds possibly leading to an irreversible deterioration due to phase separation.

RAB brazes consist of a noble metal (Ag, Pd, Au, Pt) as matrix and an oxide component (typically CuO) that partially dissolves in the molten noble metal [31–34,36,40,41]. Like in AMB, the oxide compound modifies or reacts with the surface of the (ceramic) substrate, and the newly formed surface is wetted by the molten filler. RAB joining can be carried out in air.

A disadvantage of using an Ag-CuO braze is that often a relatively thick layer (>20 μm) of metal oxides is formed as reaction product during the brazing. Especially for ferritic steels used for SOC applications (e.g. Crofer 22 APU), a layer of Cr/Cu/Mn/Fe-oxides is found due to the reaction of the CuO and the steel surface during the brazing procedure [17,29,32,42,43]. This reaction zone has been observed to be the mechanically weakest part in the joint and is prone to mechanical failure [34,44]. Another disadvantage of the RAB brazes is their high thermal expansion coefficient (TEC) compared to the other materials used in SOFC/SOEC stacks. Standard RAB brazes (Ag with 4% CuO) have a TEC of $20 \cdot 10^{-6}$ K$^{-1}$, while the ceramic cells and the typically used steels have TECs between $10 \cdot 10^{-6}$ K$^{-1}$ and $13 \cdot 10^{-6}$ K$^{-1}$). This difference in TEC is problematic for the mechanical integrity, as the stresses and stored elastic energy in the stack, which can drive crack propagation, are proportional to it.

To overcome the problems of a thermal coefficient mismatch and the formation of a fragile reaction layer, a composite braze sealant using Ag with $Al_2TiO_5$ as ceramic filler has been developed. $Al_2TiO_5$ was chosen because of its chemical stability and for its very low thermal expansion coefficient of 1–2 $10^{-6}$ K$^{-1}$ [45,46].

In the study presented here, the thermo-mechanical properties of the Ag-$Al_2TiO_5$ system and the chemical compatibility between this composite braze and relevant stack components (YSZ, NiO and Crofer 22 APU steel) of the braze are discussed. Also, the leak rates through a seal made of this composite braze was measured as a function of the operation temperature. Additionally, the long-term stability of the braze under SOFC/SOEC relevant conditions, including thermal cycling in SOFC/SOEC relevant atmospheres and the use as sealant in cell tests is described.

## 2. Experimental

### 2.1. Materials and sample preparation

Samples for differential scanning colorimetry (DCS) and dilatometry measurements were prepared by mixing Ag powder (1 μm, Sigma-Aldrich) and $Al_2TiO_5$ powder (Sigma-Aldrich). The mixed powders were pressed (2t, uniaxial pressing) into rods with a diameter of 7 mm and ~1.5 cm in length. Samples with 5 wt%, 10 wt %, 15 wt% and 17.5 wt% of $Al_2TiO_5$ were produced. To obtain fully dense samples, the rods were sintered for 5 h at 900 °C in air. For dilatometry and mechanical measurements, the ends of the rods were cut parallel using a diamond saw after sintering.

For the joining as well as for the leak experiments Ag paste (CERMET SILVER CONDUCTOR 9907) from ESL Electro-Science was screen printed on the Crofer 22 APU (Thyssen Krupp) steel. Different amounts of $Al_2TiO_5$ (Sigma-Aldrich) with a particle size < 22 μm were added to the pure Ag paste. The maximum amount of $Al_2TiO_5$ added was 10 wt % (based on Ag solid load in the ink). The addition of higher amounts of ceramic filler into the commercial Ag ink was not feasible, since inks containing such high amounts of ceramic filler had a high viscosity and were no longer printable. To achieve screen-printable inks with a higher amount of $Al_2TiO_5$ powder, an in-house ink was made by mixing 80 wt % Ag powder (1 μm, Sigma-Aldrich) and 20 wt% $Al_2TiO_5$ powder (<22 μm, Sigma-Aldrich). The mixed powders were added to the remaining organic ink components (Downnol™ (Dow chemical company), BLS™ (Mayzo), Disperbyk® 180 (Altana) and Santicizer® 261 A (Ferro)). These inks were used in the long-term experiments described in 2.6.

For joining experiments, the Ag paste with the filler were screen printed on steel sheets. To obtain different thicknesses of the Ag braze, 1 to 3 layers were printed. In this multilayer printing process, the printed assembly was dried after each printing step at 120 °C in a belt furnace in air. Typically, one screen printed layer of Ag paste resulted in a 29 μm thick joint after brazing. Planar NiO-YSZ-supported solid oxide cells half cells [47] were used as “joining partners” to the Crofer sheets. The cells have 10–13 μm thick dense YSZ electrolytes and are supported by 300 μm thick NiO-YSZ layers. All materials were cut into 2 cm × 2 cm specimens and the joining was conducted by placing the Crofer plates with the screen printed braze on top the dense YSZ electrolyte or the Ni-YSZ support of the non-reduced half-cells. To ensure contact during brazing a load of 3.2 kg/cm$^2$ was applied. The assemblies were heated in air with 100 K/h to the final brazing temperature, which varied between 920 °C and 950 °C. After 20 min at the brazing temperature the samples were cooled down (60 °C/h) to room temperature.

### 2.2. Differential scanning colorimeter and dilatometry

The melting points of the composite brazes were measured using a Differential Scanning Calorimeter (DSC) Netzsch DSC 404C. Measurements were performed in argon with a heating rate of 10 °C/min up to 1350 °C. Specimens with parallel ends were used for the dilatometry, which was carried out in $N_2$-atmosphere in a Netzsch DIL 404C applying a heating rate of 3 °C/min to 800 °C and using the automatic “softening point detection” (provided in the