# REACTIVE AIR BRAZED CERAMIC-METAL SEALS FOR SOFC: MECHANICAL PROPERTIES AND LONG-TERM BEHAVIOUR

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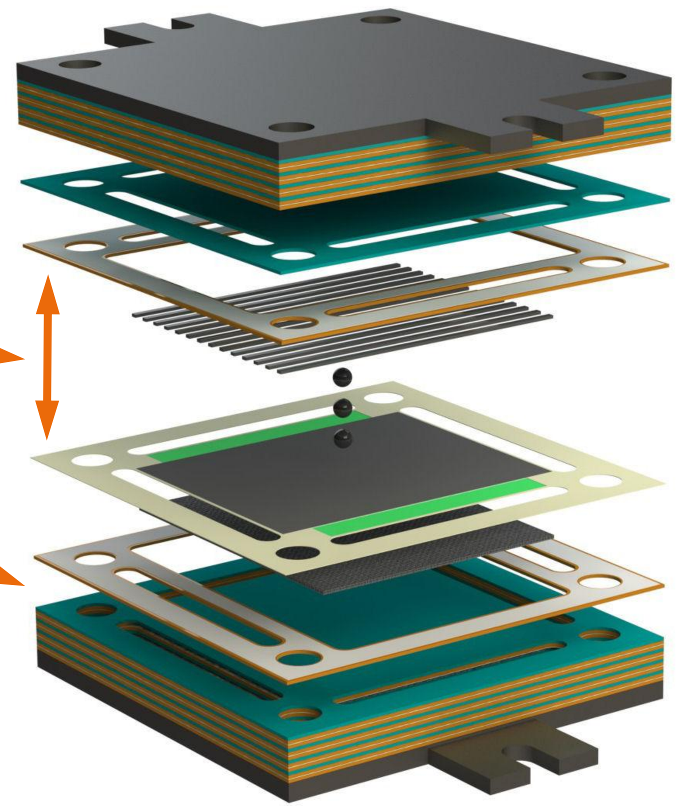
# REACTIVE AIR BRAZED CERAMIC-METAL SEALS FOR SOFC: MECHANICAL PROPERTIES AND LONG-TERM BEHAVIOUR

- Introduction
- Materials and methods
- Bending strength and microstructure
  - After brazing
  - After ageing
- Conclusions

# Introduction
## Sealing and Joining of Solid Oxide Fuel Cells (SOFC)

- Function
  - (Gas-)tight connection of stack parts
  - Examples
    - Cell and interconnect
    - Manifold sealing between interconnects
- Requirements
  - Long-term stability at operating temperature 700…850 °C
  - Chemical stability against aggressive environment ($H_2$-cont. fuel gas, off gas)



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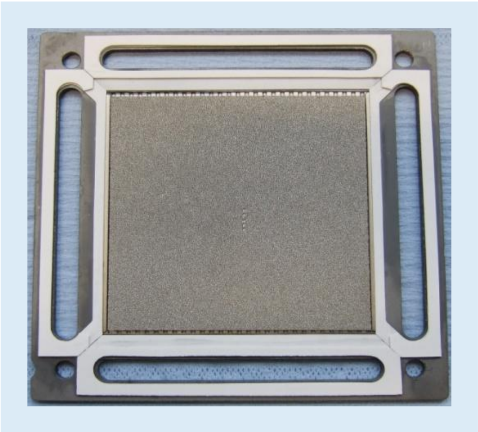
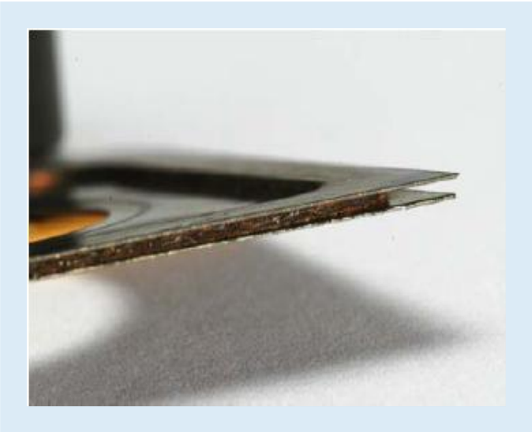
# Introduction
## Sealing and Joining of Solid Oxide Fuel Cells (SOFC)



- Glass based seals
  - Ba-Al-Si glasses and glass ceramics
  - Wide range of technologies
  - Low strength
  - Slow but steady degradation

- Brazed joints
  - Metallic brazes with active components
  - Active metal brazing / reactive air brazing
  - High strength
  - Less degradation than glass based seals?



- Compound seals
  - Hybrid materials: mica + binder / seal or elastic metal components
  - Must be compressed
  - No long-term stability

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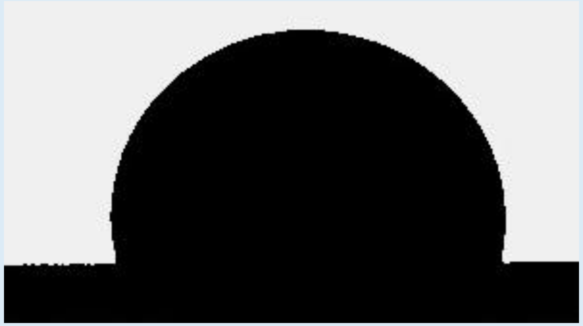
# Introduction

## Reactive Air Brazing (RAB)

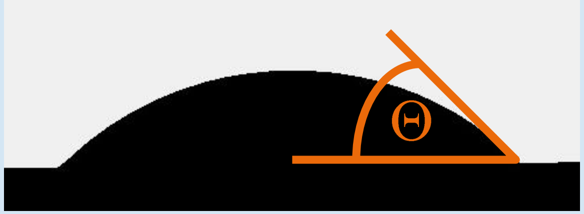
- Brazing process in air at temperatures around 1000 °C
- Braze composition
  - Noble metal (mostly Ag)
  - Metal oxide (e.g. CuO) or
    in-situ oxidation of e.g. Cu to CuO
- Wetting of the ceramic by molten metal oxide
- Modification of the ceramic surface
- Miscibility of the metal oxide in the noble metal
- Wetting by the braze filler metal

Non-wetting



Ag on $ZrO_2$ at 1000 °C in air

Wetting




Ag-4CuO on $ZrO_2$

Ag-4CuO on ferritic steel
at 1000 °C in air





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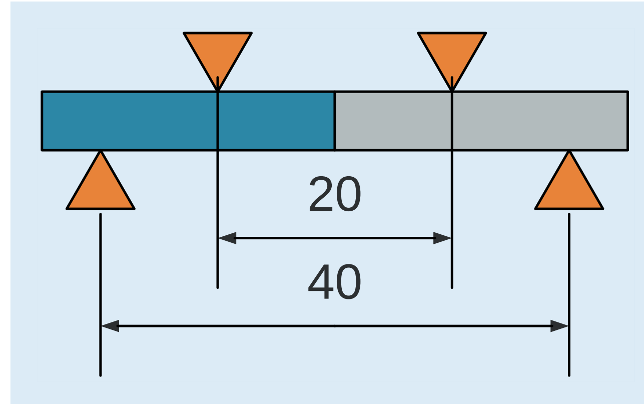
# Materials and Methods

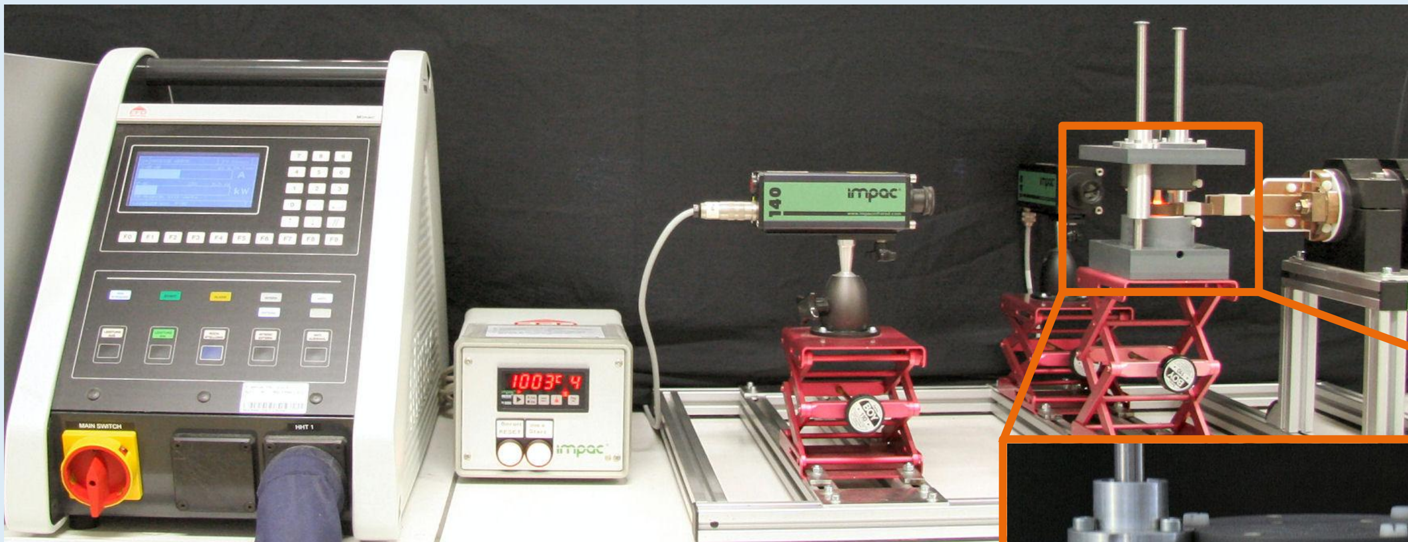


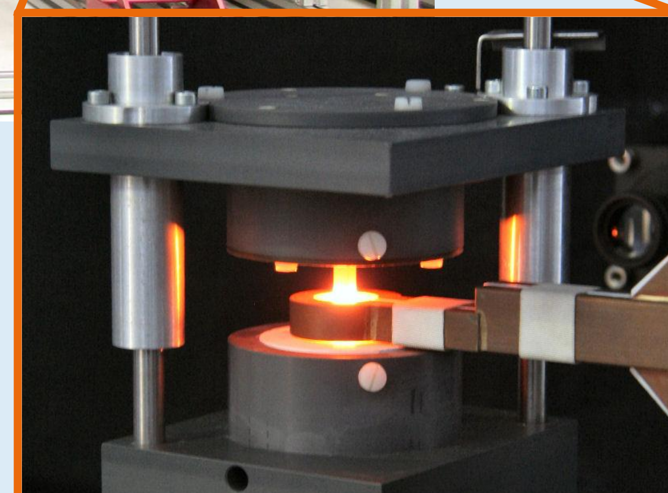

- RAB brazing pastes
  - Ag-4CuO
  - Ag-4CuO-0.5$TiH_2$
  - Ag-8CuO-0.5$TiH_2$
- Comparison of 2 brazing processes
  - Induction brazing ($t_{braze}$ = 2 min)
  - Furnace brazing ($t_{braze}$ = 18 min)
- Joining partners
  - 3 mol% $Y_2O_3$-$ZrO_2$ (3YSZ)
  - Ferritic steel
- Mechanical testing
  - 4-point bending test
  - Specimen size 5 x 5 x 50 mm
  - Ageing for 800 h at 850 °C in air
  - SEM and EDS on cross sections and fracture surfaces

Chemical composition of the metallic alloy in mass%.

| Metallic Alloy | Fe | Cr | Mn | Residual |
|---|---|---|---|---|
| Crofer 22 APU (ThyssenKrupp VDM) | bal. | 20.0-24.0 | 0.3-0.8 | La, Ti, Al, Si |

# Experimental Set-up for Induction Brazing



- Temperature cycle for induction brazing
  - 250 K/min heating rate
  - Brazing at 1000 °C for 2 min
  - 90 K/min cooling rate





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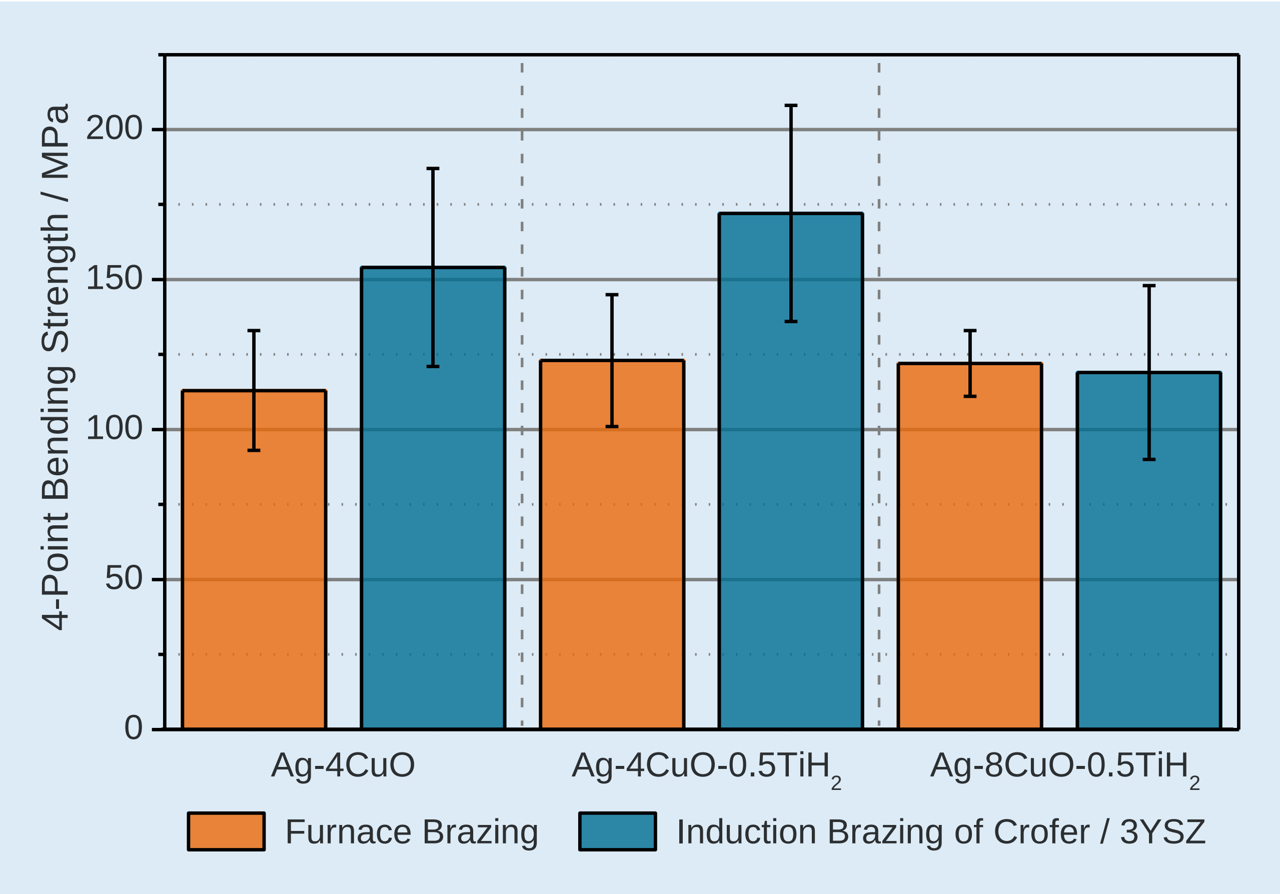
# 4-Point Bending Strength of Brazed Samples

## Comparison of Furnace and Induction Brazing




- Average values of 10 samples
- Brittle fracture of all samples
- High strength for induction brazed samples with low CuO content





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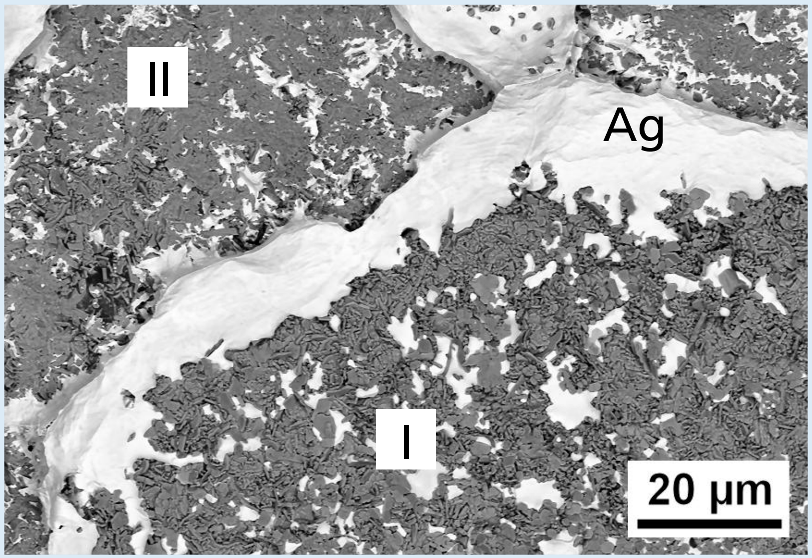
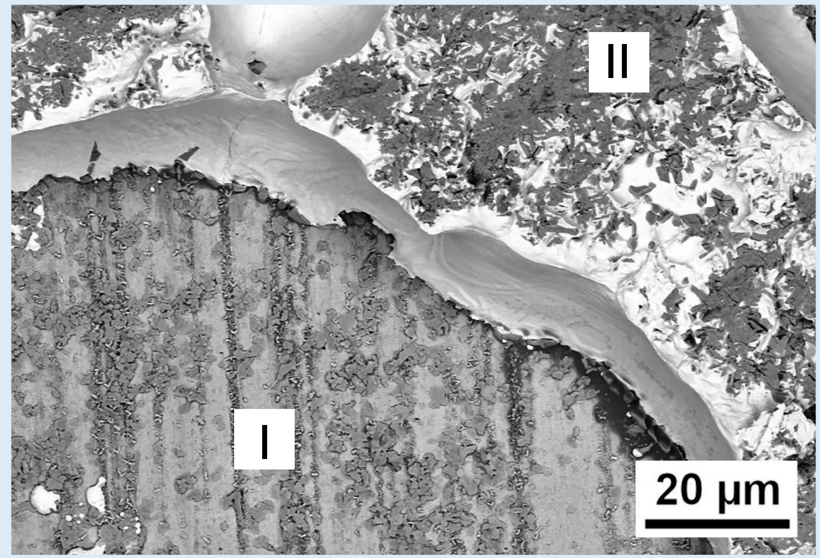
# Fractography of Induction Brazed Samples
## Crofer / Ag-4CuO / 3YSZ

Crofer side



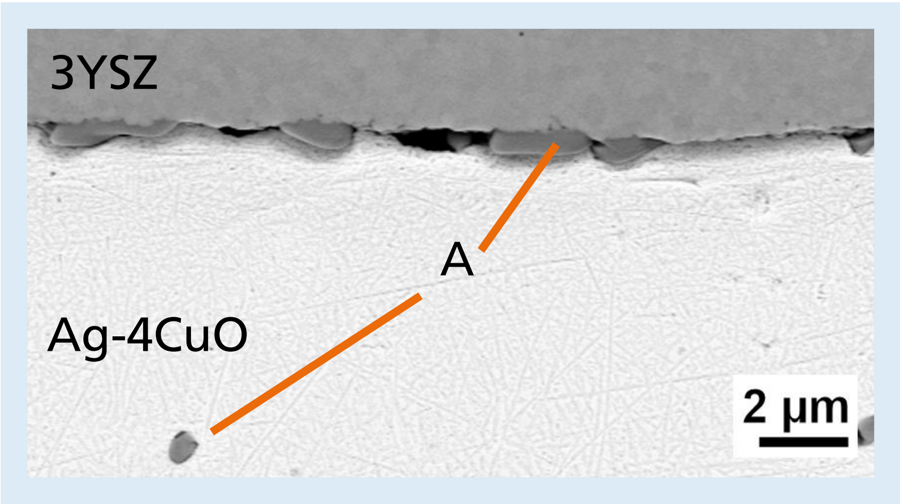

3YSZ side

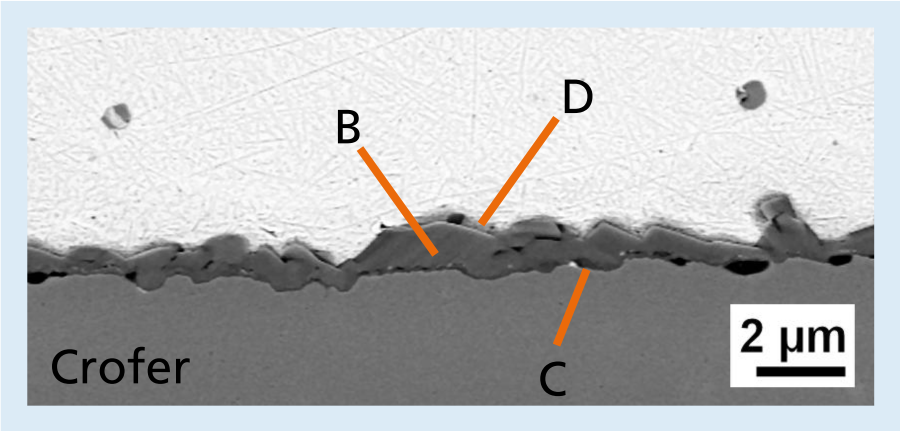



- Fracture proceeds through
  - I Reaction layer at braze-3YSZ interface
  - II Reaction layer at braze-Crofer interface
- Fracture transition inside Ag braze matrix

# Microstructure of Induction Brazed Samples

## Crofer / Ag-4CuO / 3YSZ




- Reaction layer at braze-3YSZ interface
  - Very thin, non-continuous interfacial layer
  - A Cu oxide
- Reaction layer at braze-Crofer interface (complex structure)
  - 1 µm thick, continuous layer
  - B Cu-Cr-Fe oxide
  - C Cr oxide (very thin, non-continuous)
  - D deposited Cu oxide





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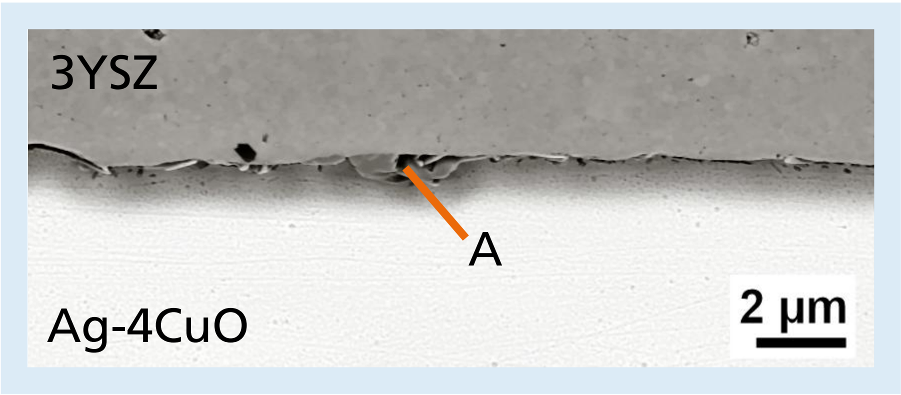
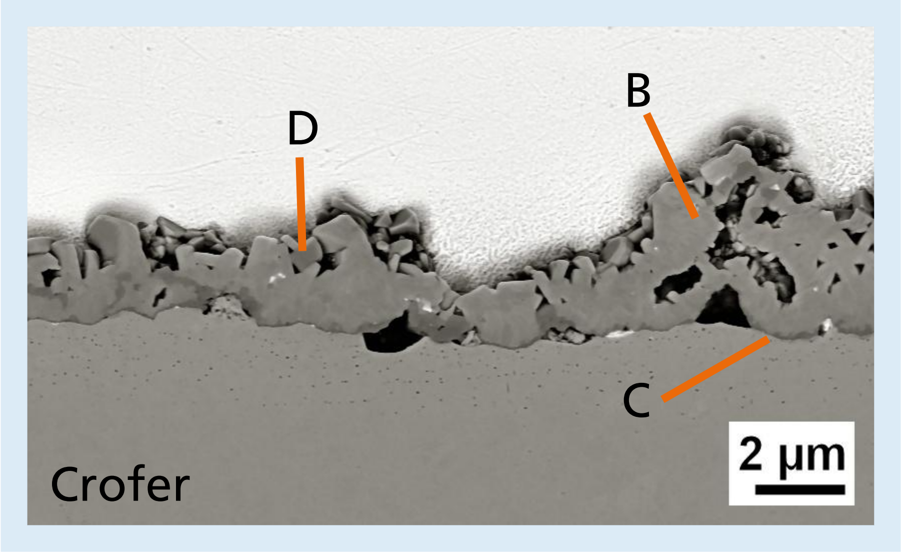
# Microstructure of Furnace Brazed Samples

## Crofer / Ag-4CuO / 3YSZ

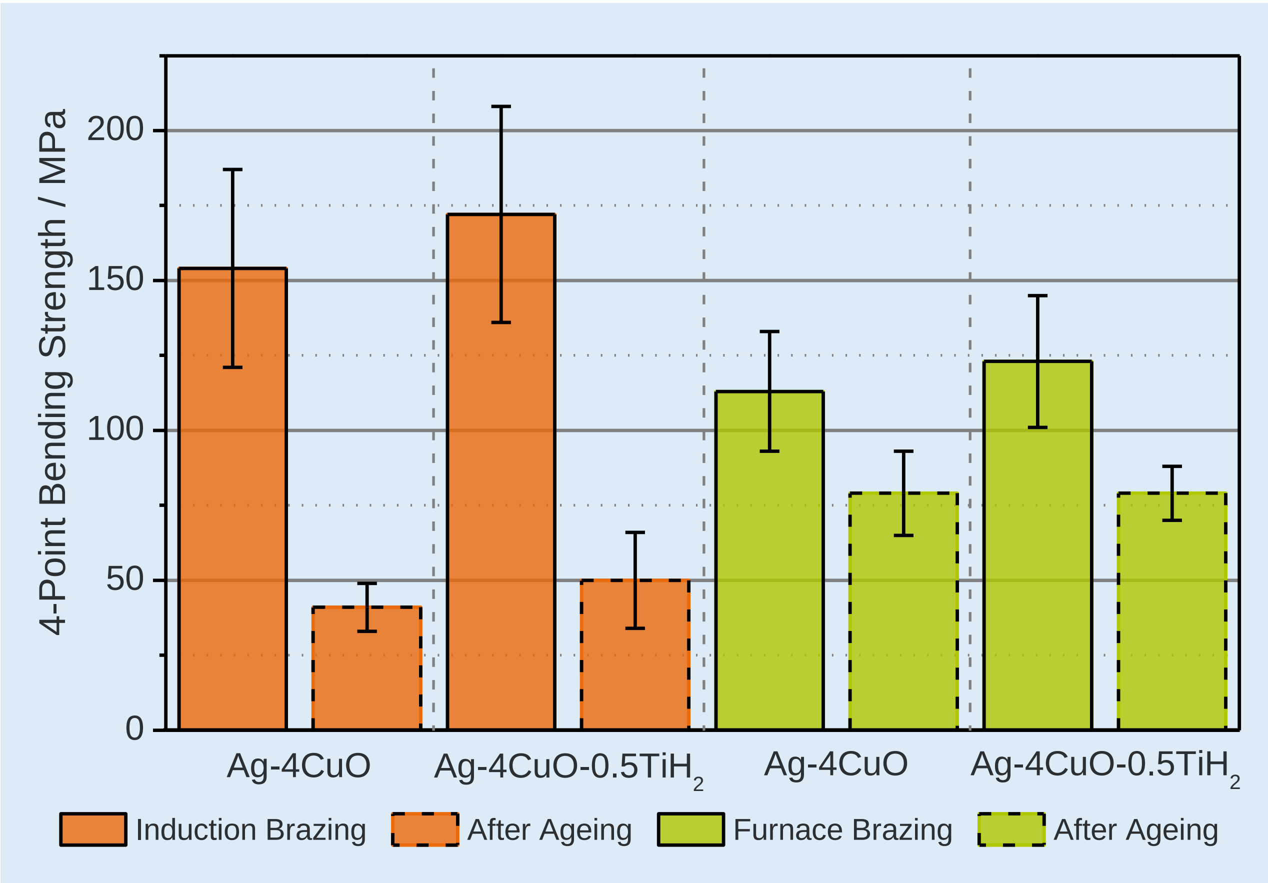



- Reaction layer at braze-3YSZ interface
  - Very thin, non-continuous interfacial layer
  - A Cu oxide




- Reaction layer at braze-Crofer interface (complex structure)
  - 4 µm thick, porous layer
  - B Cu-Cr oxide
  - C Cr oxide (very thin, continuous)
  - D Cu-Cr-Fe oxide

# 4-Point Bending Strength After Ageing for 800 h at 850 °C in Air - Comparison of Brazing Processes

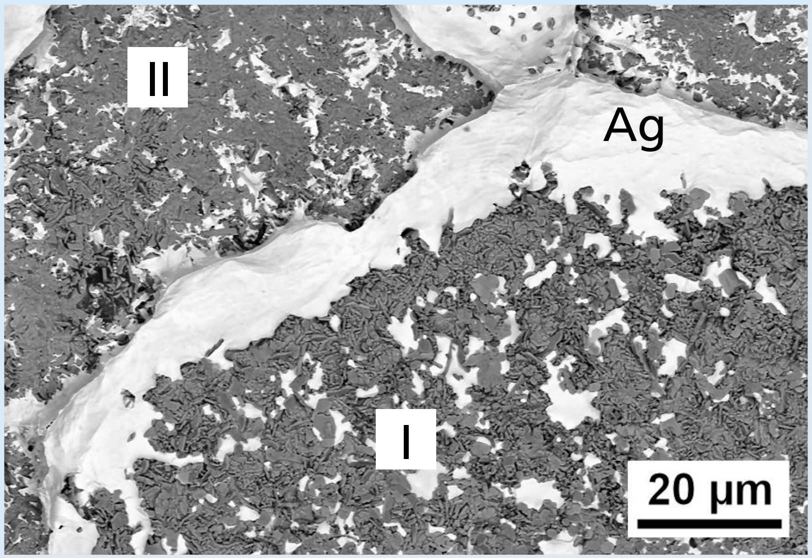



- Average values of 10 samples
- Brittle fracture of all samples
- Induction brazed samples show stronger decrease in strength

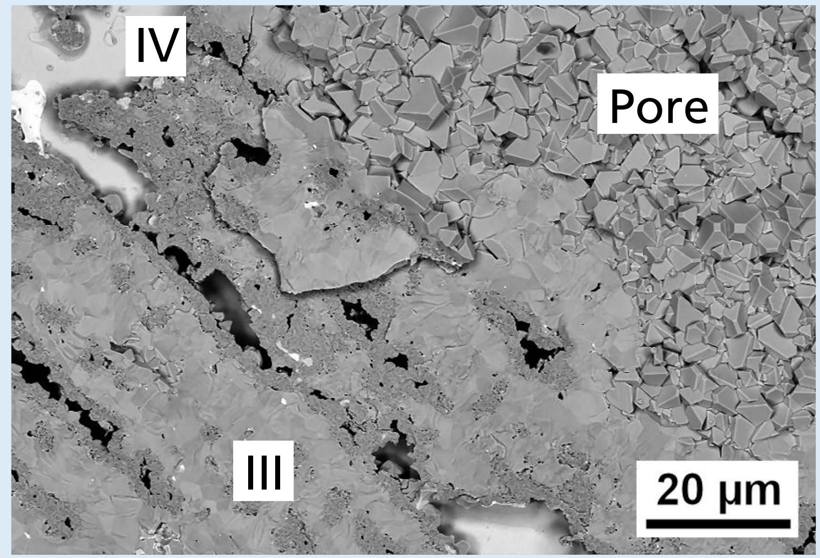
# Fractography Before and After Ageing for 800 h at 850 °C

## Comparison for Crofer / Ag-4CuO / 3YSZ

Crofer side, after brazing




Crofer side, after ageing




- Fracture proceeds through both reaction layers at
  - I Braze-3YSZ interface
  - II Braze-Crofer interface

- Fracture proceeds mainly through
  - III Reaction layer at braze-Crofer interface
  - IV Crofer (rupture of oxide layer)





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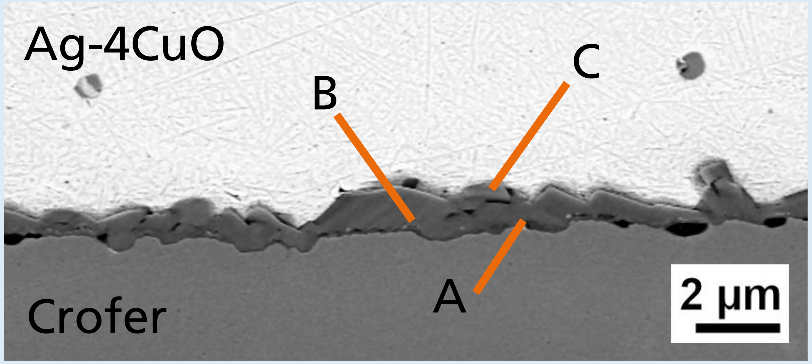
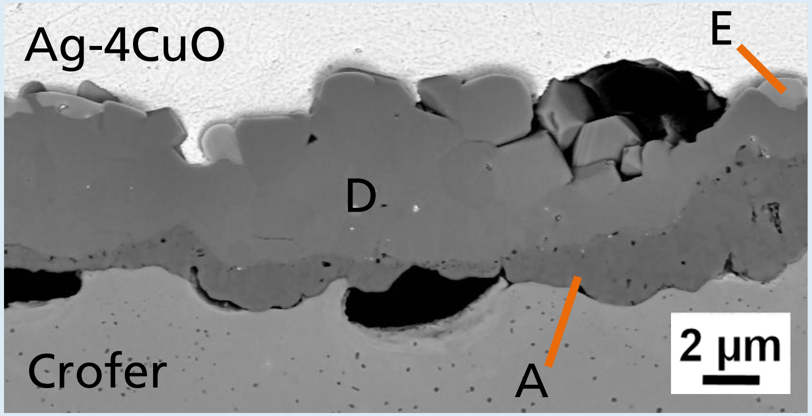
# Microstructure of Induction Brazed Samples
## Comparison for Crofer / Ag-4CuO / 3YSZ

After brazing




After ageing for 800 h at 850 °C




- 1 µm thick, continuous interfacial layer
  - A Cr oxide (very thin, non-cont.)
  - B Cu-Cr oxide
  - C Cu-Cr-Fe oxide

- Layer growth up to 10 µm with complex multilayered structure
  - Formation of pores
  - A Cr oxide (now continuous)
  - D Cr-Cu-Mn oxide
  - E Cu-Cr oxide





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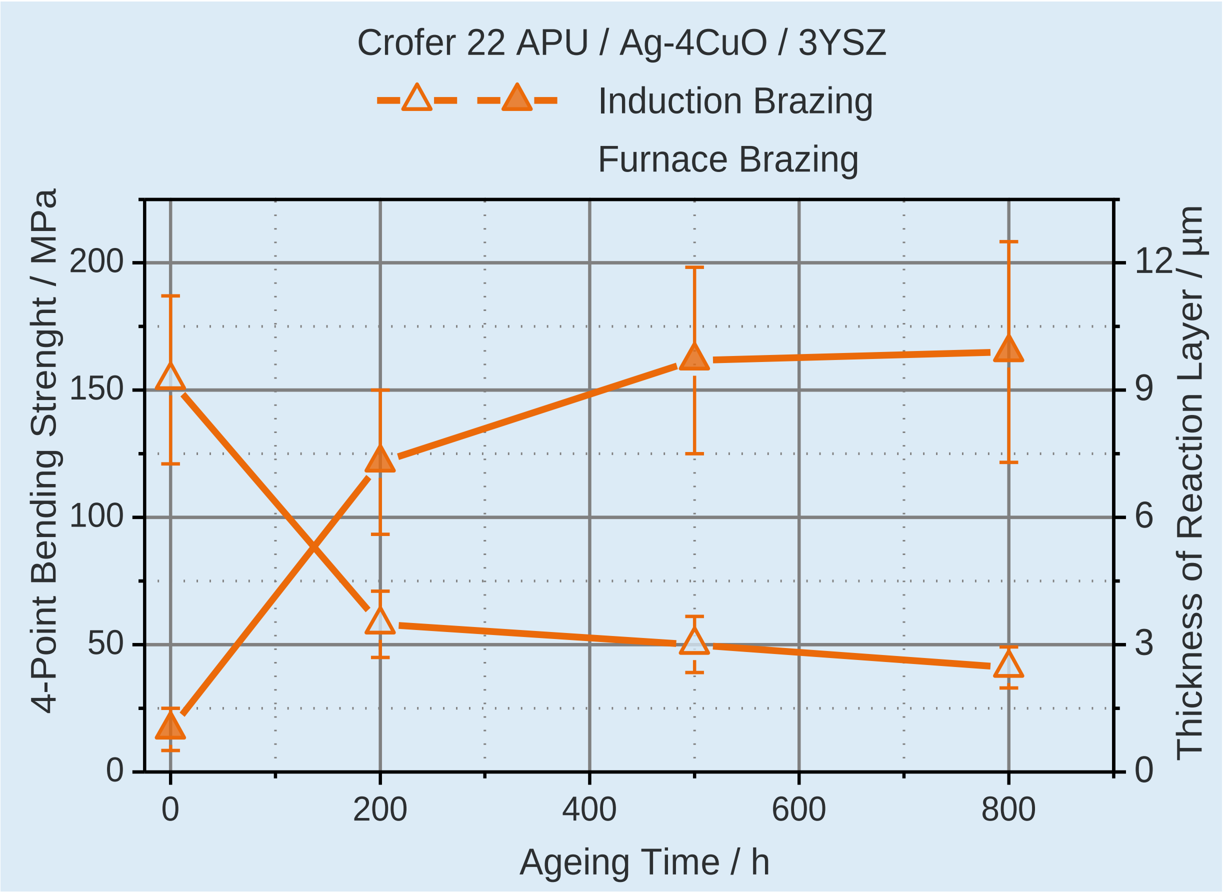
# Influence of Thickness of Reaction Layer on Bending Strength After Ageing at 850 °C in Air




- Reaction layers braze-steel grow with increasing ageing time





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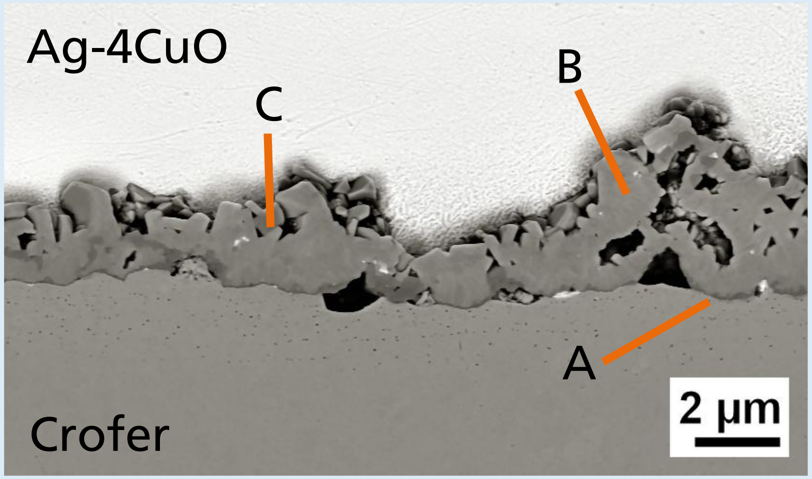
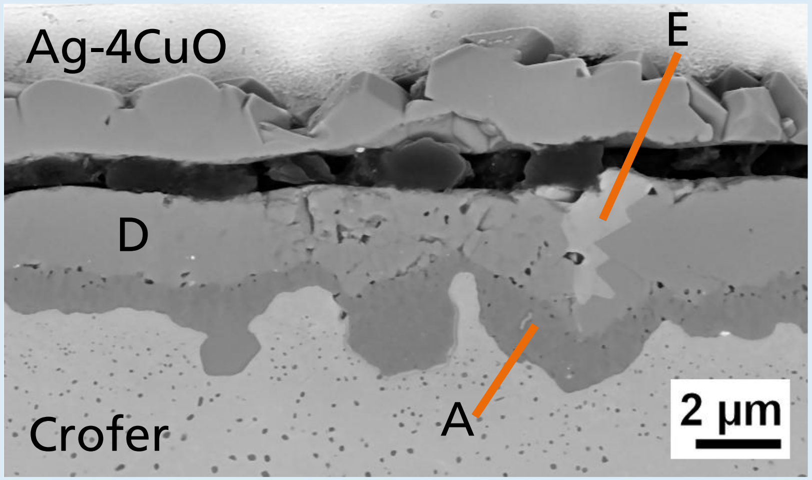
# Microstructure of Furnace Brazed Samples

## Comparison for Crofer / Ag-4CuO / 3YSZ

After brazing




After ageing for 800 h at 850 °C




- 4 µm thick, continuous and porous interfacial layer
  - A Cr oxide (very thin, cont.)
  - B Cu-Cr oxide
  - C Cu-Cr-Fe oxide

- Layer growth up to 8 µm with complex multilayered structure
  - A Cr oxide
  - D Cr-Cu-Mn oxide
  - E Cu-Cr oxide





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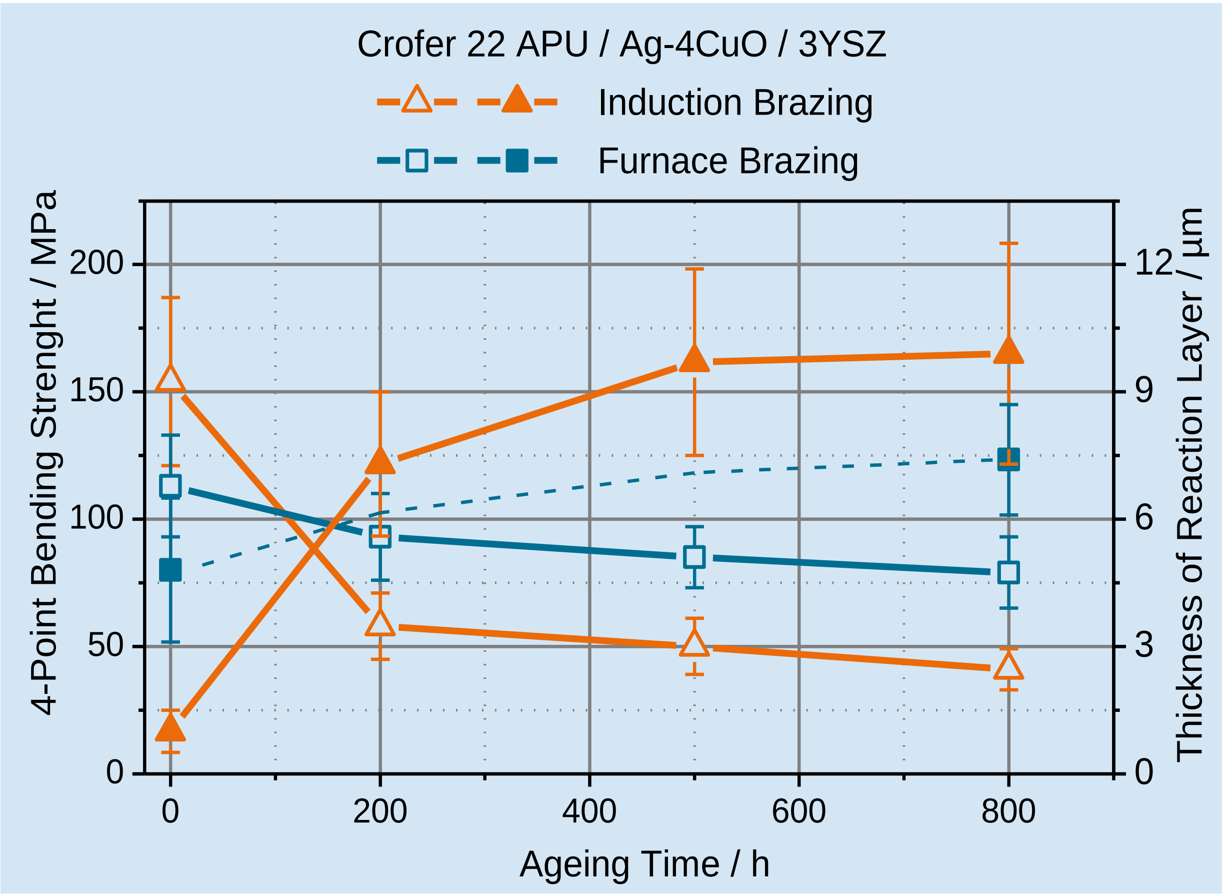
# Influence of Thickness of Reaction Layer on Bending Strength After Ageing at 850 °C in Air




- Reaction layers braze-steel grow with increasing ageing time
- Decrease of bending strength depends on
  - Pre-oxidation of Crofer
  - Initially formed Cr oxide layer
  - Brazing process





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# Conclusions

- Induction brazing yield within short processing times to ceramic-metal joints with high bending strength
- Brittle fracture in reaction layers at braze-3YSZ and braze-steel interface
- Intense growth of reaction layer braze-steel during ageing at 850 °C in air
- After ageing fracture occurs mainly in reaction layer braze-steel at lower strength
- Decrease of bending strength depends on brazing process

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EFRE

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