REACTIVE AIR BRAZING AS JOINING TECHNOLOGY FOR SOFC

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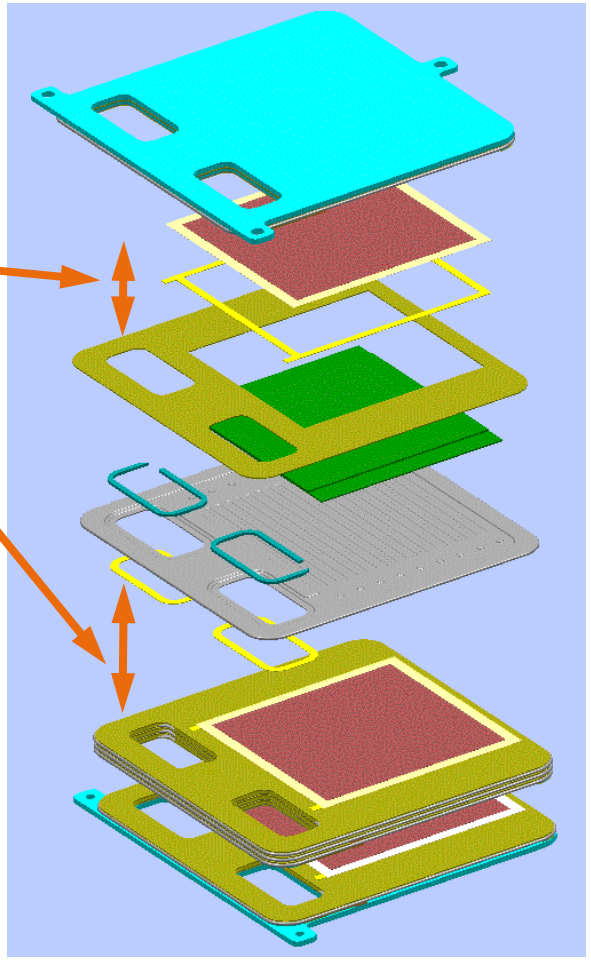
Introduction

Solid oxide fuel cells (SOFC) require (gas-)tight ceramic-metallic-connections of stack parts

- Cell and interconnect
- Manifold seals between interconnects



source: Staxera GmbH, Dresden

Requirements on seals

- Long-term stability at operating temperatures between 700...850 °C
- Compensation of CTE mismatches (temperature cycles)
- Resistance against harsh chemical environment (fuel & exhaust gas)

Methods and Experimental

Paste preparation

- CuO & Ag powders, binder
- CuO content up to 10.5 mol%
- Maximized solid content

Wetting experiments

- Hot stage microscopy of paste cylinders with 10 K/min to 1000 °C
- Measurement of wetting angles on various substrates

Joining experiments

- Screen printing on metal substrate
- Induction brazing of 3YSZ ceramic and metallic parts at 1000 °C
- Measurement of helium leak rates
- Annealing in air at 850 °C for 200, 500 and 800 h
- SEM and EDS on cross sections

Composition of the metallic alloys used for brazing experiments in wt%.

Metallic Alloy	Fe	Cr	Mn	Others
Crofer 22 APU (ThyssenKrupp)	Bal.	22.7	0.42	0.09 La, 0.07 Ti, Al, Si
ITM-LC (Plansee)	Bal.	25.4	Min.	Mo, Ti, Y_2O_3, Al, Si

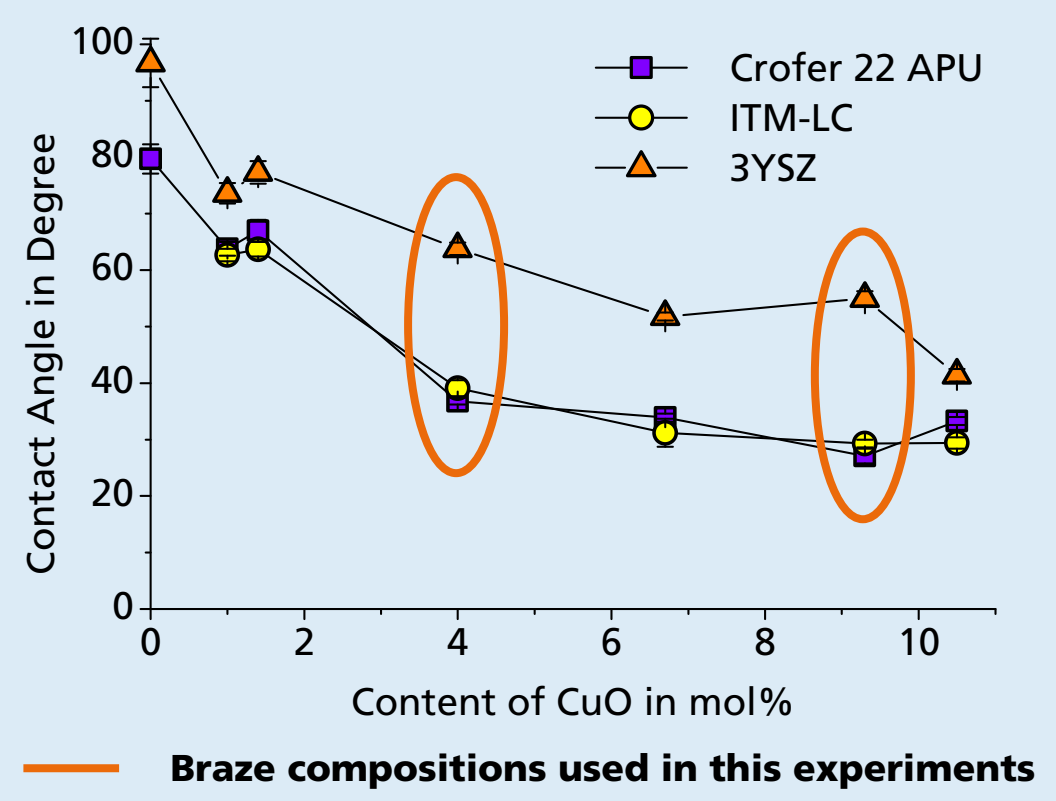
Methods and Experimental

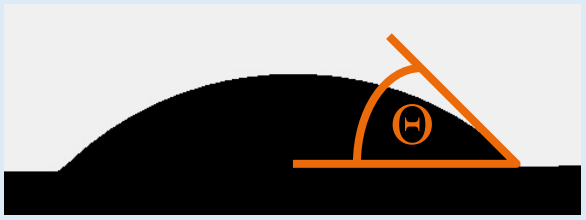
Work station for induction brazing

- Medium-frequency generator
- Heating rates up to 250 K/min
- Contact less temperature control

Wetting behaviour

Contact angle of the Ag-CuO braze compositions on Crofer 22 APU, ITM-LC and 3YSZ ceramic in air at 1000 °C.





Ag-9.5CuO on 3YSZ ceramic
in air at 1000 °C

Ag-9.5CuO on Crofer 22 APU
in air at 1000 °C

Fraunhofer IKTS

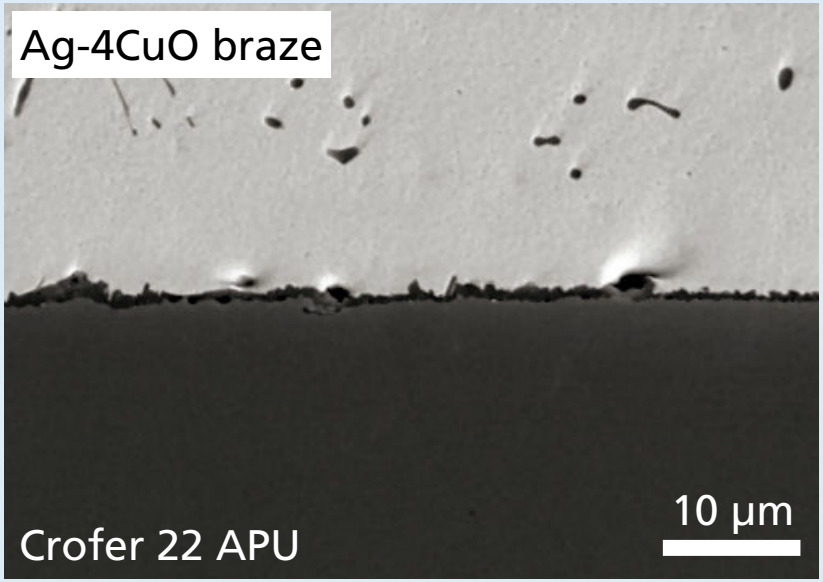
Comparison of induction and furnace brazed samples

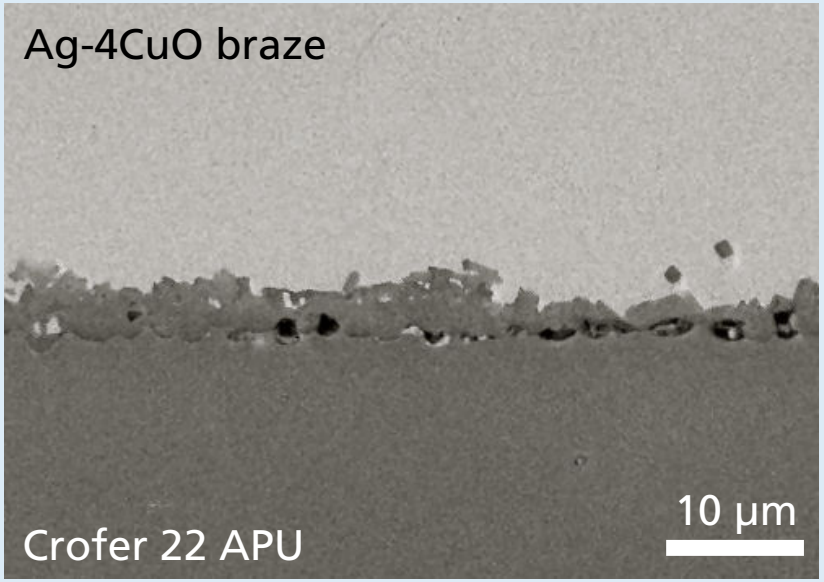
Induction brazed samples

- Thin interfacial layer (less than 1 µm)
- Layer composition: Cr-Mn-Cu oxide
- Solid inclusions of CuO in the braze

Conventional furnace brazed samples

- Layer composition: Cr-Mn-Cu oxide
- Thicker interfacial layers due to much longer brazing times
- Formation of pores at the metal surface





Comparison of induction brazed samples of Crofer 22 APU and ITM-LC

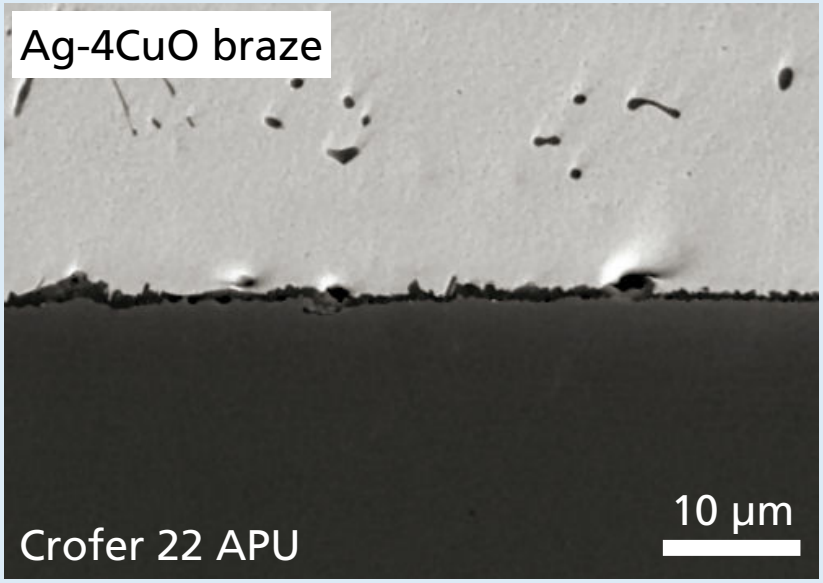
Samples with Crofer 22 APU

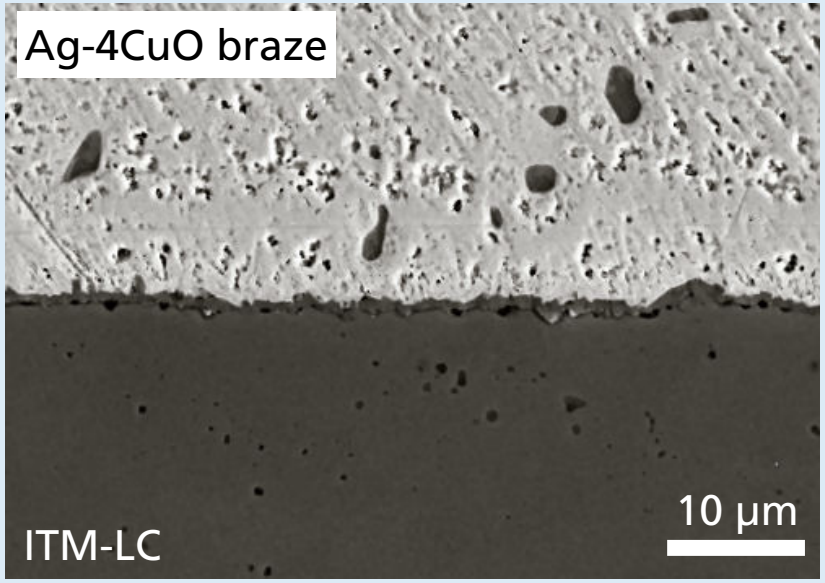
- 1 µm thin interfacial layer
- Layer composition: Cr-Mn-Cu oxide

Samples with ITM-LC

- Similar thickness of interfacial layer
- Layer composition: Cr-Fe-Cu oxide

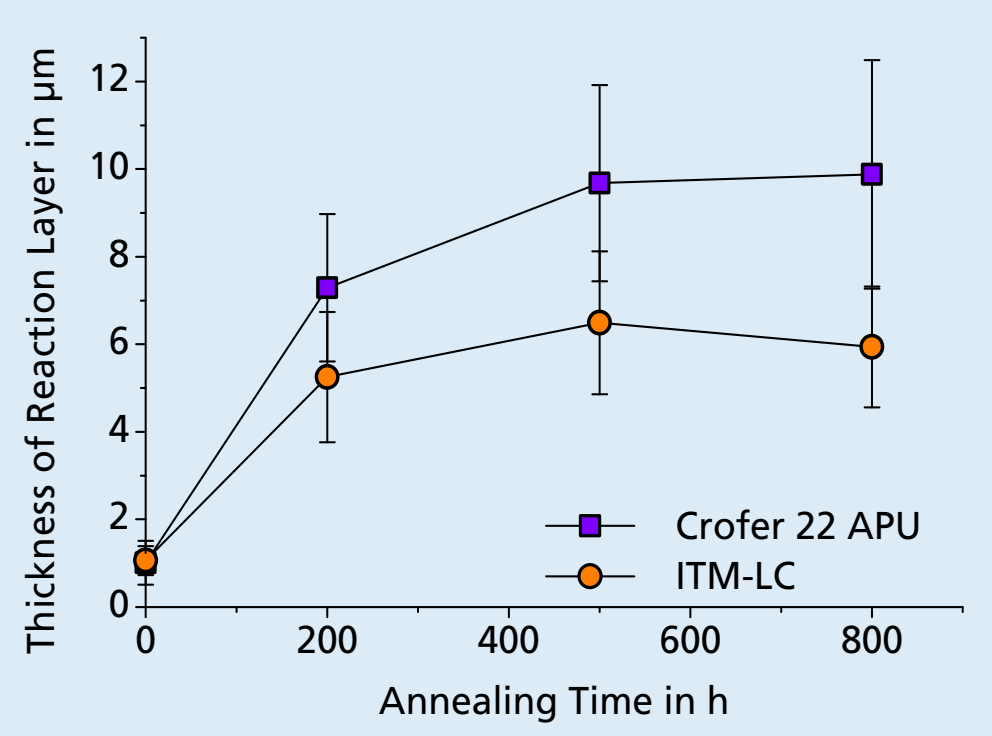
Manganese is a very reactive layer forming component of Crofer 22 APU.





Annealing of induction brazed samples in air at 850 °C

Thickness of reaction layer on Crofer 22 APU and ITM-LC brazed with Ag-4CuO after annealing in air.



- Samples showed a hermetic density (helium leak rates below 10^{-8} mbar·l·s^{-1}·cm^{-1})
- Interfacial layers grow and change their composition during annealing
  - Growth of layers according to a saturation mechanism
  - Maximum layer thickness about 10 µm

Interfacial layers remained dense and growth is saturated.

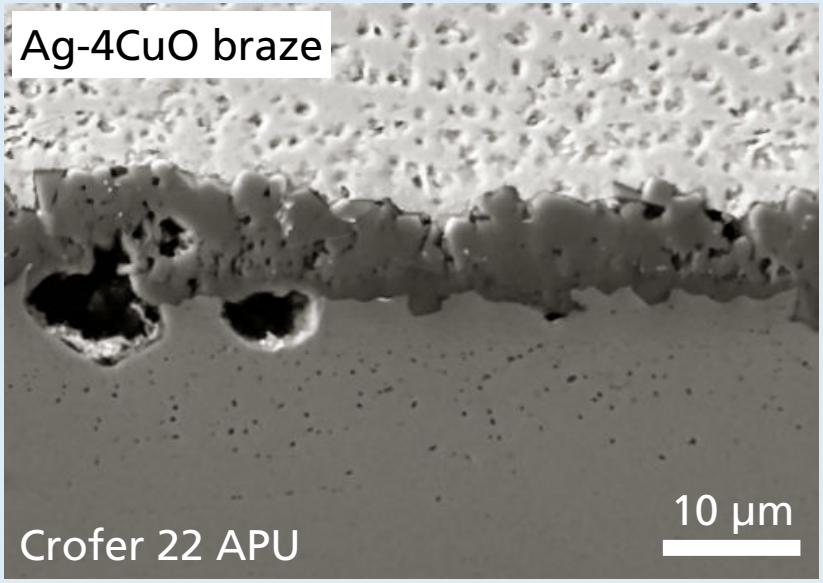
Morphology of aged interfacial layers after 800 h in air at 850 °C

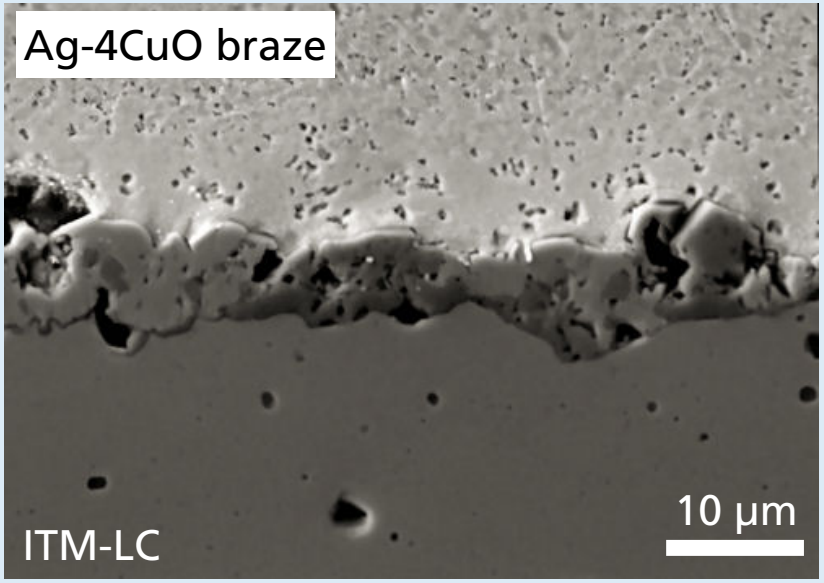
Crofer 22 APU

- 1 - 2 µm thin Cr oxide scale established after 200 h at the metal surface
- Second thicker layer: Cr-Mn-Cu oxide
- Growth of pores on metal surface

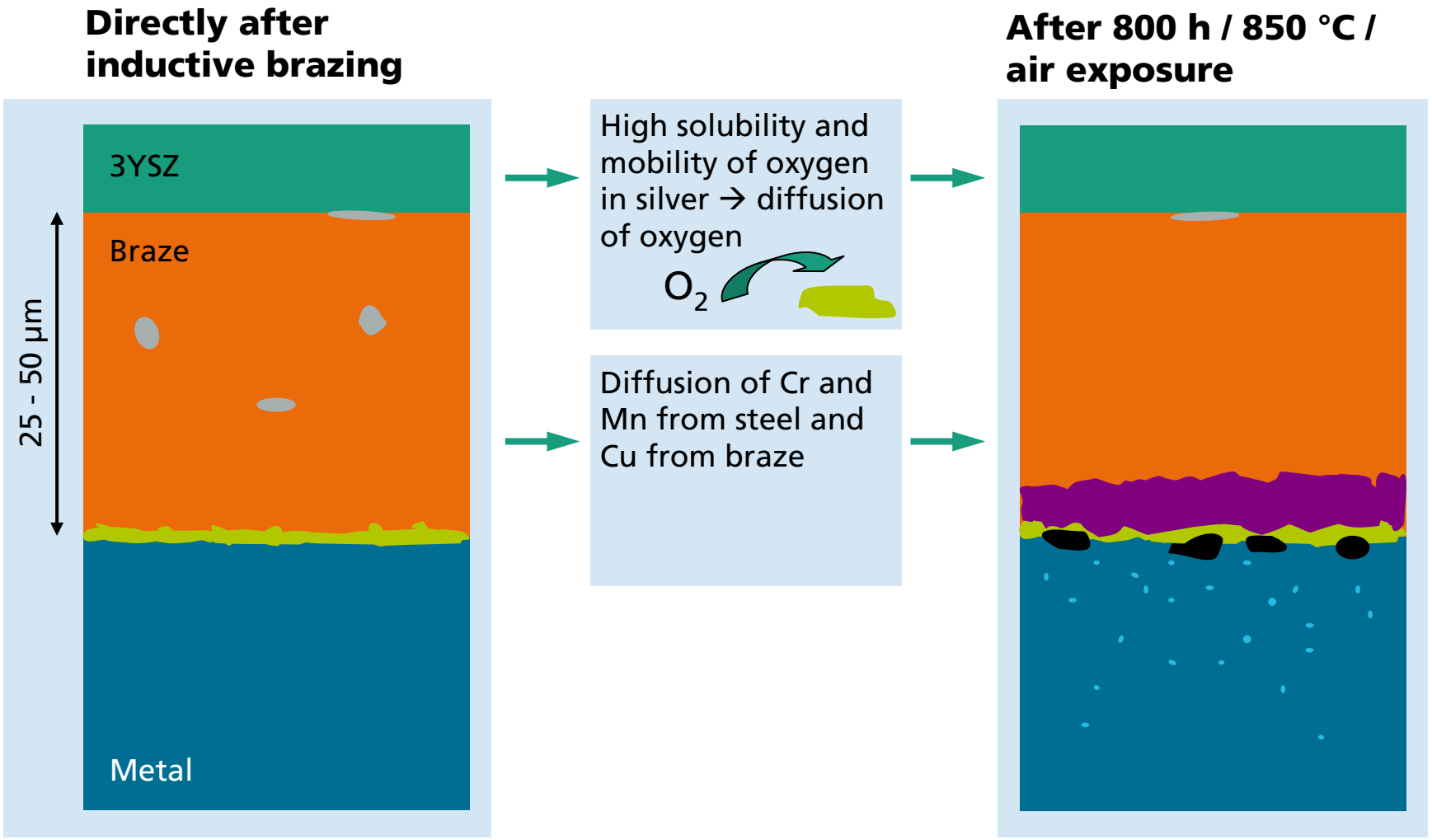
ITM-LC

- Initially formed layer grows and becomes enriched by Ag
- Additional 2nd phase: Cr-oxide particles at the metal surface (no dense layer)

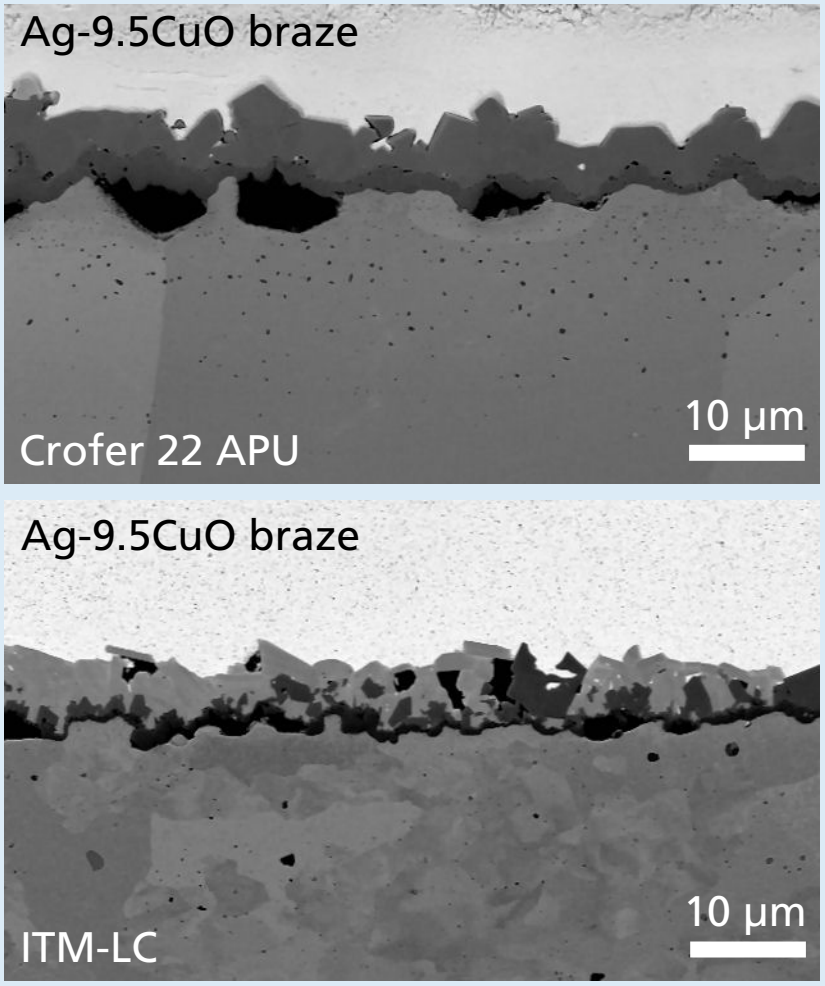




Growth of interfacial layers until saturation



Effect of increased CuO content on the braze-metal interfaces



Samples after 800 h / 850 °C / air exposure

Directly after brazing

- Thin interfacial Cr-Mn-Cu or Cr-Fe-Cu oxide layer
- Same amount of CuO inclusions in the braze as with low CuO content

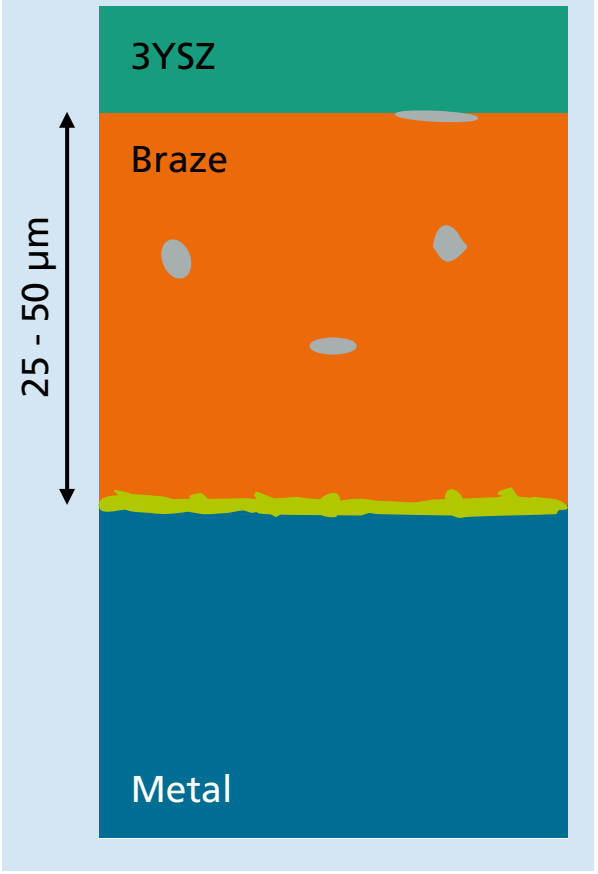
After annealing

- Growth of interfacial layers during ageing
- Similar thickness and microstructure compared to samples with low CuO content

Increased CuO content has no effect on the microstructure of the layers.

Growth of interfacial layers until saturation

Directly after inductive brazing



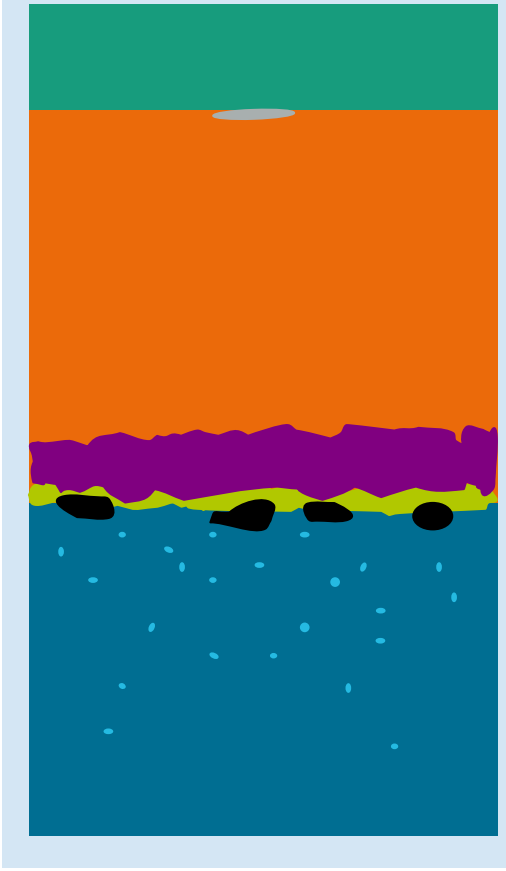
High solubility and mobility of oxygen in silver → diffusion of oxygen

O_2

Diffusion of Cr and Mn from steel and Cu from braze → growth is limited by the diffusion of metals from steel

CuO-content is not the limiting component
Crofer 22 APU: Mn
ITM-LC: ???

After 800 h / 850 °C / air exposure



Summary

- Formation of very thin interfacial layers between metal and brazing alloy by inductive brazing in comparison to furnace processes
  - Thickness less than 1 µm
  - No pore formation in the scale on metal surface

- Ageing of brazed components at 850 °C in air
  - Growth of interfacial layer according to a saturation process → 10 µm after 800 h at 850 °C in air
  - Microstructures of interfacial layers depend on type of metal substrate
  - Neither oxygen or CuO-content are responsible for the growth of the layers

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Thank you very much for your attention.

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