Compressive Seal Development: Combined Ageing and Thermal Cycling

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Outline

- Status of mica-seal development
- Technical challenges
- Current work objective
- Results of combined ageing and thermal cycling
  - Interlayer of G18 glass
  - Problem of G18 glass
  - Interlayer of modified G18 glass (G18m)
  - Interlayer of other glass with low B_2O_3
  - Interlayer of Ag foil
  - Issue of long-term Ag volatilization
- Summary and conclusion
- Future work

Current status of compressive seal

Final goals:
>40,000 hrs stability
>10^2 or 10^3 thermal cycle
No degradation to mating mat'l
Low stresses
Low cost in SOFC stack

Hybrid micas survived 800^oC
2000hr, 34 cycles @12 psi
0.03-0.04 sccm/cm @0.2psi

Hybrid micas showed low Leakage @ 6 psi and Nernst OCV

Hybrid micas survived
88 cycles@12.5 psi

Hybrid micas survived 1026 thermal cycle
between ~100^oC - 800^oC, ~2.7%H_2/Ar+3% H_2O and 100 psi

Glass-mica
composites

Infiltrated micas

Hybrid micas

Plain mica paper

Plain Muscovite mica (monolithic)

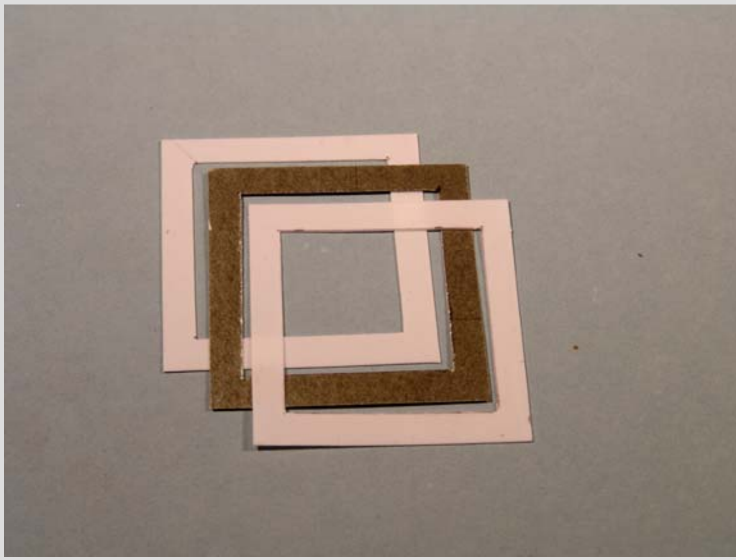
Technical challenges for compressive mica seals

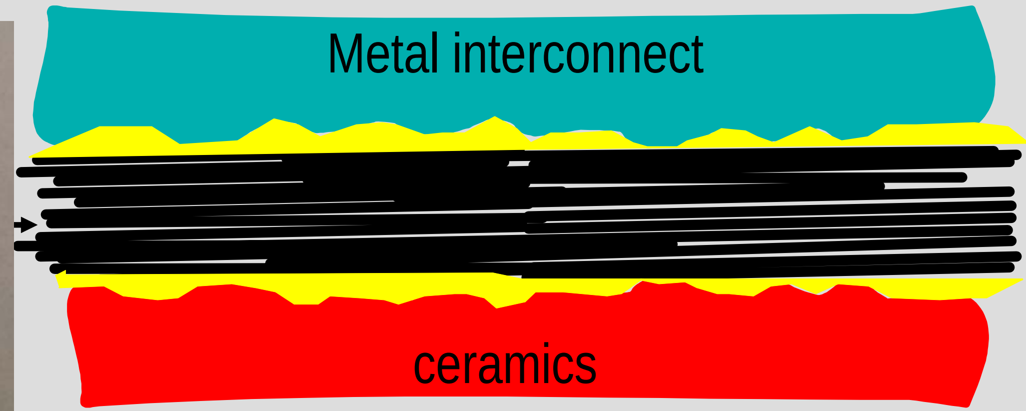
- Does the hybrid mica seal have long-term (40,000 hrs) mechanical, thermal, and chemical stability in SOFC environments of high humidity, ~40% ?
- Combined ageing and thermal cycling stability?
- Will the compressive stresses evenly distributed through multiple cells in actual SOFC stacks?
- Will the compressive stresses cause undesirable creep or plastic deformation and degradation of the metallic stack components?
- Will hybrid mica seals survive long-term thermal cycling (10^2-10^3 cycles) in SOFC environments and still maintain low leak rates?
- How low can the applied compressive load be?
- Will they survive thermal cycling with temperature gradients?

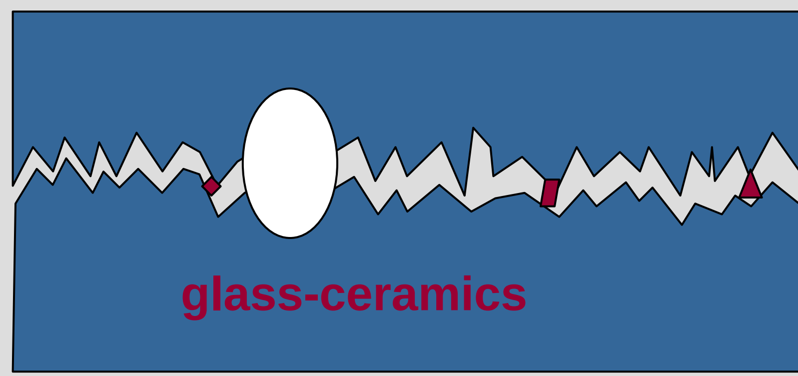
Current work objective

The objective was to evaluate the combined ageing and cycling effect on hybrid Phlogopite mica seals with respect to materials and interfacial degradations in a simulated SOFC environment.

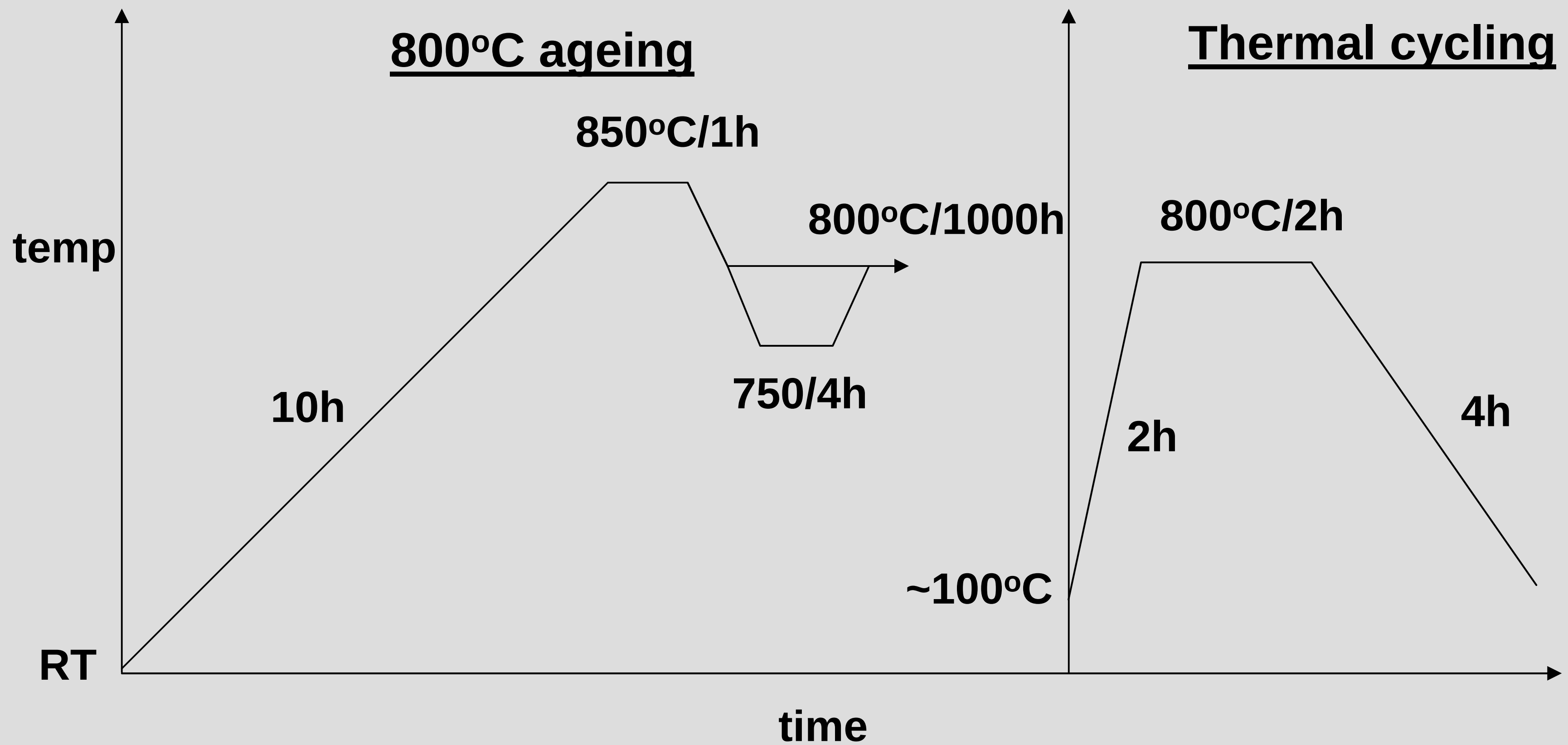
Hybrid Phlogopite mica





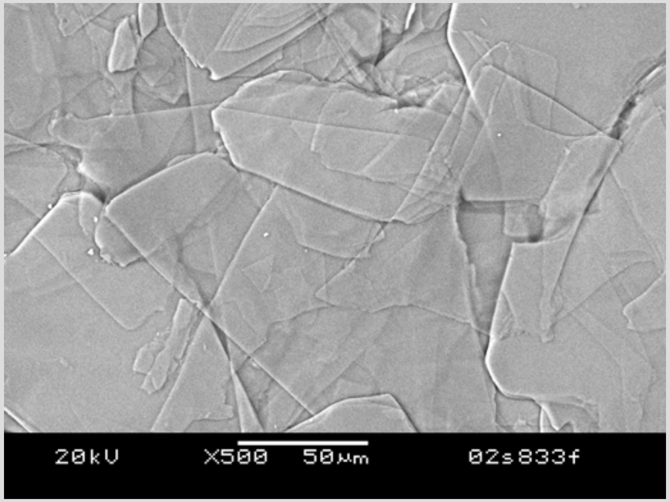


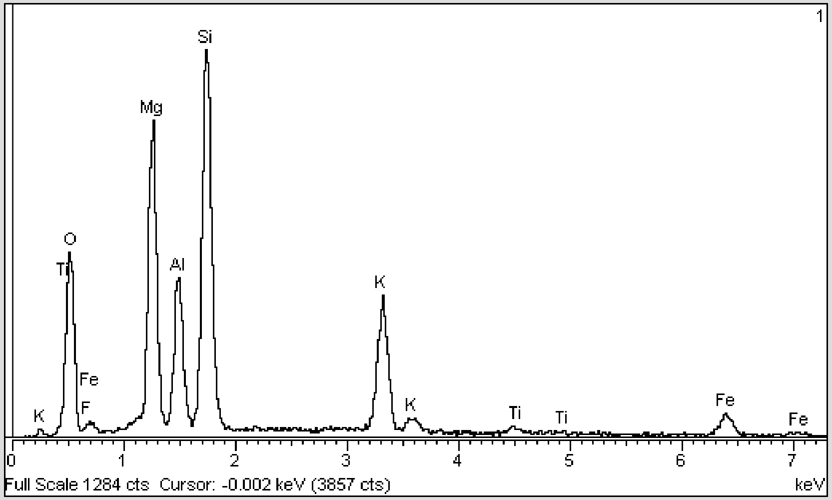
Experimental: ageing and short-term thermal cycling



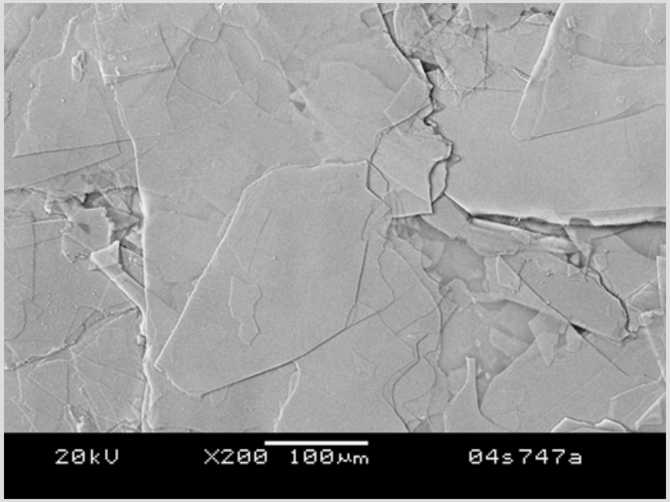
Phlogopite micas

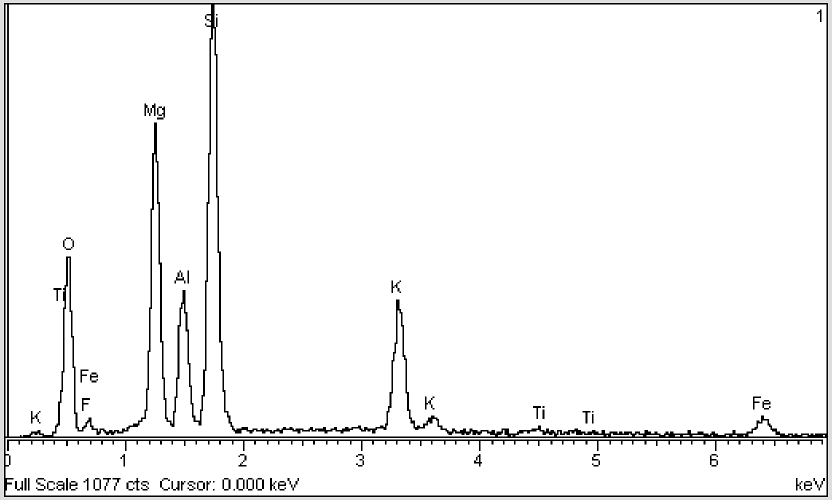
PH-A: cogebi, cogemica





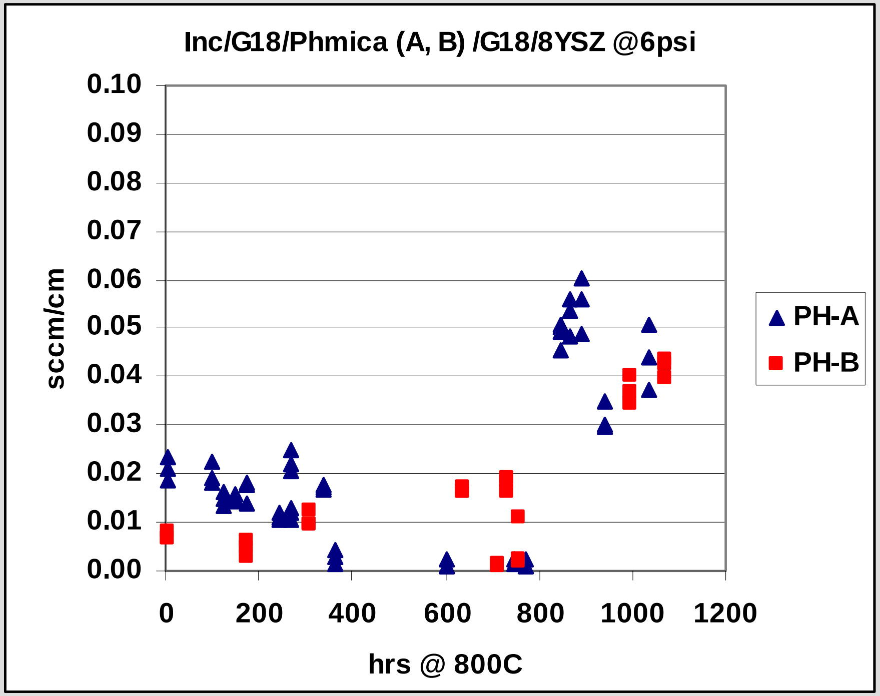
PH-B: McMaster-Carr



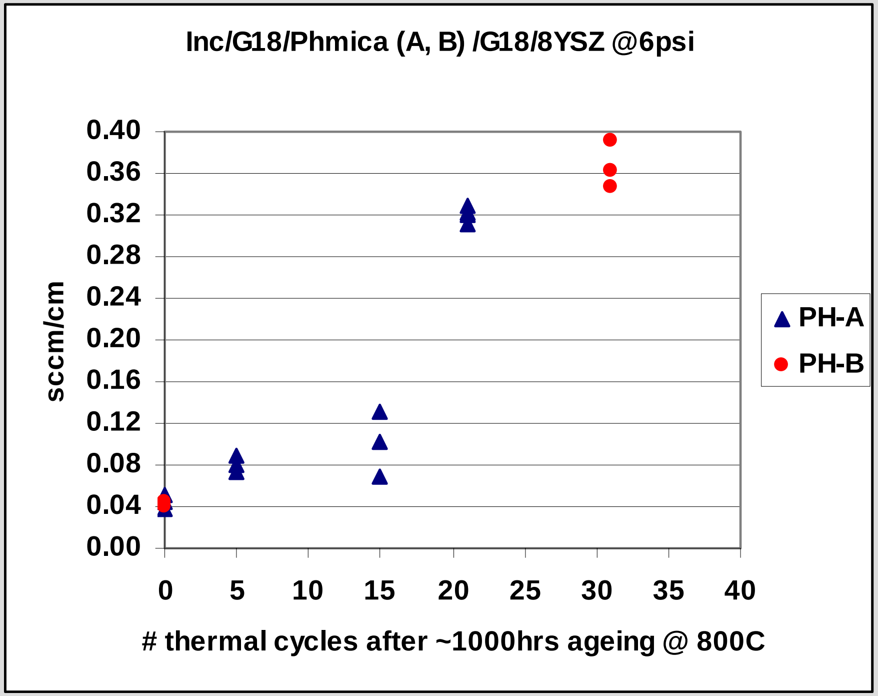


Combined ageing and thermal cycling of hybrid mica with G18 glass interlayers

Inc/G18/PH-A or PH-B/G18/8YSZ @ 6psi with flowing ~2.7%H_2/Ar+~3% H_2O



800°C ageing

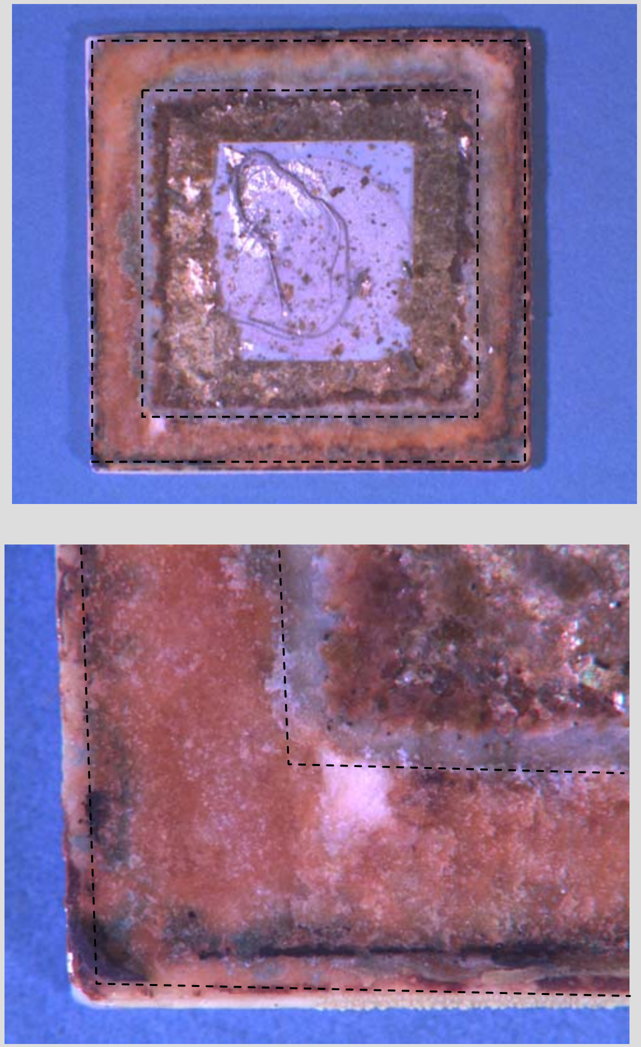


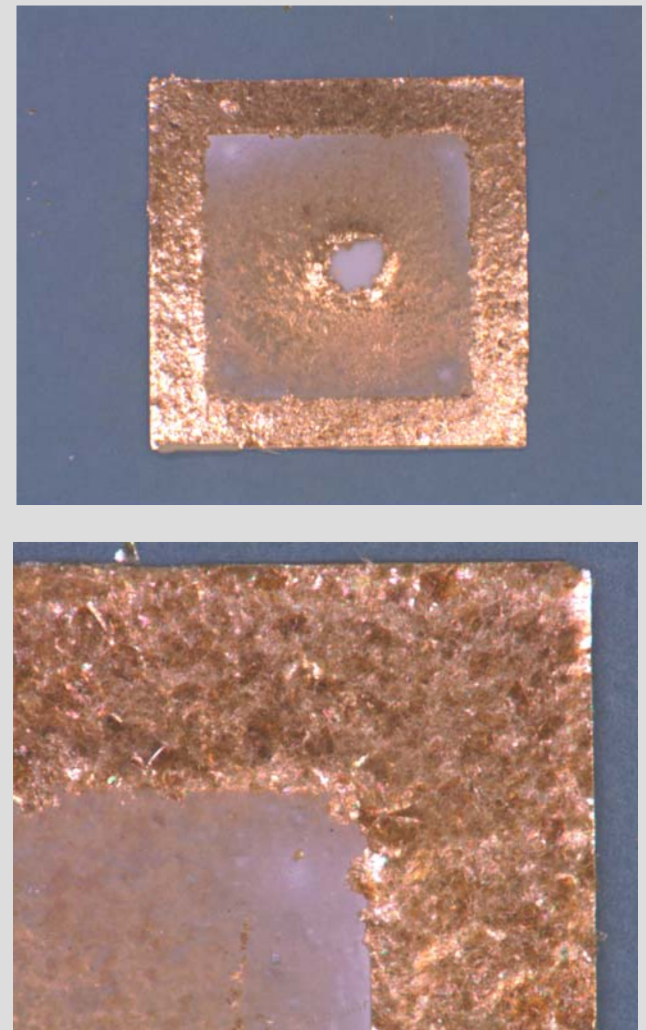
thermal cycling

PH-A: Cogebi, cogemica, PH-B: McMaster Carr

fracture surface of aged and cycled hybrid mica with G18 glass interlayer

PH-A
Mica
1036hrs
21 cycles

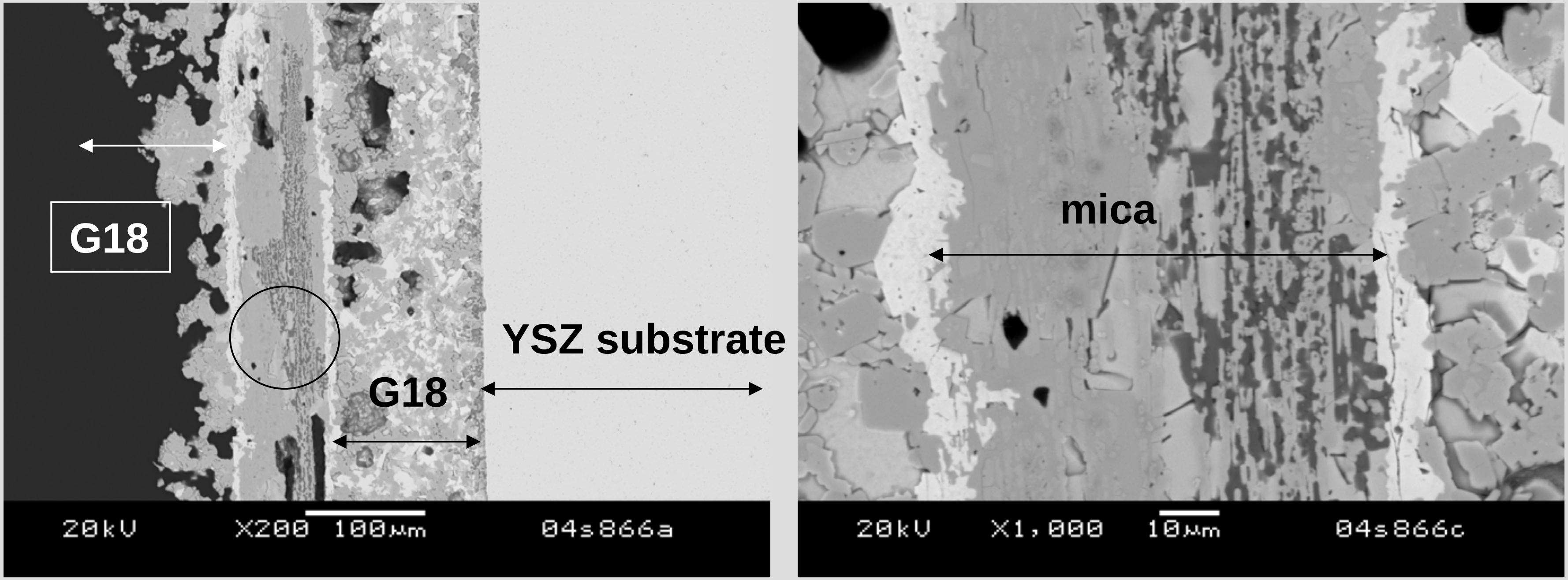




PH-A
Mica
31 cycles
No ageing

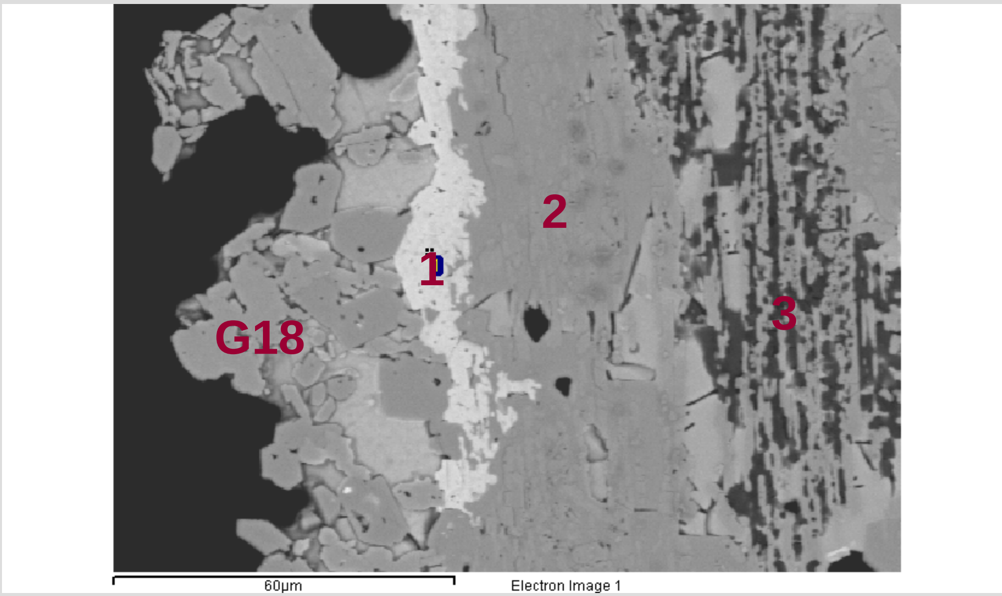
Cross-section of aged and cycled hybrid mica with G18 glass

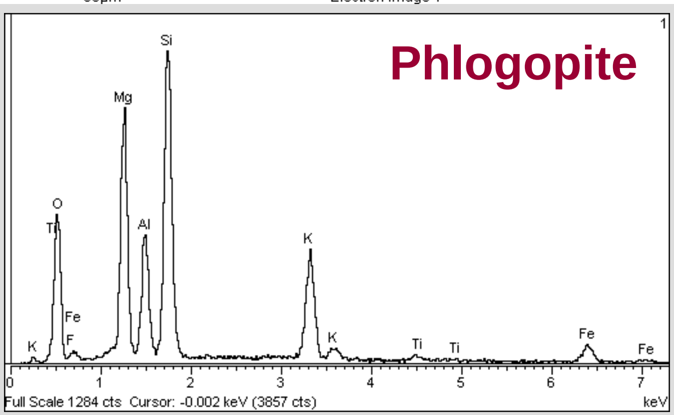
Pressed @6psi after 1036 hrs ageing and 21 cycles

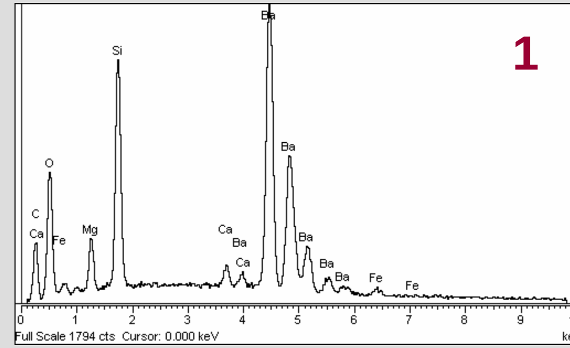


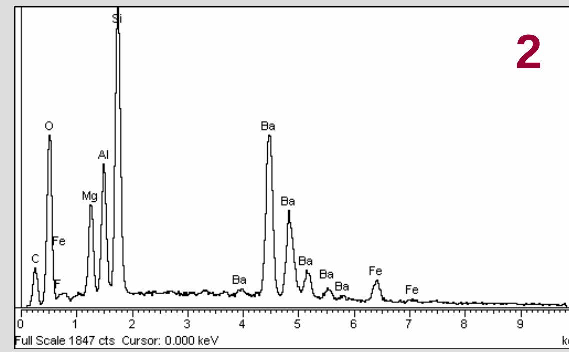
- **Fracture occurred along with the G18 glass near the Inconel600 side**
- **Thick G18 glass showed undesirable porous microstructure**

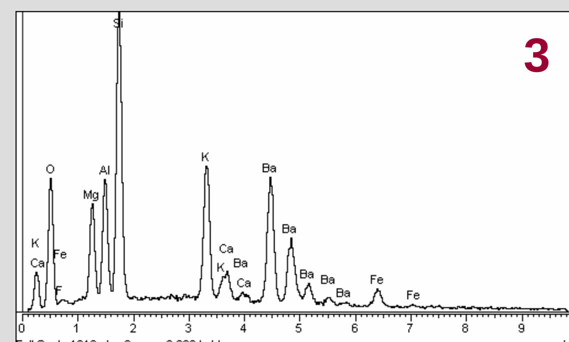
Reaction of G18 with mica









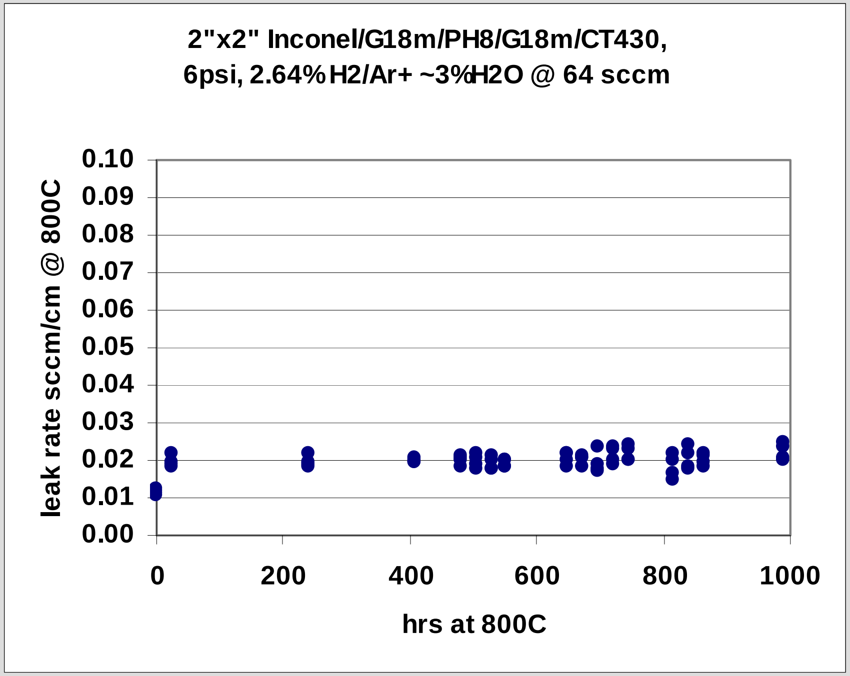


Approaches to minimize mica degradation

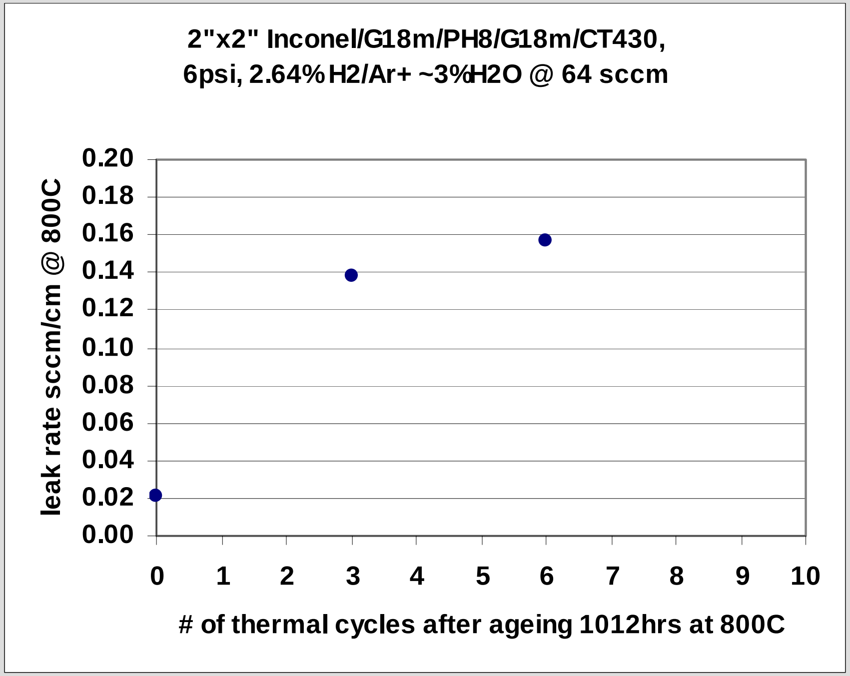
- Promote crystallization more rapidly in the G18 (Ba-Ca-Al silicate) by adding nucleation agent
- Use less reactive glass G-M (less B_2O_3)
- Use of non reacting metallic foils (Ag)

Ageing and thermal cycling of hybrid mica with modified G18m glass interlayers

Inconel/G18m/PH8/G18m/CT SS430 @6psi



800^{o}C ageing

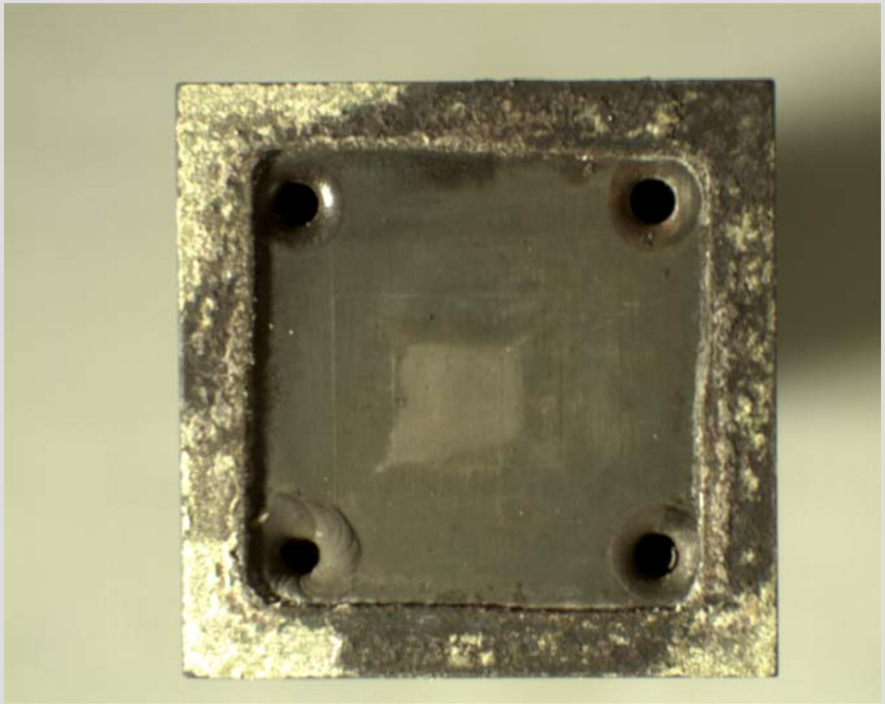


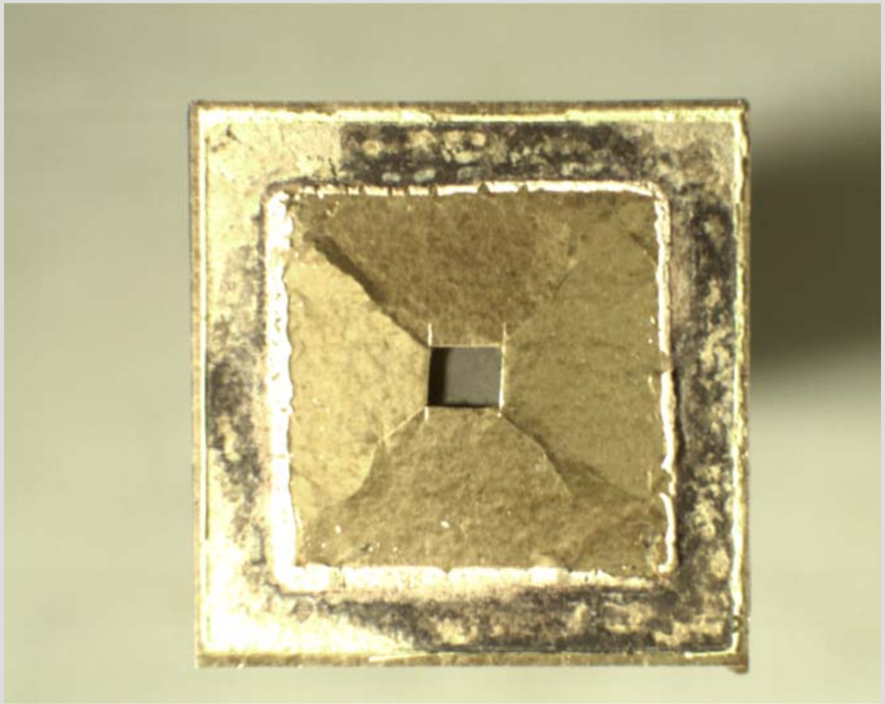
thermal cycling

Rapid increase in leakage suggests fracture through G18m interlayer near Inconel

fracture surface of aged and cycled hybrid mica with G18m glass

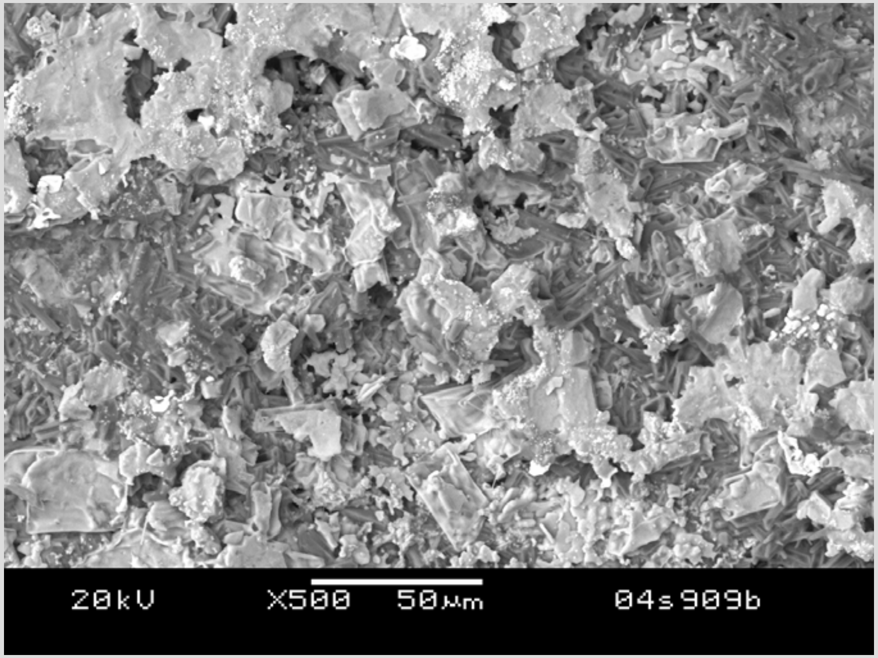
Inconel/G18m/PH8/G18m/CT SS430 @6psi, 800^{o}C 1012hrs and 6 cycles

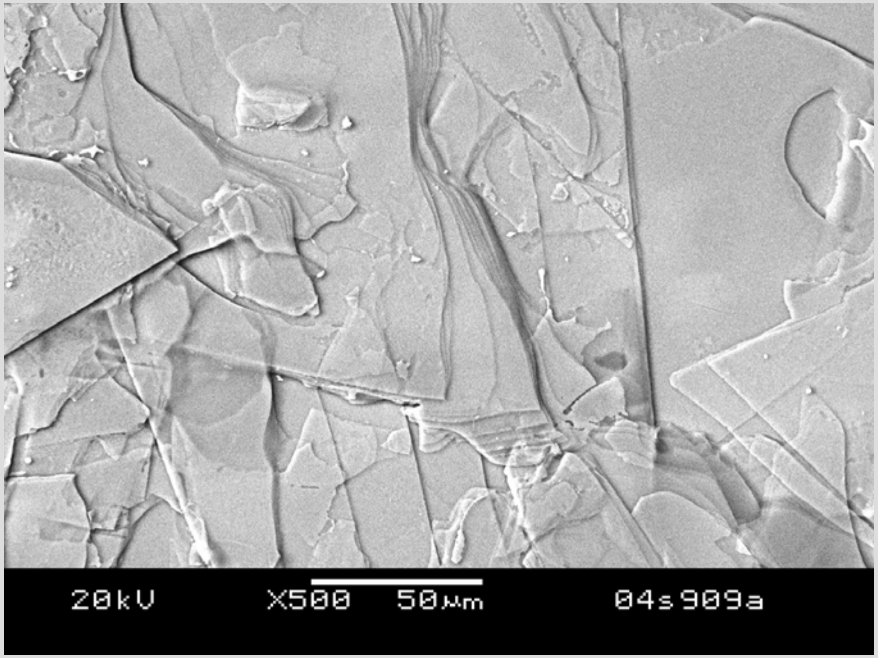




fracture surface of aged and cycled hybrid mica with G18-M glass

Inconel/G18m/PH8/G18m/CT SS430 @6psi, 800ºC 1012hrs and 6 cycles



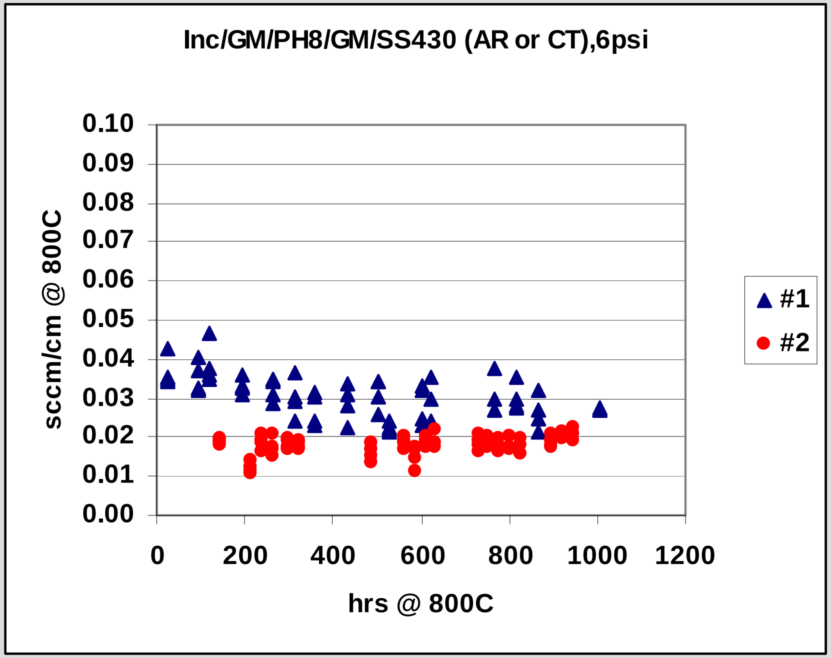


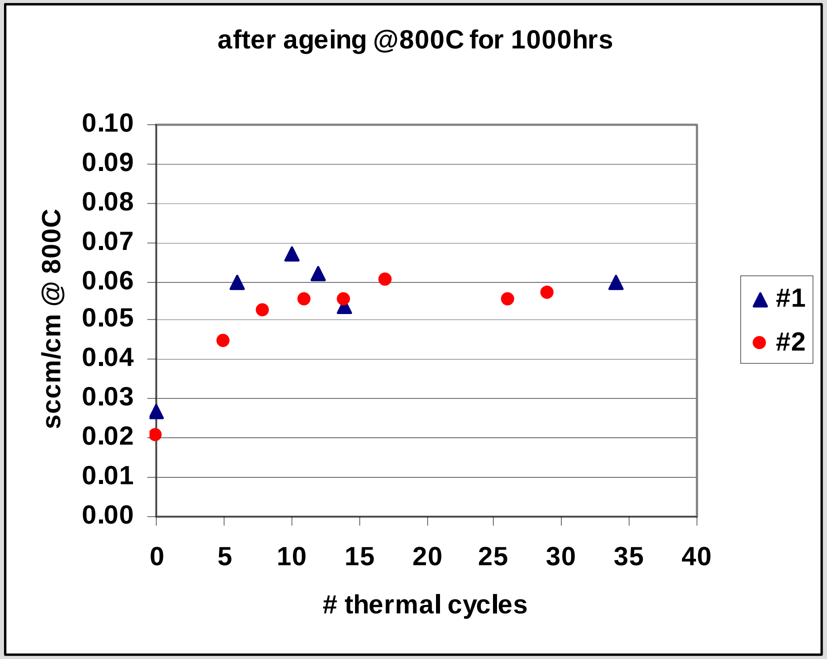
on the fracture surface
crystallized interlayer glass

underneath the fracture surface
Intact mica flake

Ageing and thermal cycling of hybrid mica with glass of low B_2O_3 (G-M) interlayers

GM glass contains lower B_2O_3 than G18 (Ba-Ca-Al silicate)



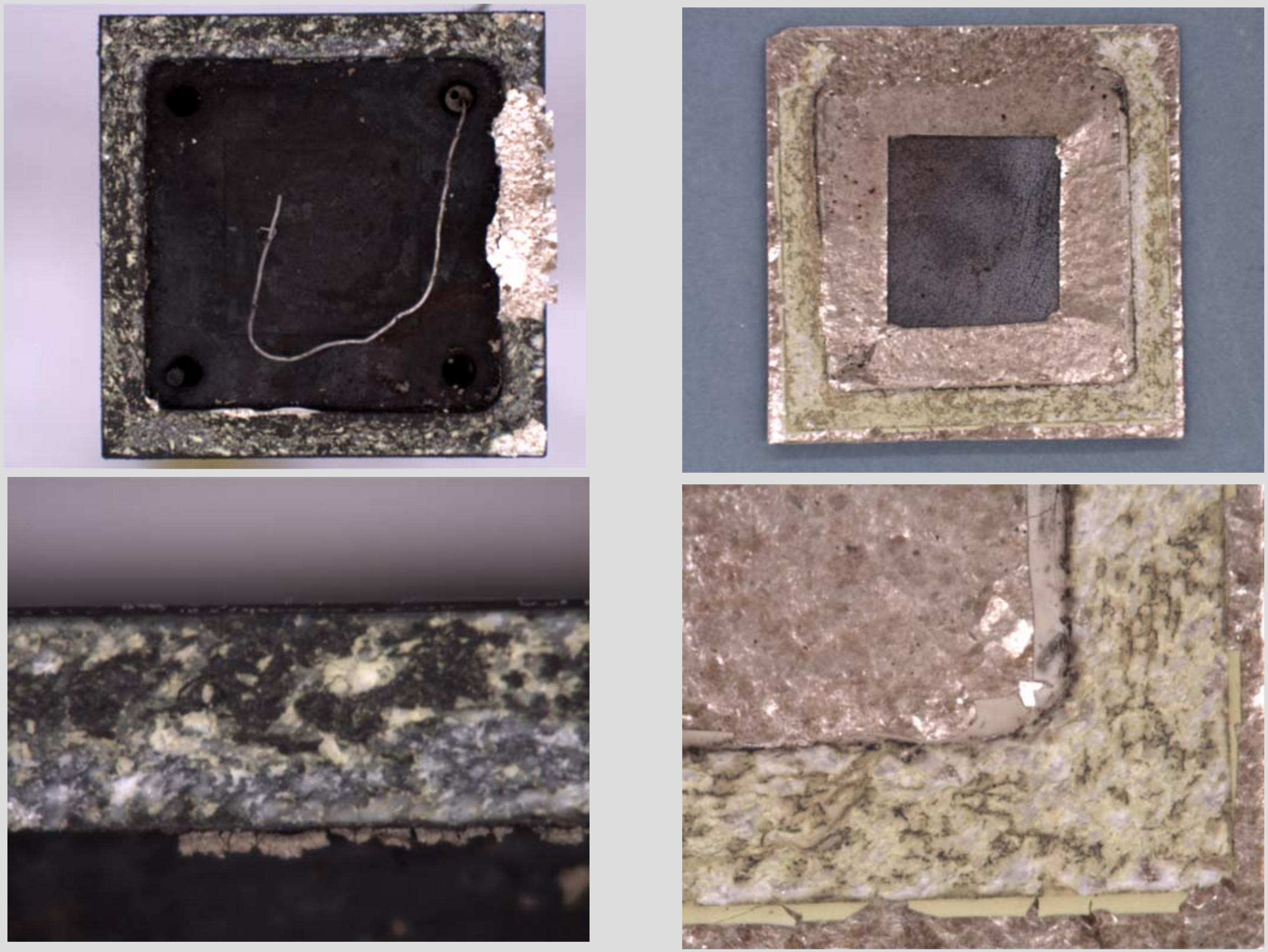


800^{o}C ageing **thermal cycling**

fuel loss = 0.6 % @0.06 sccm/cm, 0.2 psid, 0.7V, 0.5 W/cm^2, 800^{o}C, 80% fuel utilization of pure hydrogen of a 6"x6" SOFC cell

SECA target: fuel loss <1% @ 0.1 psid after 10 thermal cycles for 6"x6"

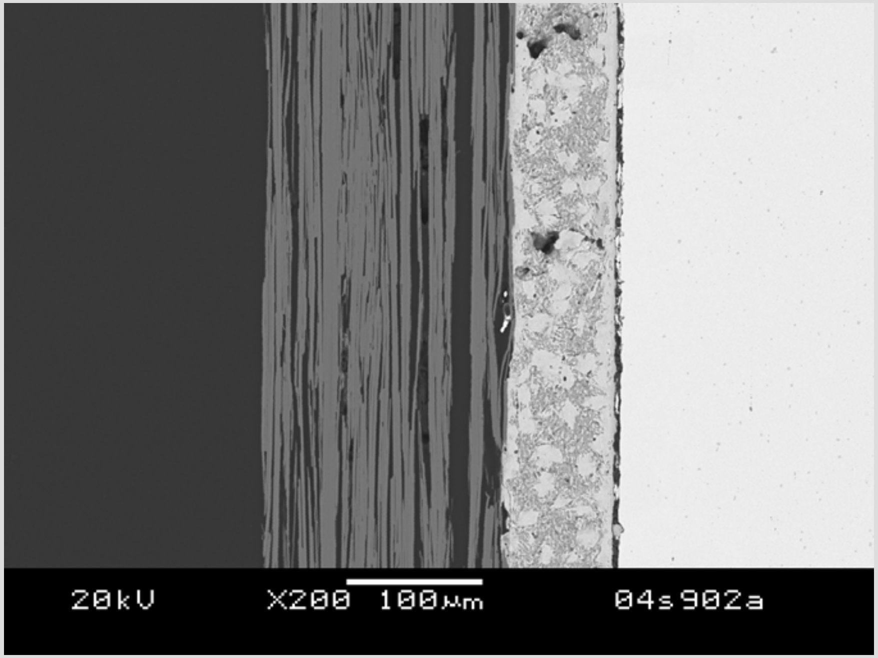
fracture surface of aged and cycled hybrid mica with G-M glass

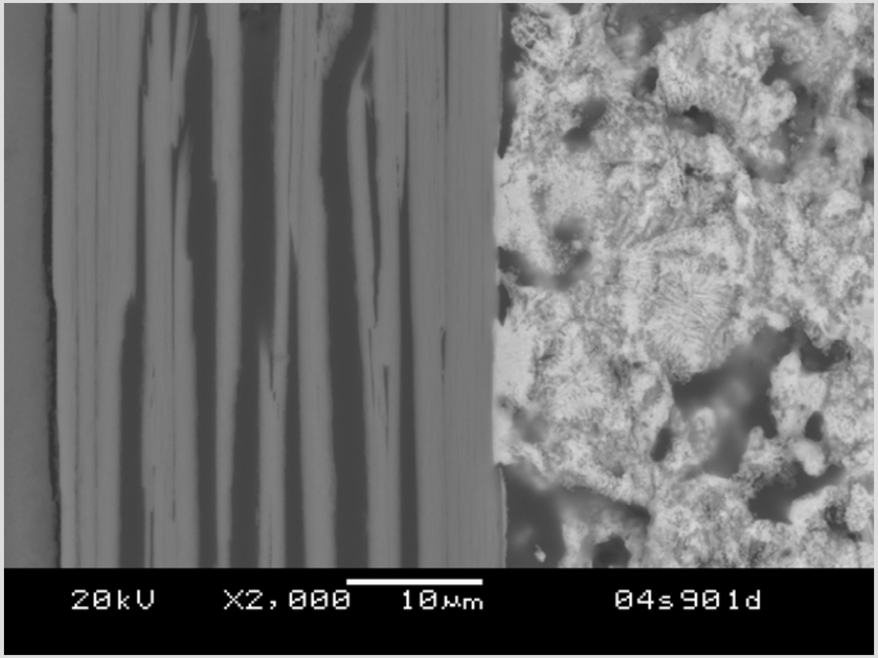


800°C/1000hr, 34 cycled @6psi

No degradation of mica with glass G-M

Inconel/GM/PH8/GM/CT SS430 @ 6psi after 1000 hrs 800^{o}C and 34 cycles





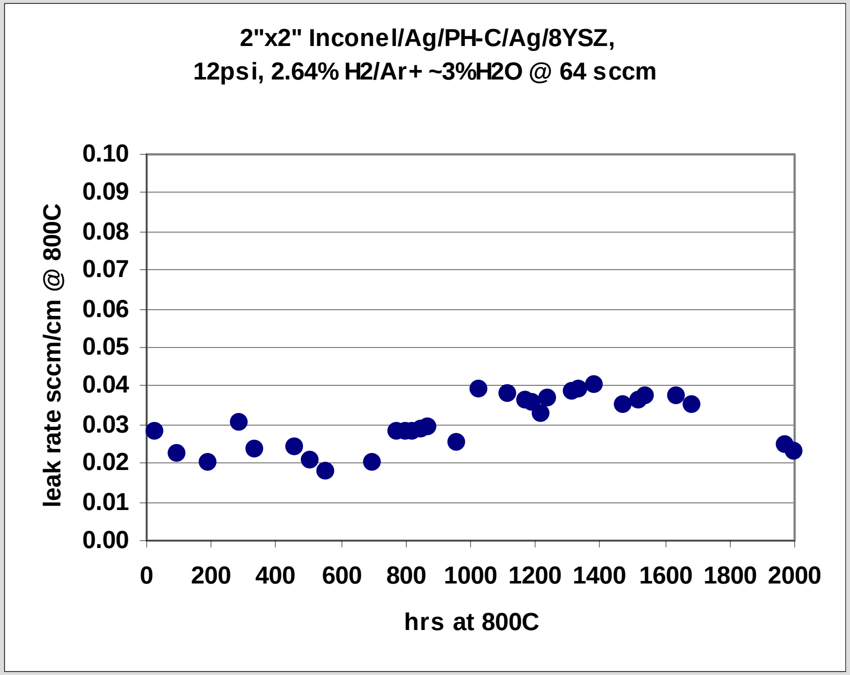
No reaction of Phlogopite mica with glass G-M
Lower leakage vs cycling likely due to denser G-M microstructure

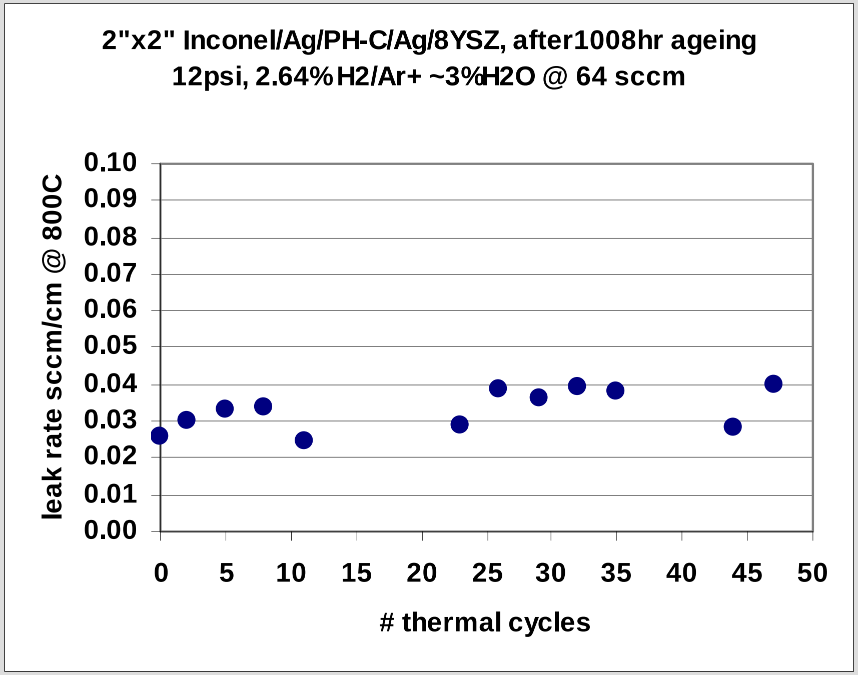
Concerns when using glass interlayers with metals of high CTE

- Very high residual stresses (~300 MPa) from CTE mismatch between Inconel600, 16.7 ppm/^{o}C and crystallized G18, 11~12 ppm/^{o}C.
- The interlayer has to be thin and dense

Ageing and thermal cycling of hybrid mica with Ag interlayers

Inconel/Ag/Phlogopite/Ag/8YSZ @12psi



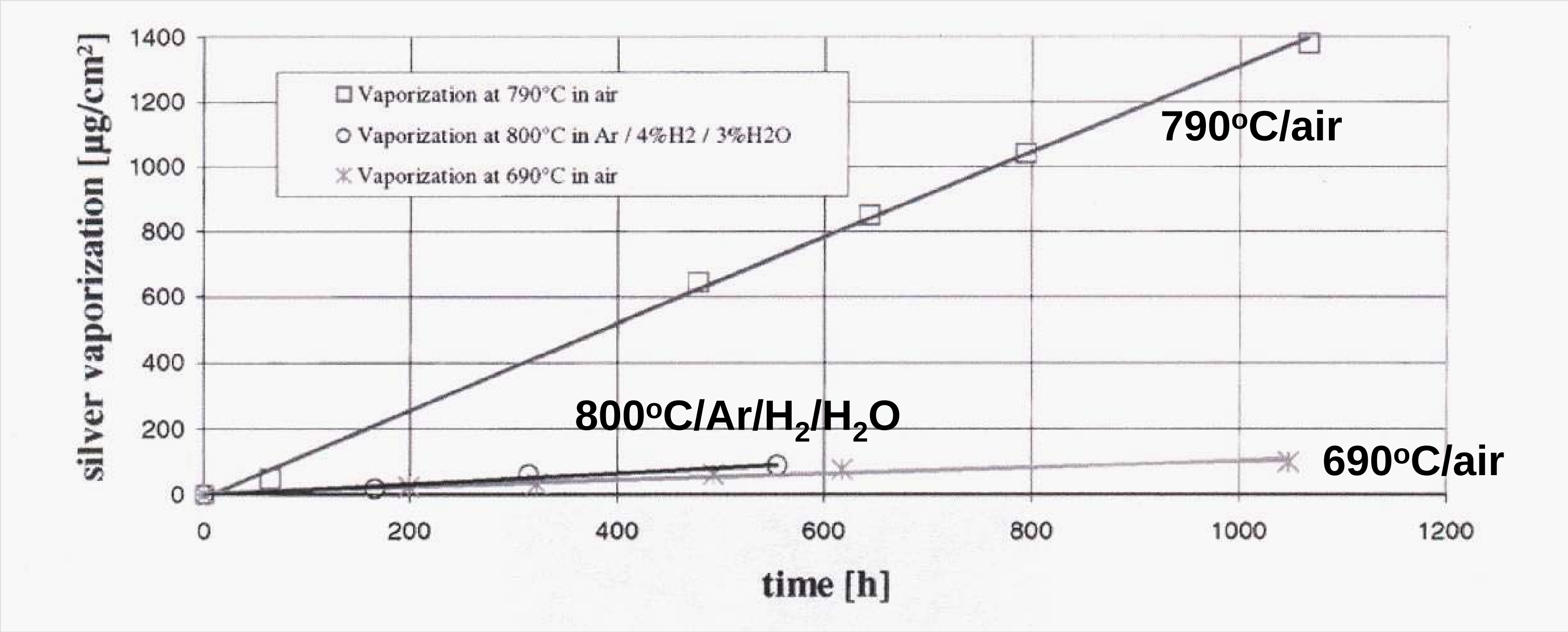


fuel loss = 0.4 % @0.04 sccm/cm, 0.2 psid, 0.7V, 0.5 W/cm^2, 800^{o}C, 80% fuel utilization of pure hydrogen of a 6”x6” SOFC cell

SECA target: fuel loss <1% @ 0.147 kPa (0.1 psid) after 10 thermal cycles for 6”x6”

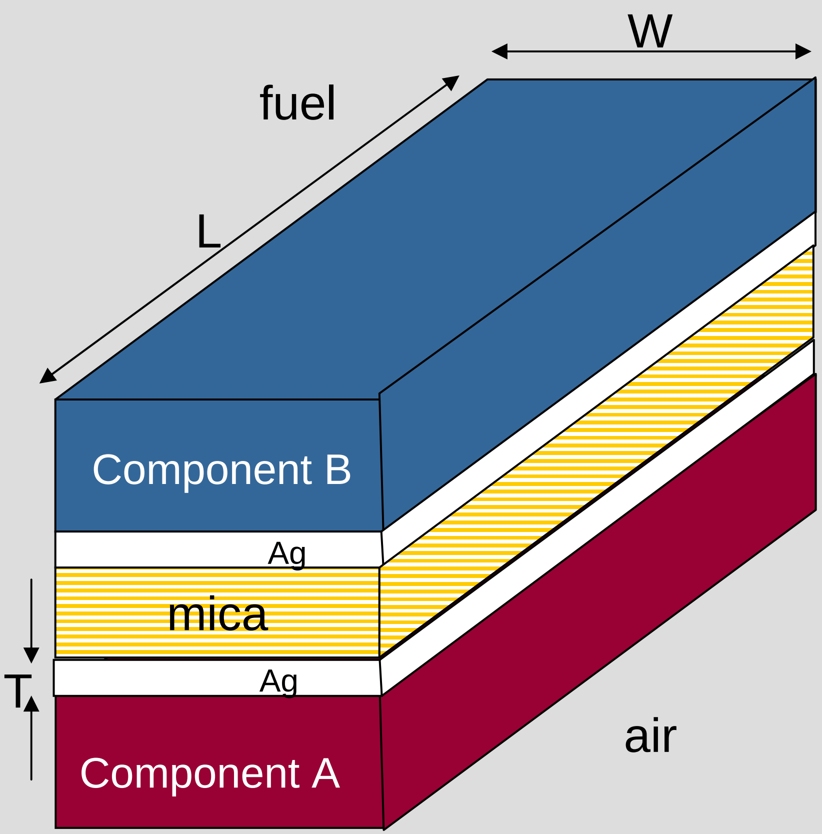
Issue of vaporization loss of Ag

From Meulenberg etal J. Mater. Sci., 36 [6] 3189-3195 (2001)



690°C/air: 0.094 µg/cm²/h	**2.16% @40,000hrs**
790°C/air: 1.29 µg/cm²/h	**28.7% @40,000 hrs**
800°C/Ar/H_2/H_2O: 0.161 µg/cm²/h	**2.33% @40,000 hrs**

Insignificant loss of Ag in hybrid mica assembly @ 790-800ºC



For a width (W) = 0.5 cm
ρ(Ag) = 10.5 g/cc

Ag loss on fuel side
=40,000(aTL)/(ρTWL) = 0.12%

Ag loss on air side
=40,000(bTL)/(ρTWL) = 0.98%

- Ag loss from free exposed edges
- No reaction of H_2 and O_2 by diffusion through lattice
- No diffusion loss to metals

Summary and conclusion

- Hybrid mica with G18 glass interlayers showed severe reaction during ageing and led to poor thermal cycle stability.
- Three approaches to minimize the reaction of interlayer glass with mica were proposed: G18m, G-M, metallic foils.
- Interlayer of modified G18m showed good chemical compatibility with mica for 1000 hrs, but poor thermal cycle stability.
- Interlayer of glass G-M of low B_2O_3 also demonstrated good chemical compatibility over 1000hrs, and thermal cycle stability of leakage ~0.06 sccm/cm over 35 cycles @ 6psi. Fuel loss <0.6%.
- Interlayers of Ag foil exhibited good thermal cycle stability over 2000 hrs with leakage of ~0.04 sccm/cm over 47 cycles @ a compressive stress of 12 psi. Fuel loss <0.4%.
- Calculation of vapor loss of Ag at 790-800^{o}C showed minute (~1 wt%) loss for 40,000 hrs; however, the effect of Ag on I-V performance/degradation remains to be verified.

Future work

- Finish ongoing ageing and short-term cycling tests in pure hydrogen fuels
- Post-mortem microstructure and interfacial degradation characterization
- Study the effect of SOFC environment (high water content) on the degradation of candidate sealants
- Development of new novel seals with tailored nano-microstructure and engineered interfacial structure for optimum strength and leakage

Possible degradations of hybrid mica during ageing with glass inter-layers