Rigid Seals for SOFC

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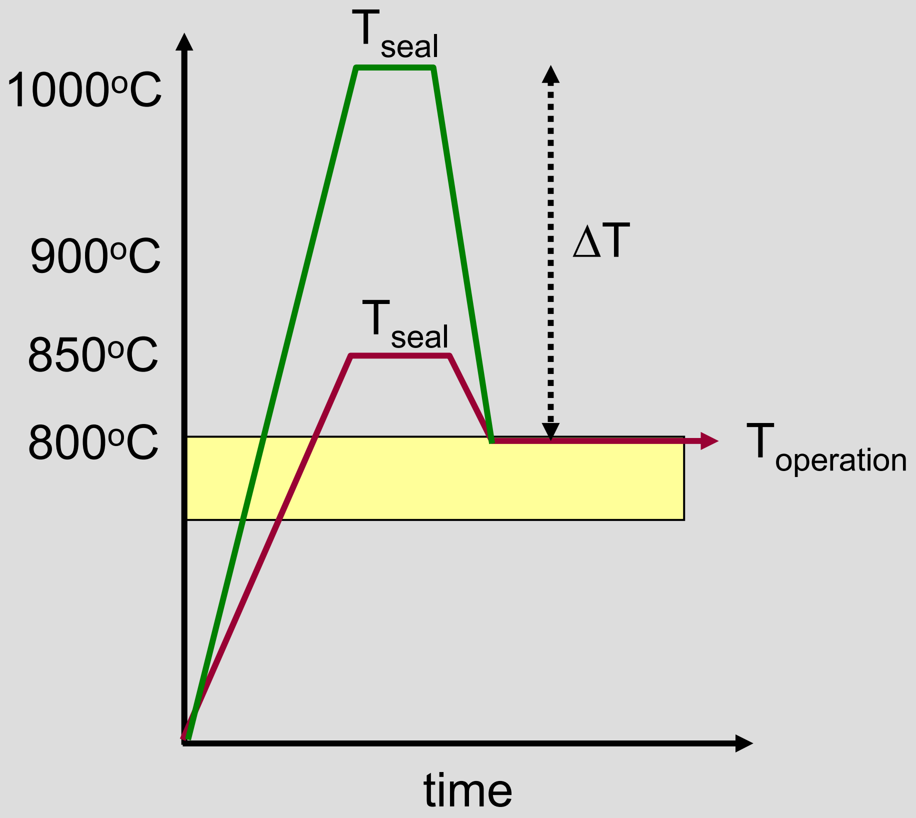
“Refractory” Glass-Ceramic Seals for SOFC

- **Objective**
  - To develop reliable, CTE-matched “refractory” sealing glasses (with higher sealing temperatures than typical SOFC sealing glasses) to minimize seal reactivity and increase seal stability. Higher sealing temperatures may also electrical contact and bonding of cathode/interconnect interfaces.
- **Approach**
  - Glasses are fabricated in-house by melting of raw materials.
  - Evaluation includes sealing temperature, crystallization behavior, CTE, chemical compatibility, leak testing, isothermal and thermal cycle stability.
  - Standardized tests allow for meaningful comparison between different sealing materials (PNNL or other SECA participants).



Background

- **General Issues:**
  - Matching CTE ($\sim 12.5 \times 10^{-6}/^{o}C$)
  - Minimal interfacial reaction (metal and ceramics)
  - Long-term thermal stability (crystallization rate and products)
  - Wetting properties
  - Volatility in dual atmosphere, moist environments
  - Mechanical integrity during thermal cycling
  - Electrically insulating
- **State-of-art glass: G18 (Ba-Ca-Al-B-Si-O)**
  - Sealing temperature ≤ 850ºC
  - Decrease in CTE from ~12.5 ppm/^{o}C to ~11.0 ppm/^{o}C after 750^{o}C/1000h aging, due to phase transformation: hexagonal celsian ($BaAl_2Si_2O_8$ CTE~8 ppm/^{o}C) to monoclinic celsian (CTE ~3 ppm/^{o}C)
  - Reaction with interconnect alloys to form $BaCrO_4$

Conclusions

- New "refractory" sealing glasses have been developed. Optimized glasses exhibit stable, matching CTE in the as-cast glass, short-term crystallized samples, and aged samples.
- Studies of weight loss, XRD, and microstructure showed good stability of candidate glasses after aging for 1000-2000 h at 800-900^{o}C.
- For several candidate glasses, sealed alloy/bilayer coupons tested in dual environment retained hermetic sealing after 1000 h at 800-850^{o}C.
- No interfacial reactions observed at glass/YSZ interface. However, $SrCrO_4$ was found at the glass/alloy interface when sealed at 900-950°C.
- To prevent undesirable interactions during long-term operation, protective coatings may be required.
- Preliminary results for aluminized Crofer22APU showed no chromate formation at glass/alloy interface after aging at 800°C/1000h in air
- Larger (11cm x 11cm) samples showed hermetic behavior in some cases; however, they failed after 10 thermal cycles in dual atmosphere environment. Recent improvements in sealing process are expected to improve future results.

Approach: Development of glass compositions

- Starting composition: G-18: Ba-Ca-Al-B-Si-O glass
- YS series:
  - Replaced Ba w/ Sr, decreased B, added Y
  - Higher sealing temps, but unstable CTE (decreased over time)
- YSO series:
  - Removed Al from YS series to avoid possible formation of Sr-based celsian phase
  - Improved CTE stability (in ~11.5 ppm/ºC range)
  - Sealing temperature ~950ºC
- YSP series:
  - Included some Ba to raise CTE
  - Improved CTE stability (in ~12.5 ppm/ºC range)
  - Sealing temperature ~1000ºC

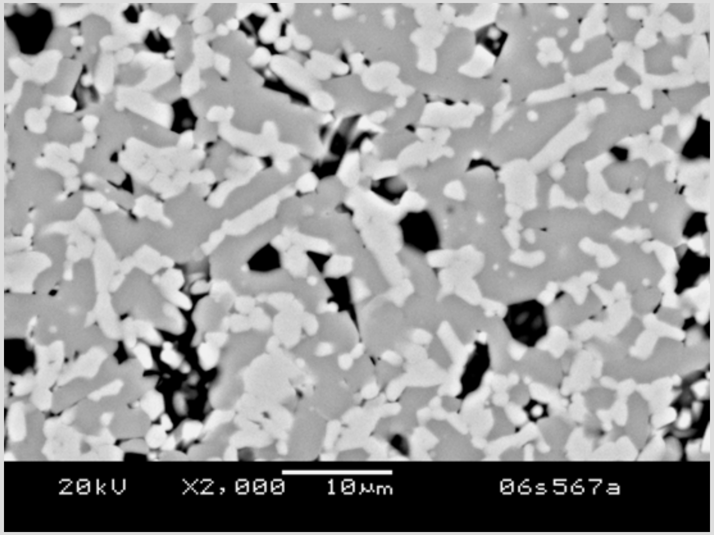
Properties of YSO-1 Glass

Composition (mol%):

42.5% SrO, 10% CaO, 6% Y_2O_3, 7.5% B_2O_3, 34% SiO_2

CTE (ppm/ºC):

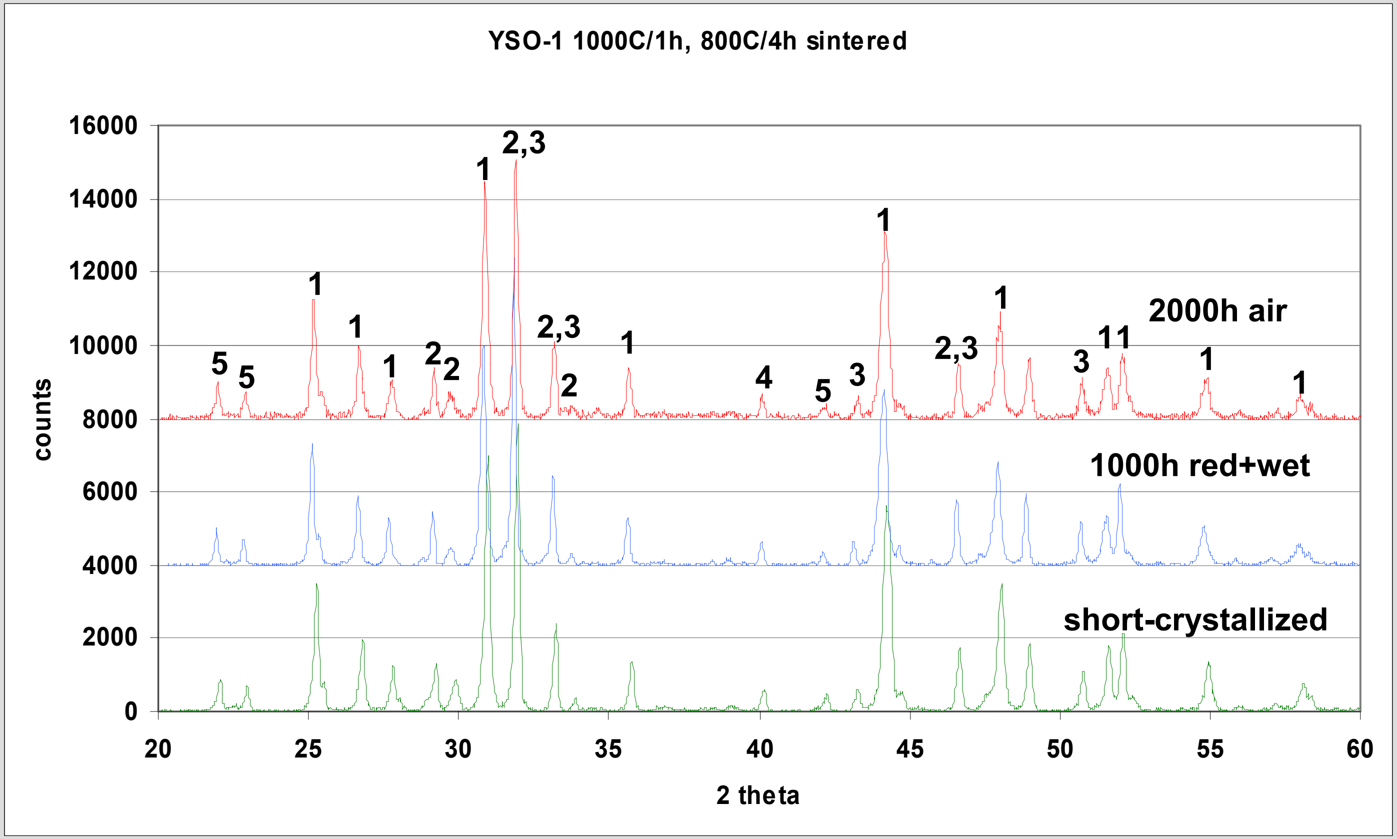
Glass: 12.1; Crystallized: 11.7; 1000 hrs: 11.5; 2000 hrs: 11.6



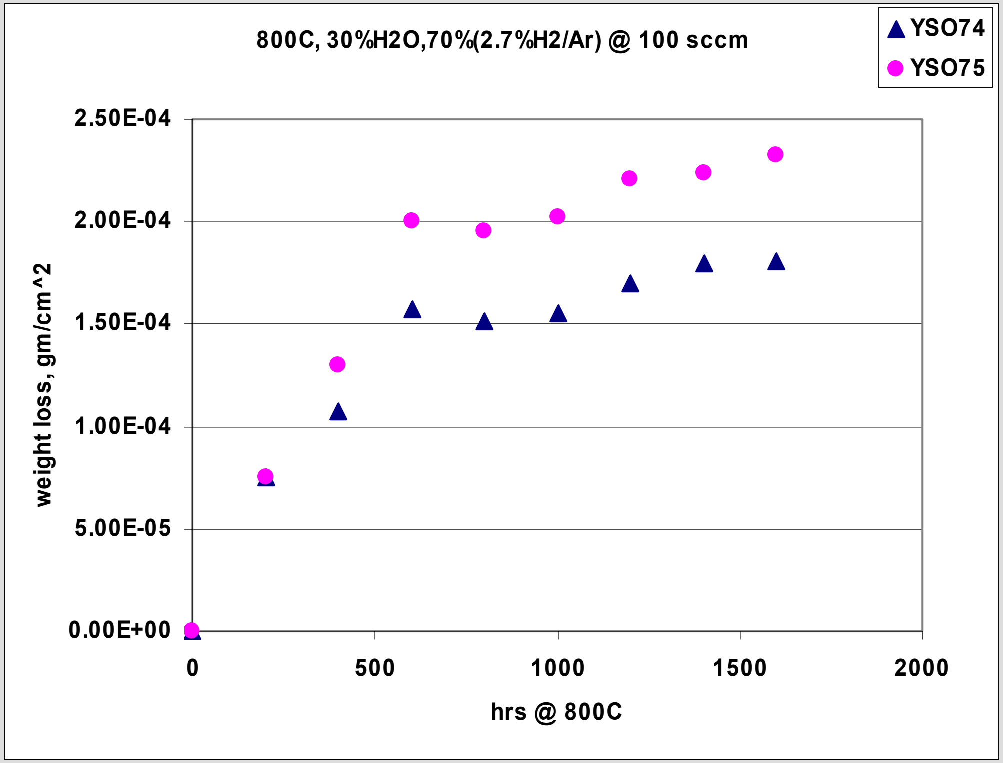
YSO-1 900°C/2000h air aged

Thermal stability of YSO-1: Crystallization Products

1:$SrSiO_3$, 2:Ca_3SiO_5, 3:Ca_2SiO_4, 4:SrB_2O_4, 5:Y_2SiO_5



Thermal stability of YSO glass: weight loss in wet reducing environment

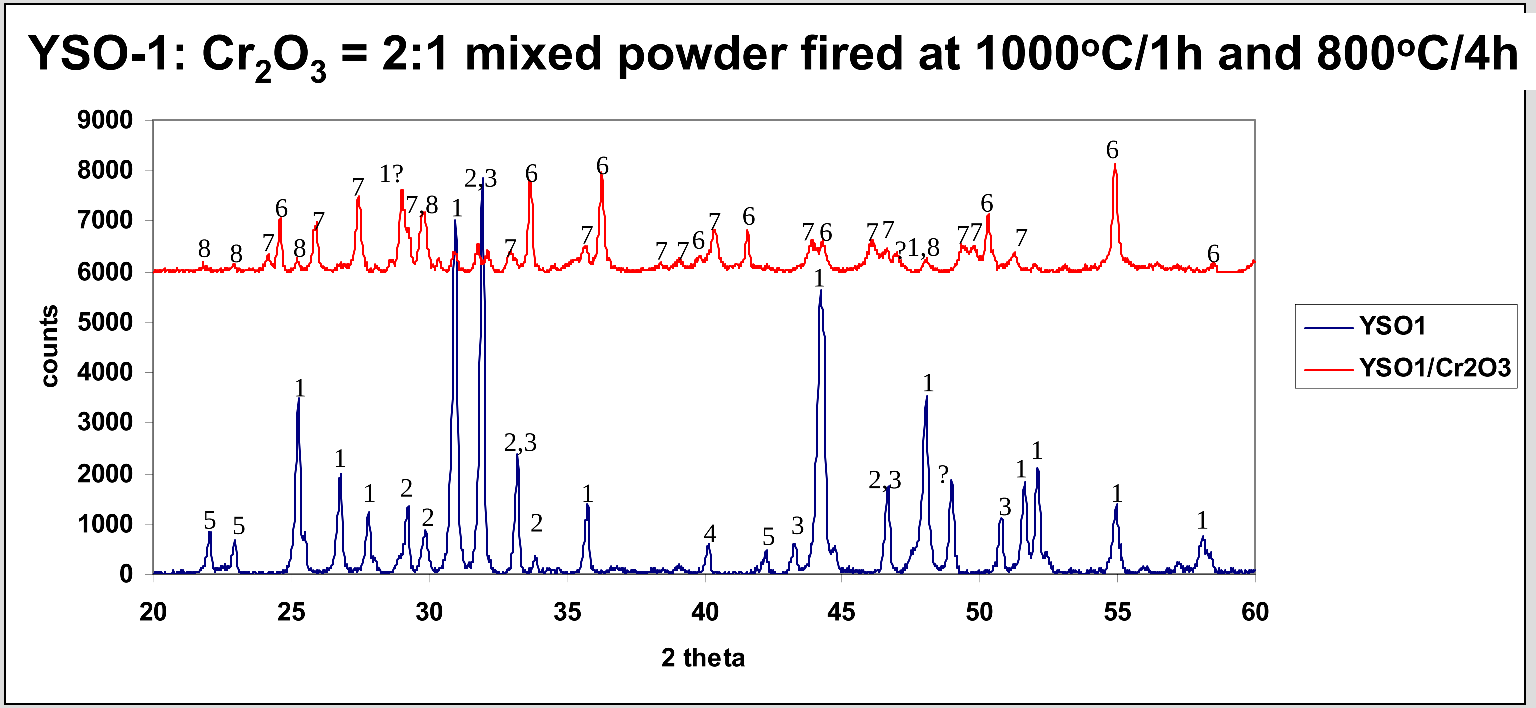


1. 2 stages of weight loss
2. Estimated loss rate to be 3.1-3.6x10^{-8}g/(cm^2.h)
3. Total material loss in 40,000 hrs @800C <0.1 wt%

Glass/alloy interfacial stability

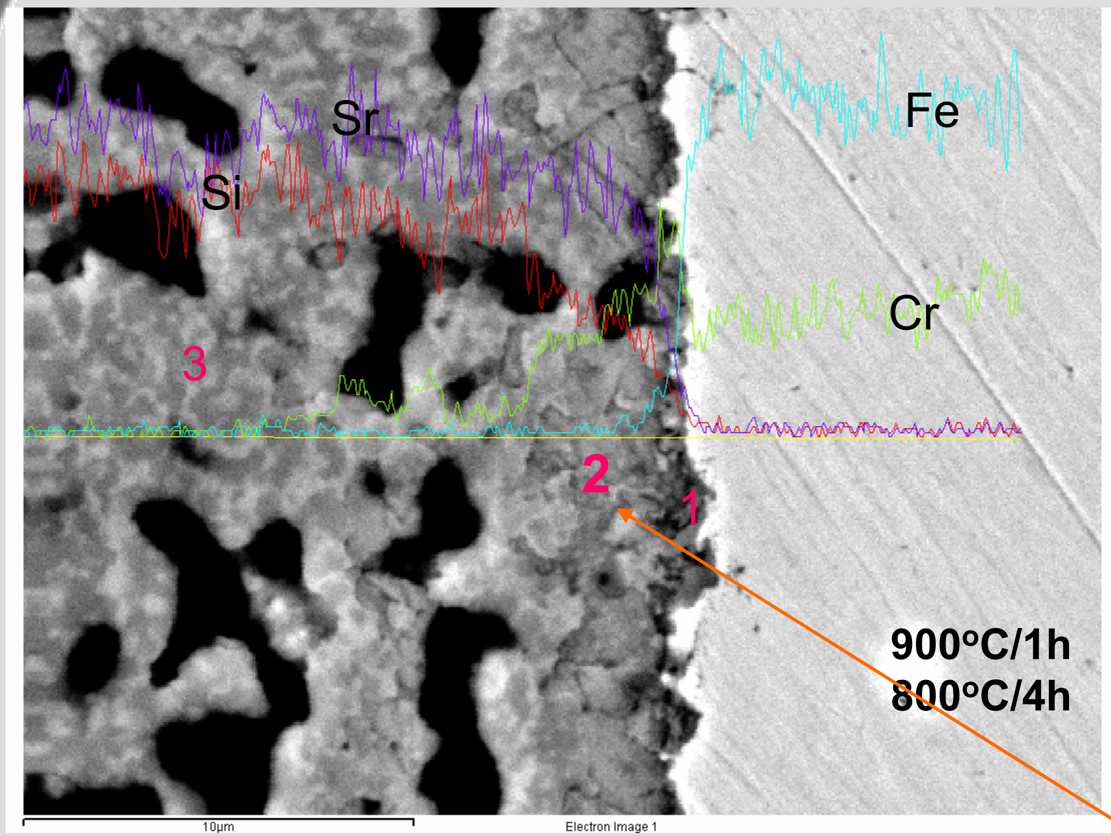
$2SrO + Cr_2O_3 + 1.5O_2 = 2SrCrO_4$ $\Delta G = -156$ kJ/mole

$2SrSiO_3 + Cr_2O_3 + 1.5O_2 = 2SrCrO_4 + SiO_2$ $\Delta G = -24$ kJ/mole



1: $SrSiO_3$, 2: Ca_3SiO_5, 3: Ca_2SiO_4, 4: SrB_2O_4, 5: Y_2SiO_5,
6: Cr_2O_3, 7: $SrCrO_4$, 8: $CaSiO_3$

Glass/alloy interfacial reaction



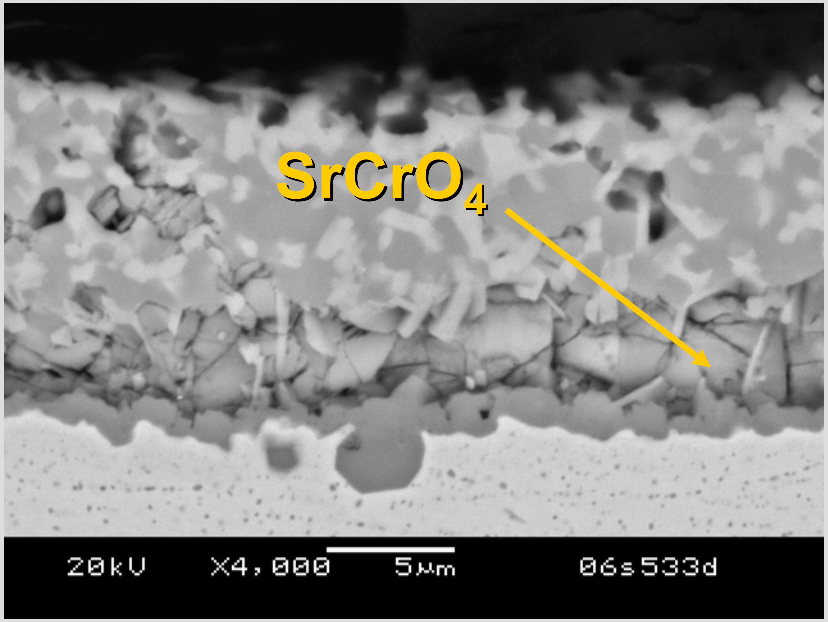
Element	#1	#2	#3
O K	38.2	49.0	47.7
Si K	0.0	1.8	23.0
Ca K	0.0	1.1	5.4
Al K	1.2	0.0	0.0
Ti K	0.4	0.0	0.0
Cr K	28.5	24.7	0.0
Mn K	1.0	0.0	0.0
Fe K	26.2	1.3	0.0
Sr L	4.5	22.3	18.6
Y L	0.0	0.0	5.3

#2: $SrCrO_4$

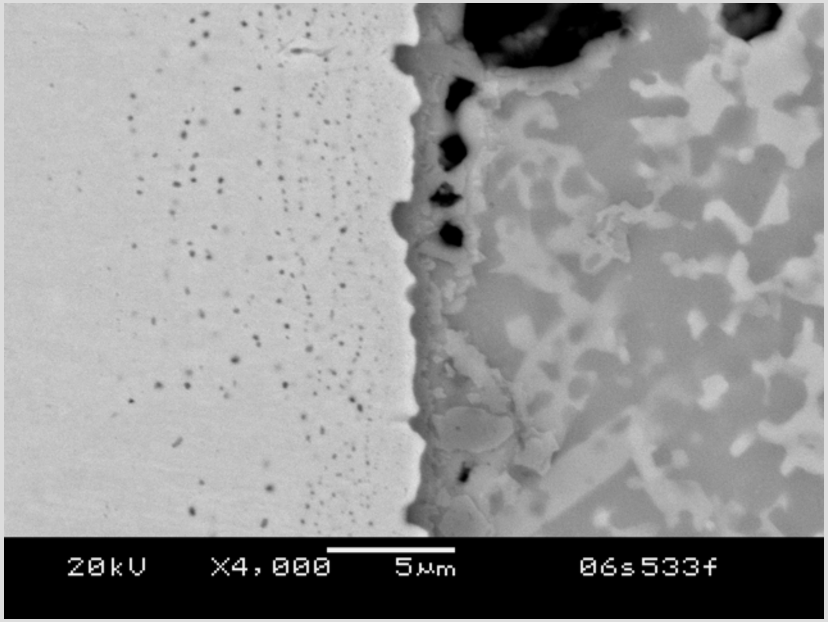
YSO-1 Crofer22APU

Dual atmosphere test: air side

YSO-75 850°C/500hr in dual environments (30%H_2O/70%H_2 vs. air)



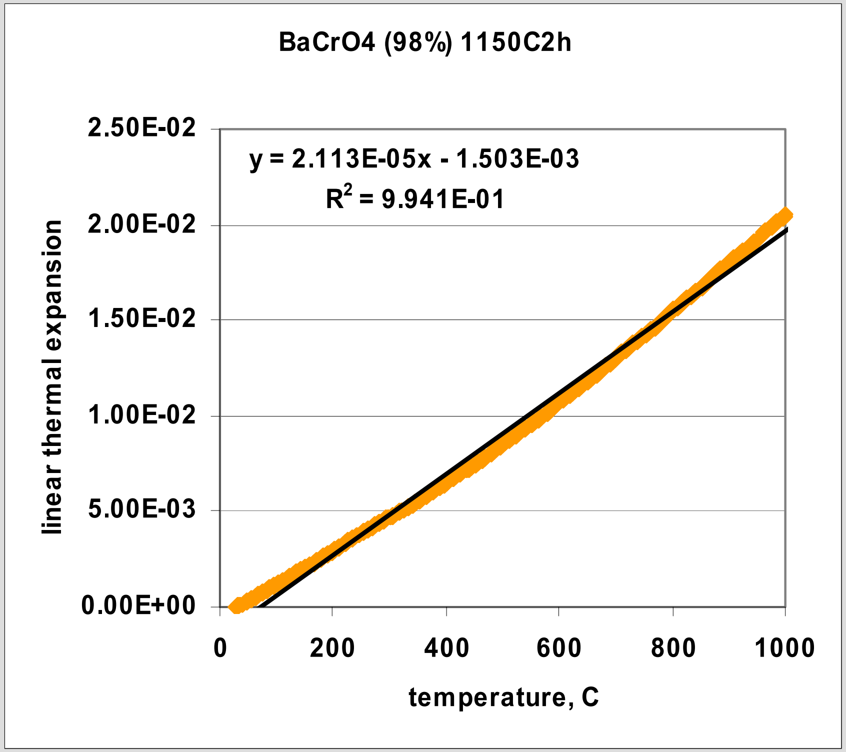
Near seal edge

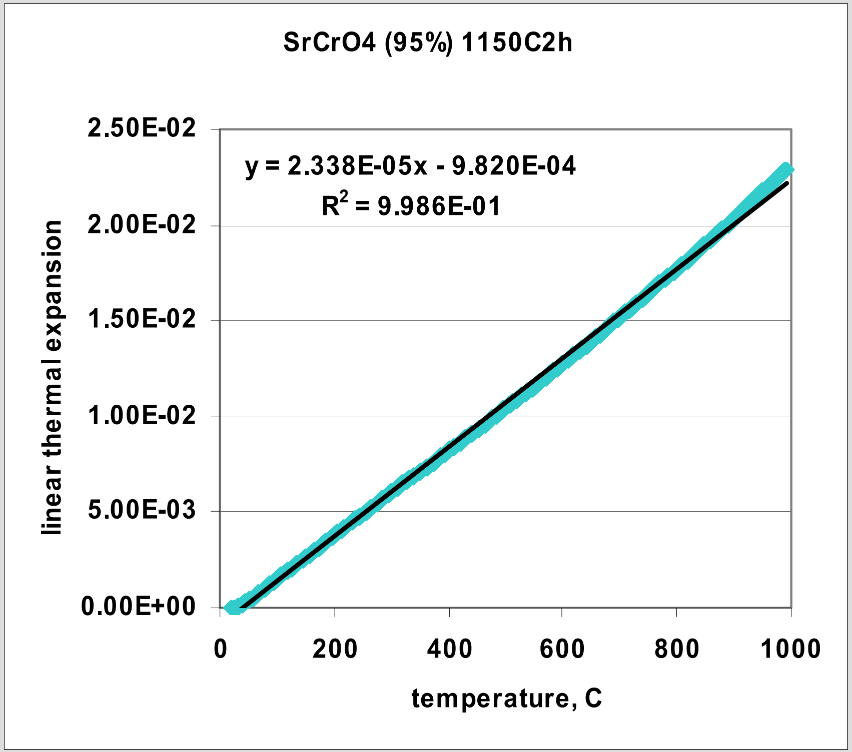


Interior of seal

3.8 cm x 3.8 cm anode-supported bilayer sealed onto 5 cm x 5 cm Crofer22APU; Aged at 850°C for 500 hrs

Thermal Expansion of $BaCrO_4$, $SrCrO_4$



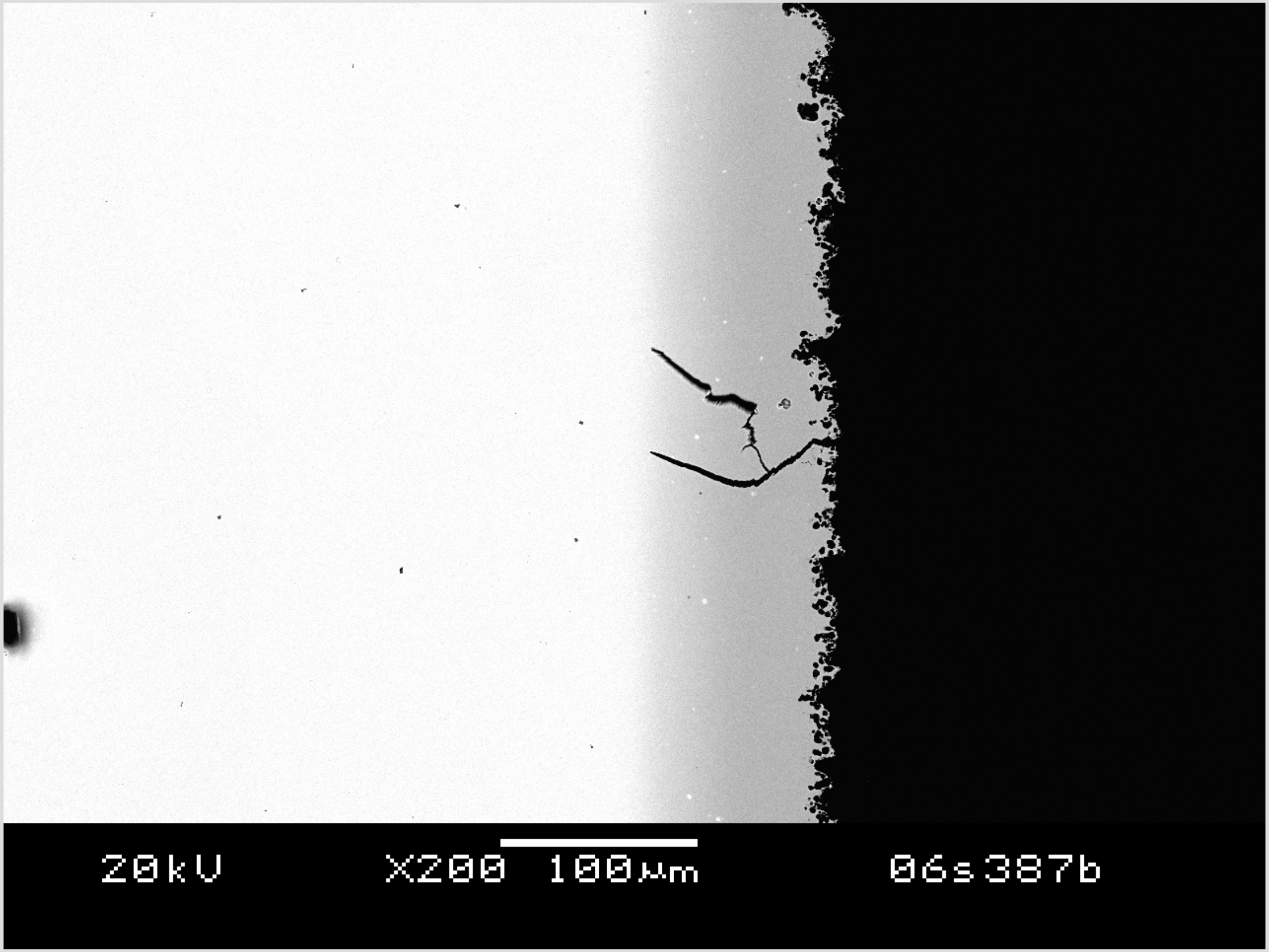


Protective coating to prevent seal / alloy interaction

- Aluminizing of alloy
  - Established commercial process
  - Possible formation of low CTE celsian-like phase (similar to $BaAl_2Si_2O_8$), as observed in Al-containing glasses such as G18?

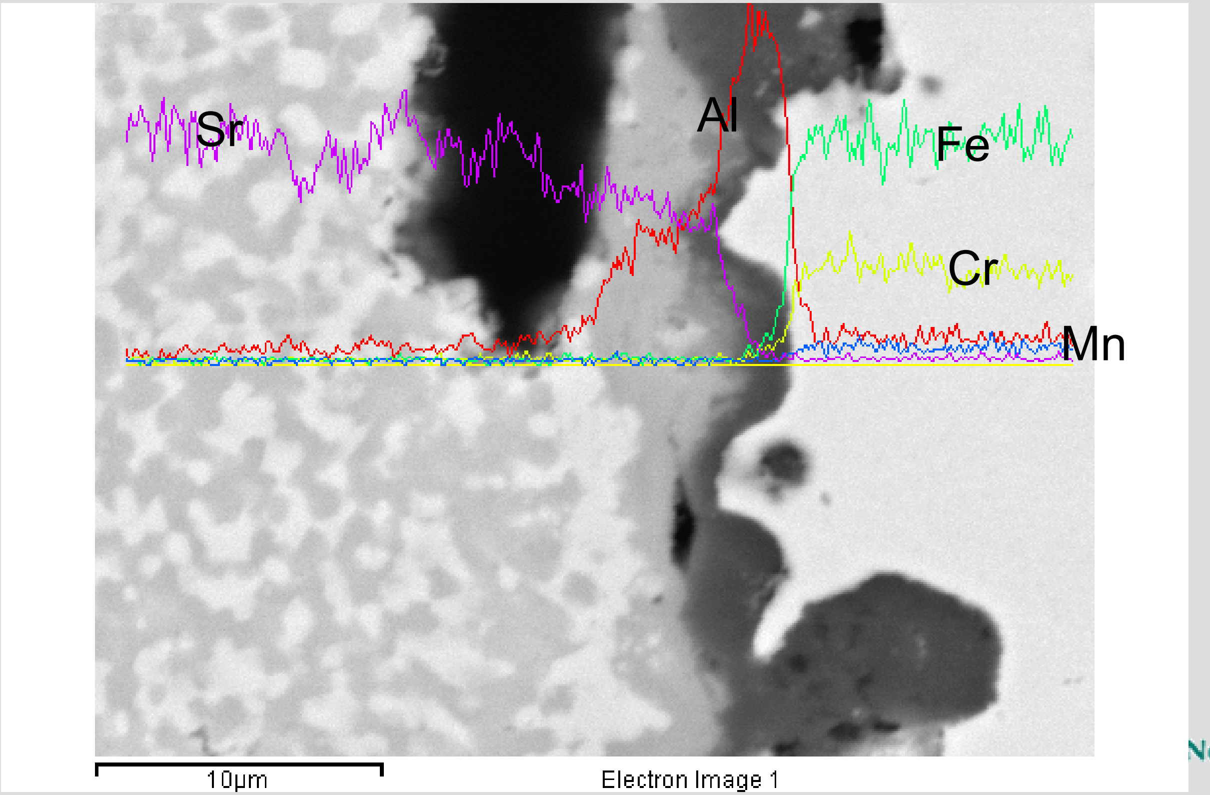
- Mn-Co spinel
  - Potential to use one coating for both active and seal areas of interconnect
  - Chemical compatibility with glass?
  - Unstable in reducing fuel environment

Aluminized Crofer22APU



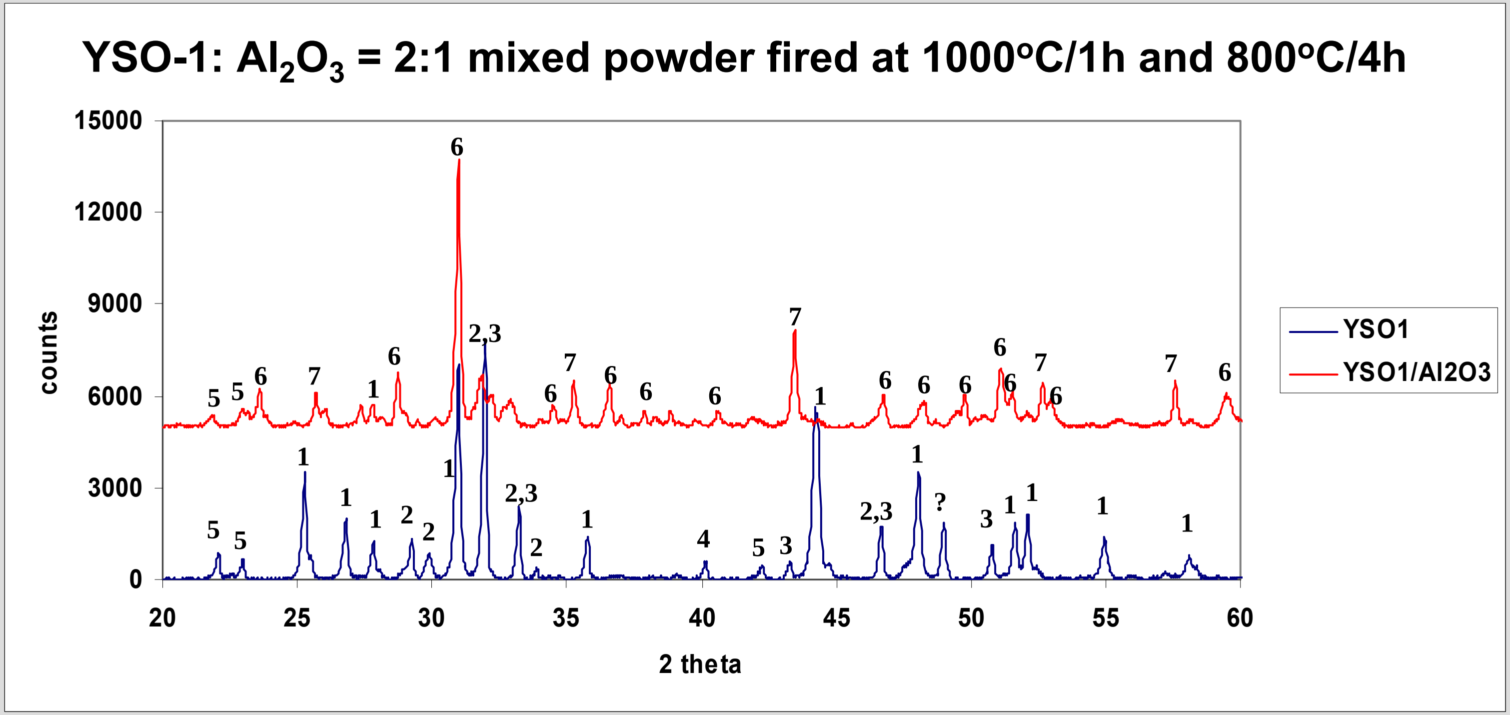
Aluminized Crofer22APU/Glass Interface

- YSO75 sealed at 950ºC/2h followed by 800ºC/4h in air; aged in air 800ºC for 1000 h
- Preliminary room temperature leak tests showed good hermeticity after 1000 hours and 10 thermal cycles (800ºC; air or reducing atmosphere)
- **Alumina layer effectively blocked the diffusion of Cr, Mn, Fe into glass-ceramic**
- No $SrCrO_4$ formation at alloy/glass interface (edge or interior)
- Possible dissolution of Al into glass-ceramic seal



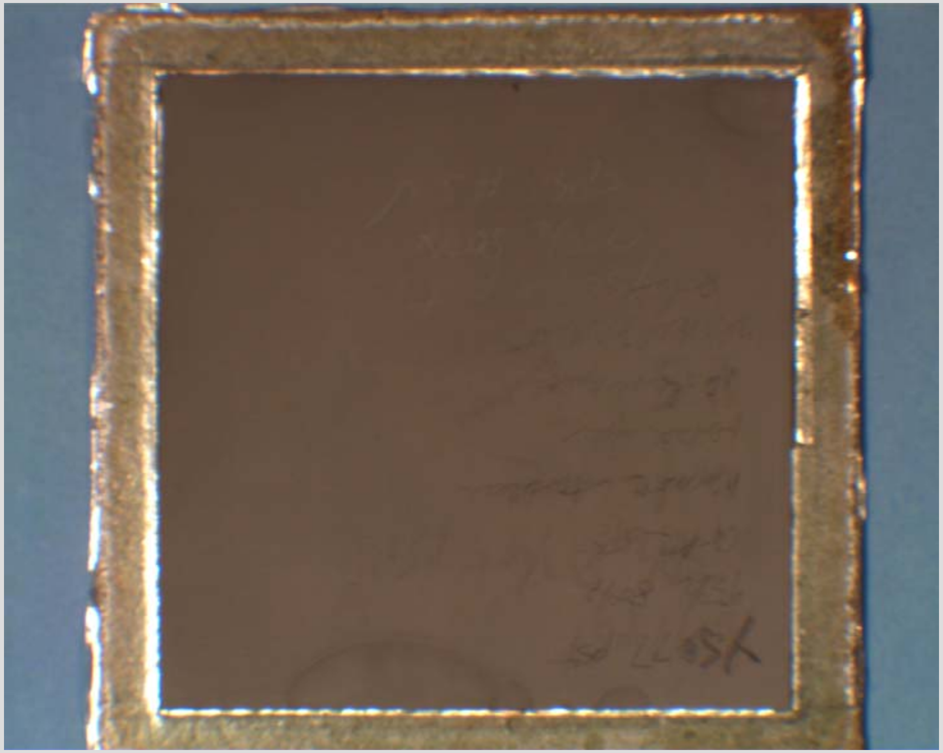
Reactivity with Al_2O_3

1: $SrSiO_3$, 2: Ca_3SiO_5, 3: Ca_2SiO_4, 4: SrB_2O_4, 5: Y_2SiO_5, **6: $Sr_2Al_2SiO_7$**: 7: Al_2O_3



Scale-up of seal testing

- 11cm x 11cm Crofer22APU with 9.5cm x 9.5cm ceramic bilayer sealed in air
- Only 2 out of 8 specimens hermetic after sealing
- Recently improved sealing process (furnace issues resolved, improved seal fabrication)



Future work

- Evaluate the interfacial chemical compatibility and mechanical integrity of aluminized Crofer22APU with candidate sealing glasses.
- Evaluate the interfacial chemical compatibility and mechanical integrity of $(Mn,Co)_3O_4$ spinel-coated Crofer22APU with candidate sealing glasses.
- Implement scaled-up seal testing
- Study the behavior of coated alloys with candidate sealing glass in a simulated SOFC environment with DC electrical loading.
- To investigate effect of transition element additions on chromate formation reaction.

Conclusions

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