Cathode-Interconnect Interfacial Properties

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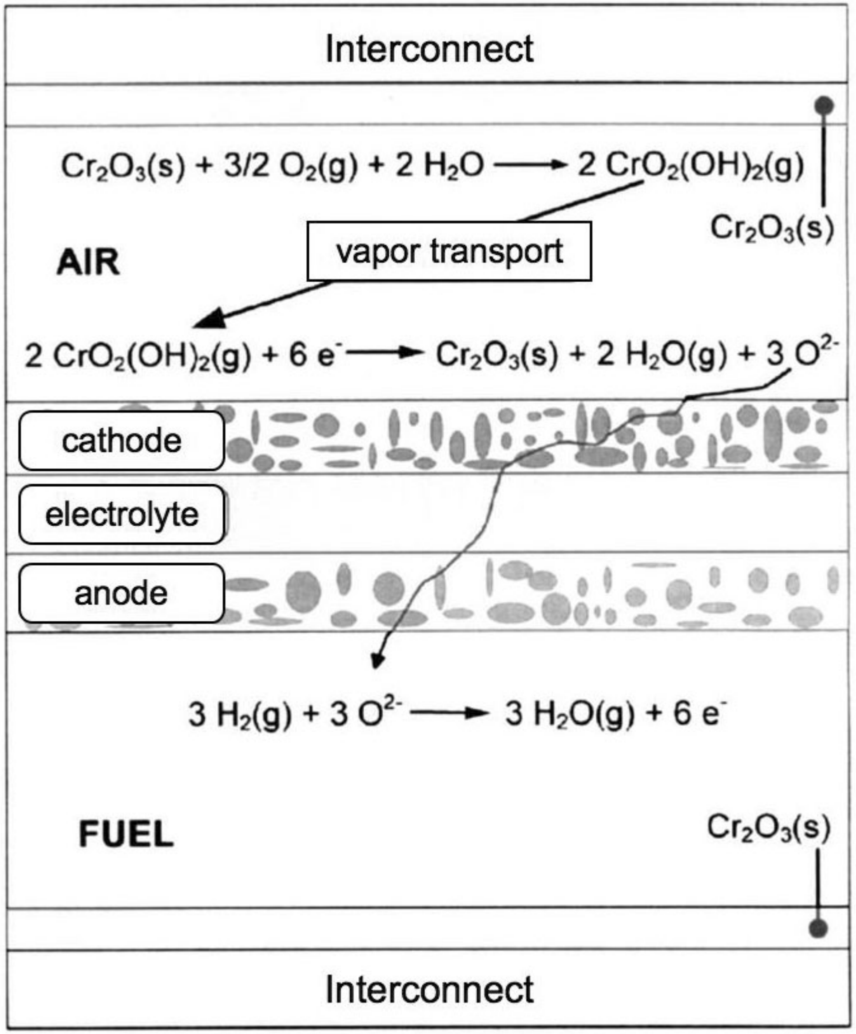
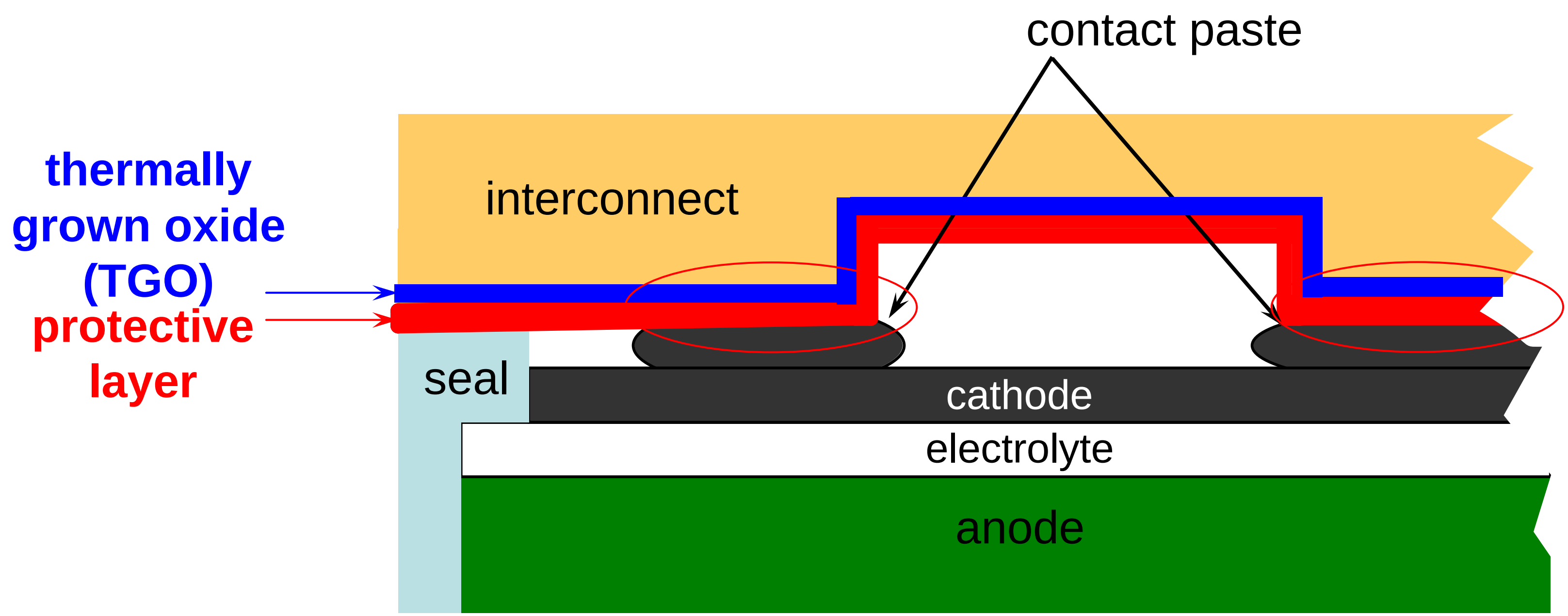
Background – Chromium poisoning



K. Hilpert, D. Das, M. Miller, D. H. Peck and R. Weiss, *J. Electrochem. Soc.*, **Vol. 143**, No. 11 (1996) pp. 3642-3647

Background - Cathode side interfaces



- Protective layer has several requirements*

  - diffusion barrier, thermomechanical/chemical stability etc

- Complex system with several interfaces
- Degradation may be related to debonding due to thermal cycling

* Wang et al., *Surface and Coating Technology*, 2006

Approach

- Phase ID and phase evolution in protective layer during processing*

  - Processing includes reduction and re-oxidation (specimen preparation - PNNL)

  - Phase transitions effect the stress development in layers

  - Phases in thermally grown oxide (TGO) identified

- Fracture Characterization of the interconnect-cathode interfaces as a function of processing conditions

  - Processing includes reduction, re-oxidation and pO_2 cycling**

  - Effect of sintering temperature, volume fraction of pore former and geometric parameters

  - Energy release rate as a function of processing conditions

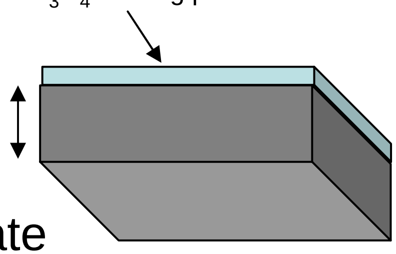
* Wang et al., *J Electrochemical Society*, 2005.

** McCarthy et al., *J Power Sources*, 2008.

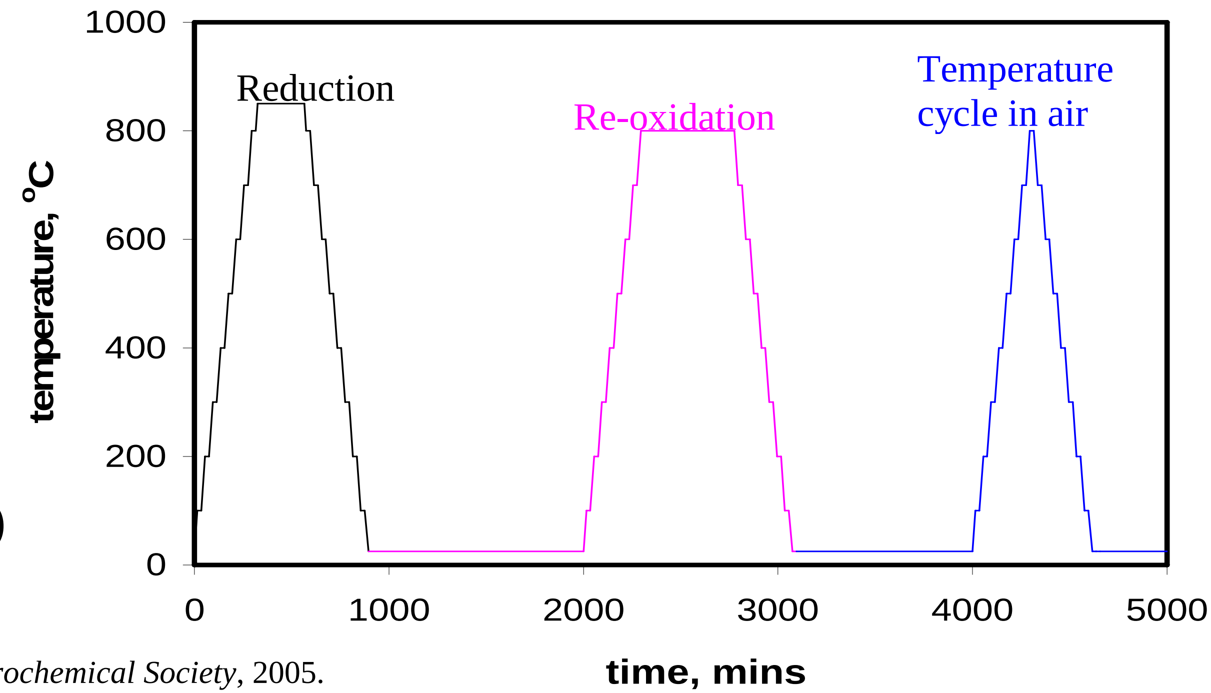
Phase Evolution Study

In-situ XRD on protective layer

15 μm screen printed
(Co,Mn) oxide spinel layer
glycine nitrate combustion synthesis using $MnCO_3$ and Co_3O_4 starting powders.



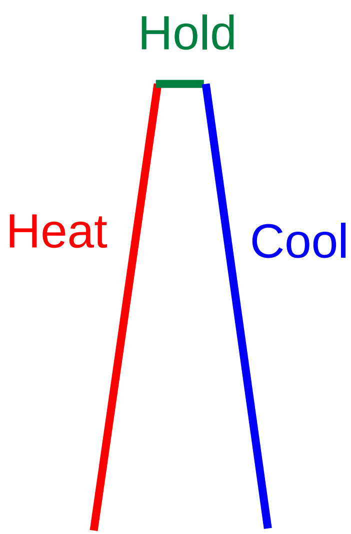
0.3 mm
Metal Substrate
(Crofer or AL441
With Roughness, R_a ~ 0.3 μm)



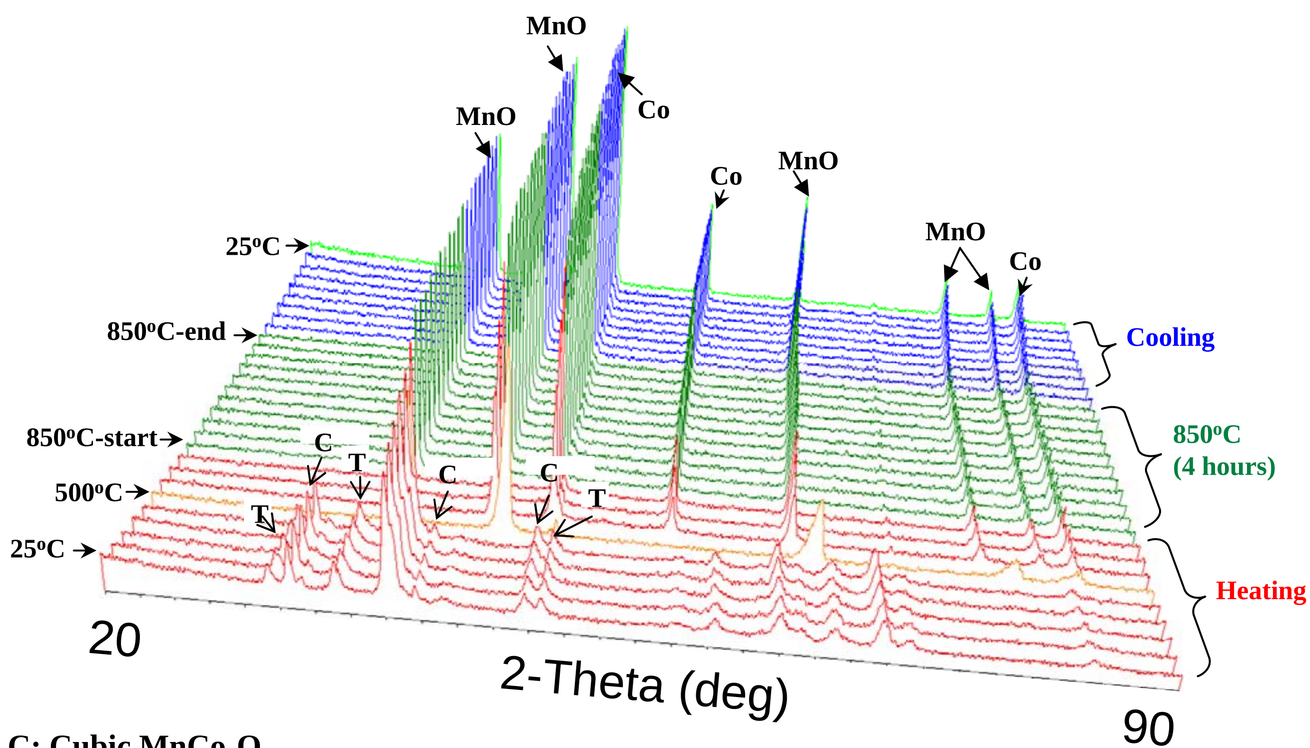
Processing conditions from Wang et al., *J Electrochemical Society*, 2005.

	Reduction	Oxidation
Heating/Cooling Rate	5 °C/min	5 °C/min
Measurements during heating/cooling	Every 100 °C (20mins scan)	Every 100 °C (20mins scan)
Holding temperature/time	850 °C (4 hours)	800 °C (8 hours)
XRD scan time during holding	20 mins	20 mins
Environment	Wet 4%H_2 96%N_2 (13.3 cc/min)	Air

Results – Phase evolution for reduction cycle



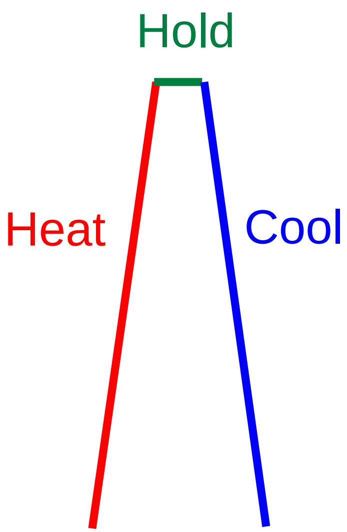
Protective layer phases on Crofer substrate



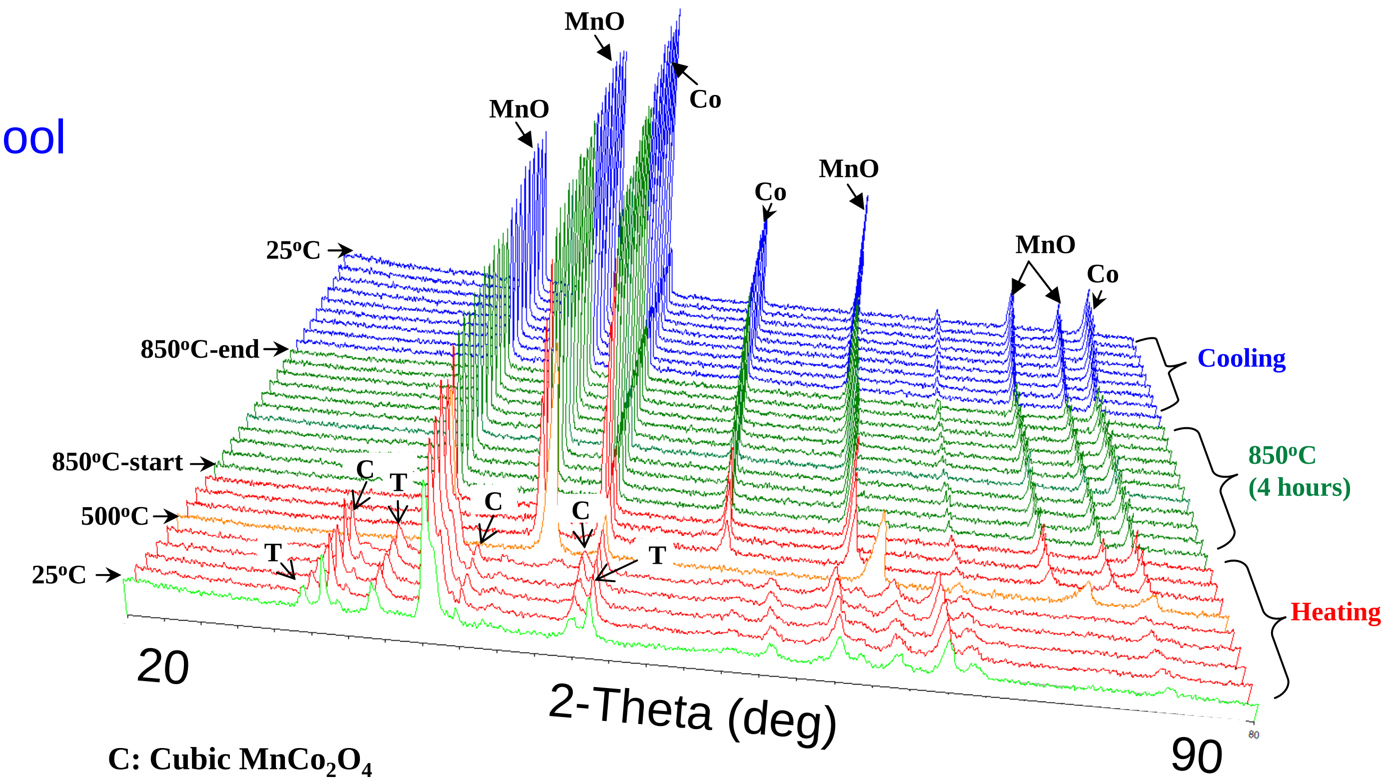
C: Cubic $MnCo_2O_4$
T: Tetragonal $CoMn_2O_4$ or $(Co,Mn)(Co, Mn)_2O_4$

- C + T oxide phases until 400 °C → Transition state 400 – 600 °C → Co + MnO
- Co + MnO are present at the end of the reduction process

Results – Phase evolution for reduction cycle



Protective layer phases on AL441 substrate



C: Cubic $MnCo_2O_4$
T: Tetragonal $CoMn_2O_4$ or $(Co,Mn)(Co, Mn)_2O_4$

- The evolution of the phases in AL441 is the same as the Crofer substrate

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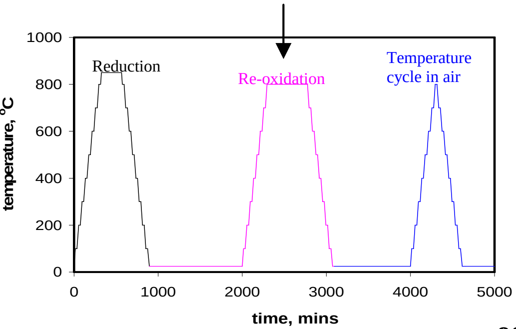
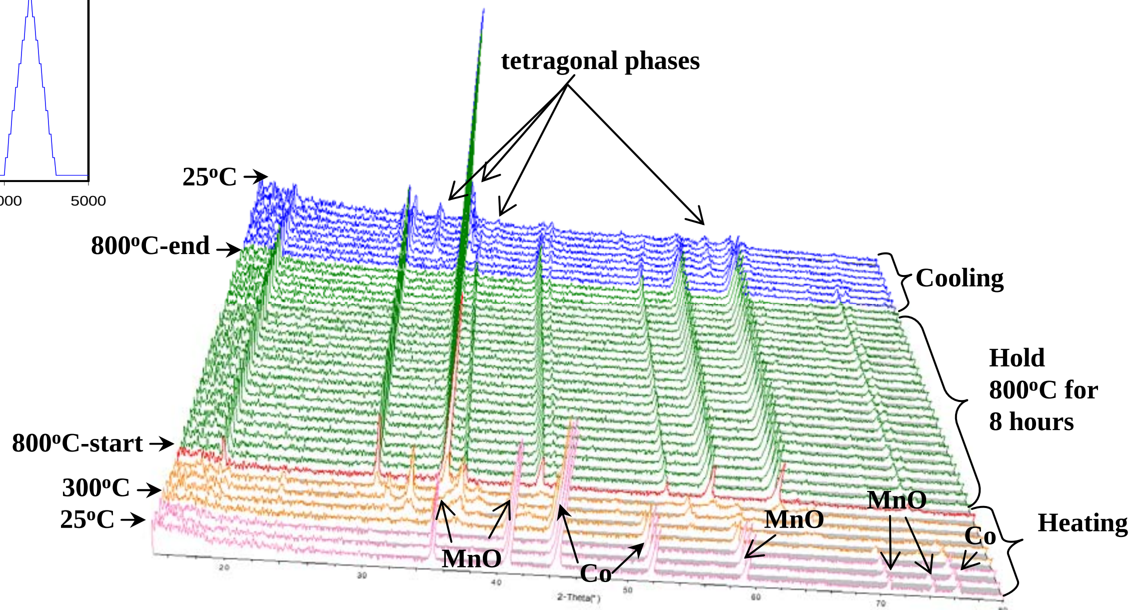
Results – Phase evolution for re-oxidation cycle



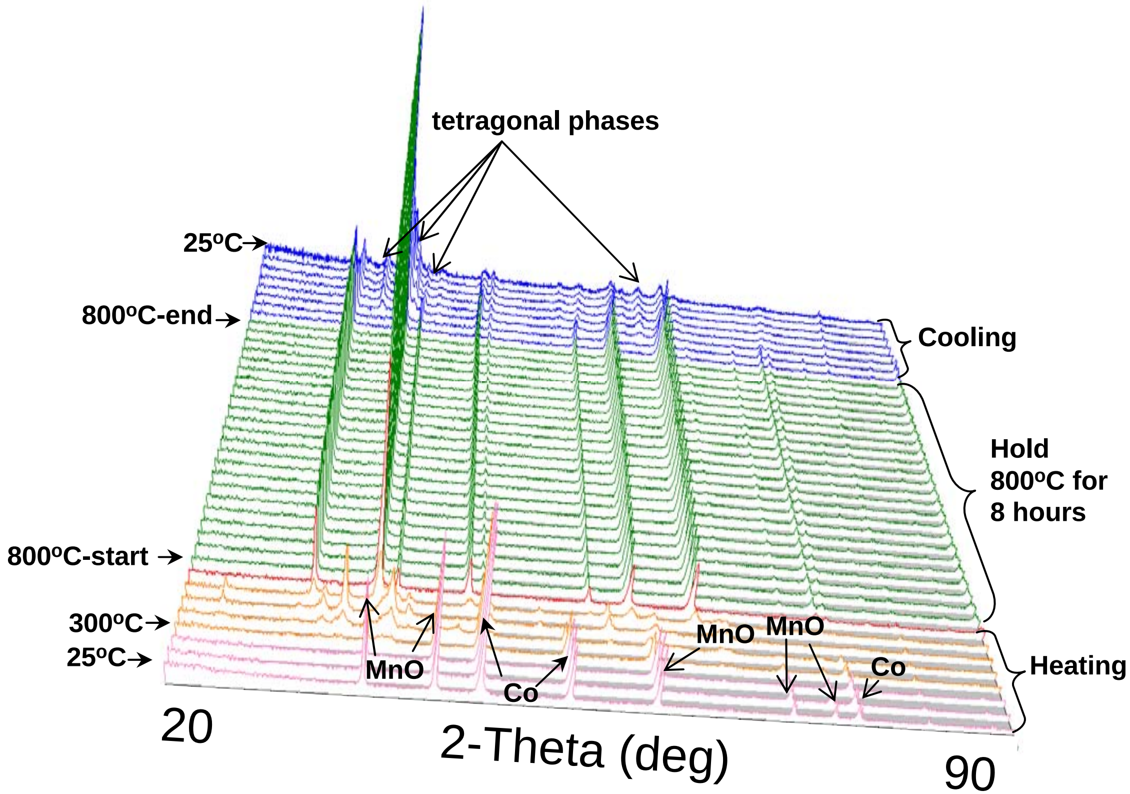
Protective layer phases on Crofer substrate



- Co and MnO start oxidizing at 300 °C
- 400 – 500 °C – Co → $CoO + Co_3O_4$; MnO (c) → Mn_2O_3 (c) → Mn_3O_4 (t)
- 500 °C phases → Tetragonal $CoMn_2O_4$ or $(Co,Mn)(Co, Mn)_2O_4$ + Co_3O_4 (c) + Mn_2O_3 (c) + Mn_2O_4 (o)
- 700 °C and above only cubic $MnCo_2O_4$ is present
- During cooling tetragonal phase appears at 600 °C and cubic and tetragonal spinel phases co-exist below 500 °C

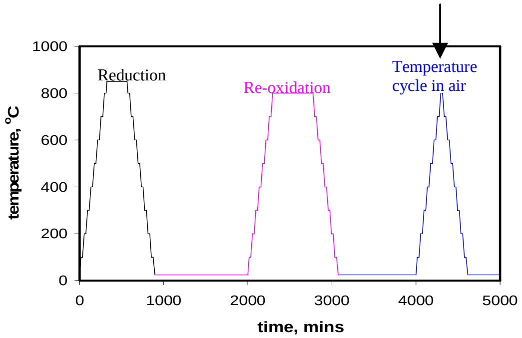
Results – Phase evolution for <u>re-oxidation</u> cycle

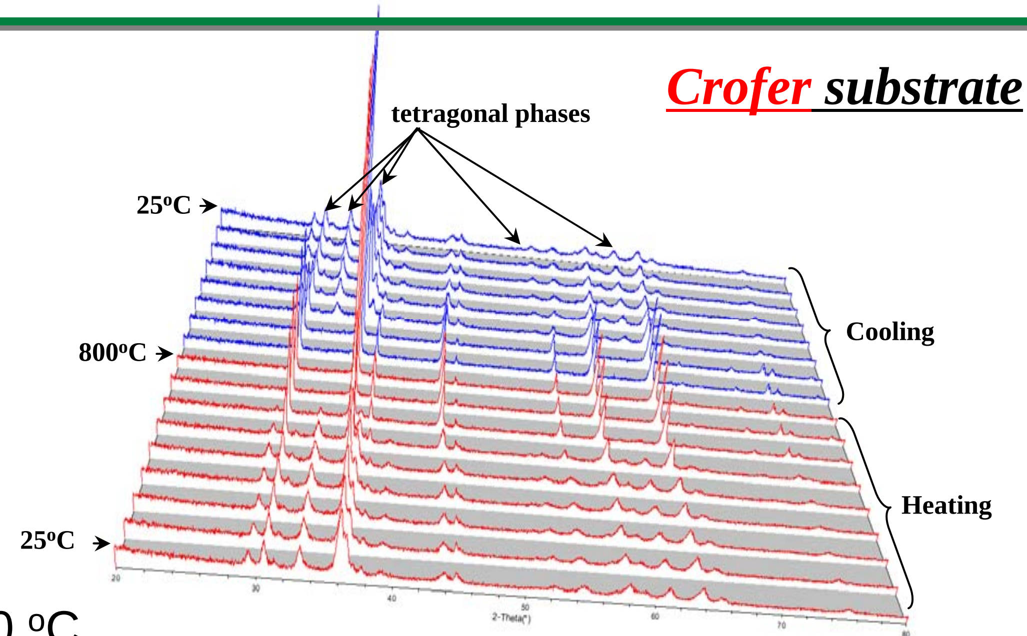
<u>Protective layer phases on AL441 substrate</u>



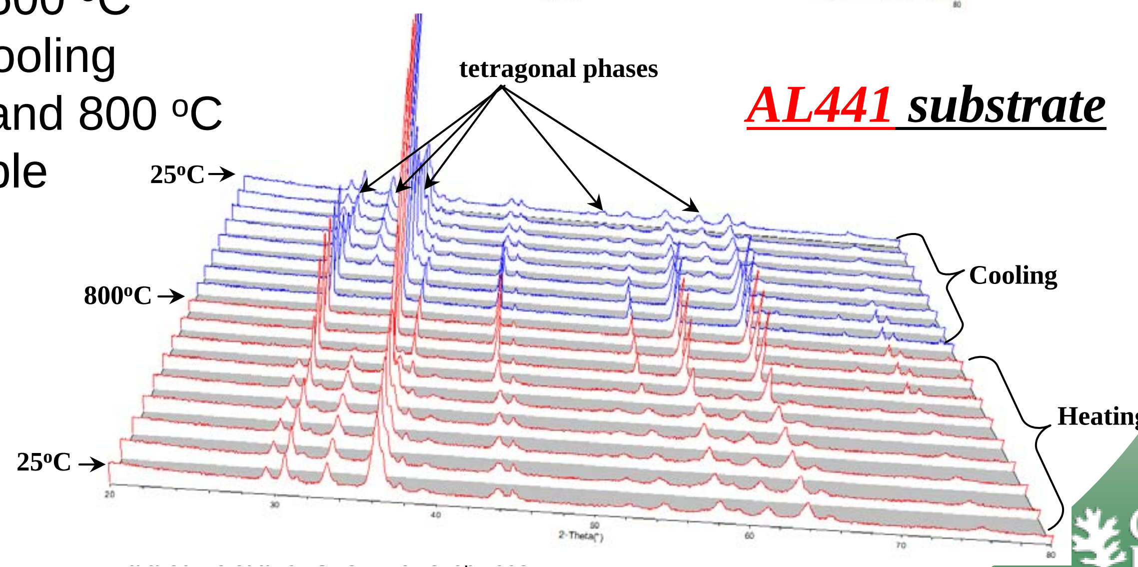
- The evolution of the phases during re-oxidation in AL441 is the same as evolution of the phases on Crofer substrates
- The phase transformations would affect the stress development inside the layers

Results – Phase evolution for Temperature cycle





- C + T oxide phases until 600 °C
  - during heating/cooling
- Only cubic phase at 700 and 800 °C
- Transformation is reversible for one cycle



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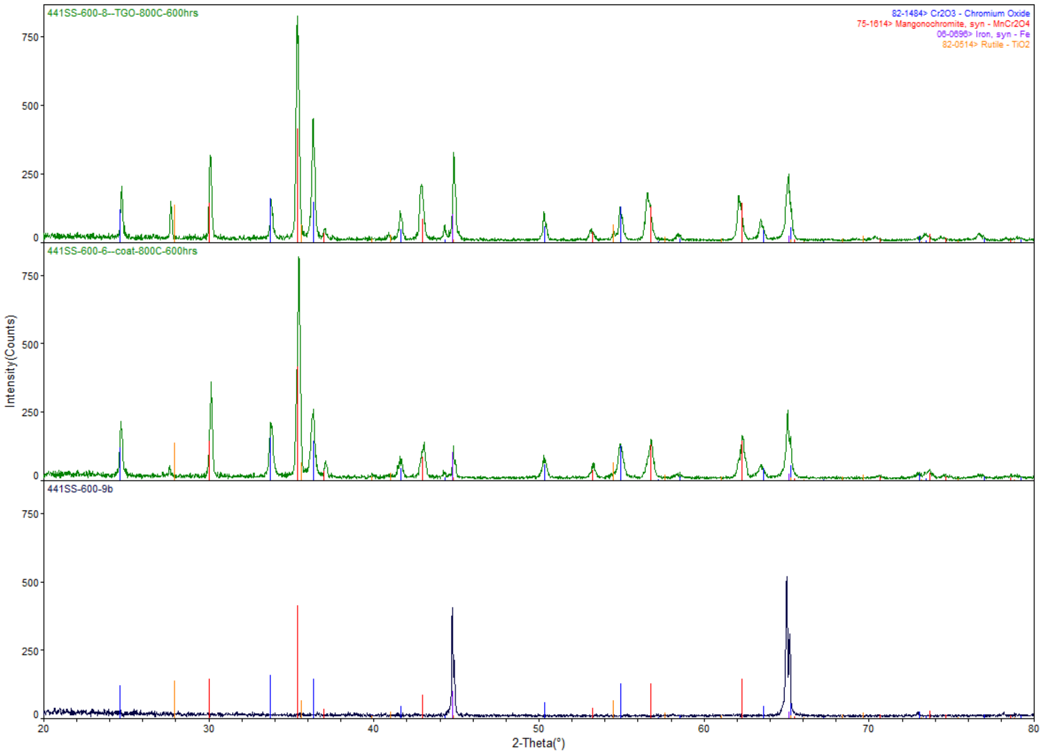
Phases in thermally grown oxide (TGO) layer

600-8 (441)

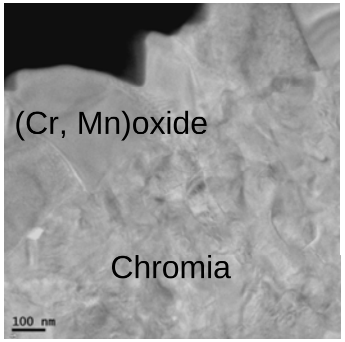
600-6 (441)

600I-3 (Crofer)



Sample I.D.	Material	Surface roughness R_a , µm	Phases identified through XRD
600-8	441 stainless steel	0.08	Cr_2O_3, $MnCr_2O_4$, **TiO_2**
600-6		0.63	
600I-3	Crofer 22 APU	0.1	Cr_2O_3, $MnCr_2O_4$,

Treatment
800 °C for 600 hours



Phases confirmed by TEM analysis (for Crofer)

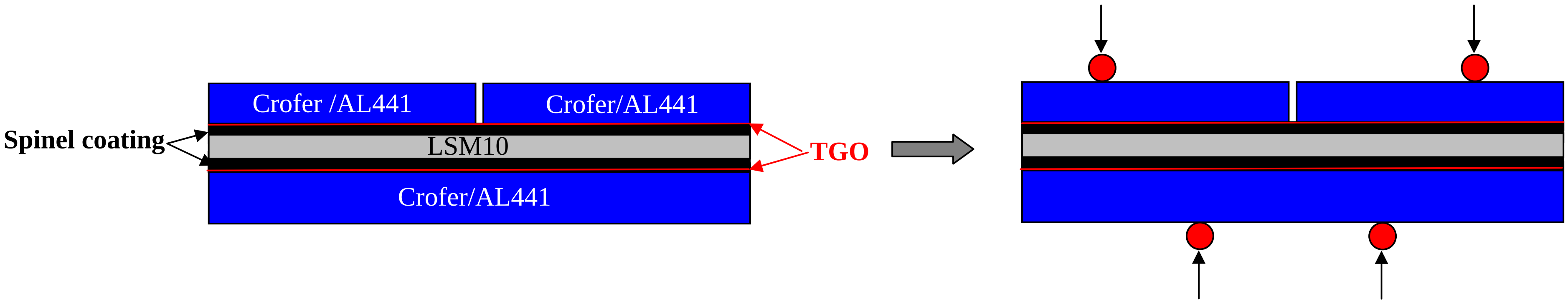
- Titanium oxide present on Al441 but not on Crofer

Summary - Phase evolution for protective layer

- The phase transformations in the spinel protective layer due to reduction, re-oxidation and temperature cycling were identified.
- Under oxidizing conditions, the cubic spinel $MnCo_2O_4$ is stable at elevated temperatures whereas both cubic and tetragonal phases co-exist at lower temps.
- The phase evolution is important to quantify the residual stresses in the layers.
- Residual stress measurements are in progress at NSLS.

Interfacial Characterization

Sample preparation and testing



- AL441, Crofer22
  - Cut and ground to either 30 or 15 mm in length and 300 µm in thickness with high values of flatness and parallelism
- 15 µm spinel protective layer screen printed
  - Same reduction and re-oxidation procedure as described for phase ID study
- Commercial LSM paste screen printed
  - Sandwich specimen sintered with total LSM layer thickness 60 – 70 µm
  - Variables – Sintering conditions (air/cyclic pO_2), temperature, concentration of pore former, thickness of LSM, aging and thermal cycling.

Calculation of Strain Energy Release Rate

- **Four point bending based interfacial fracture energy calculation***

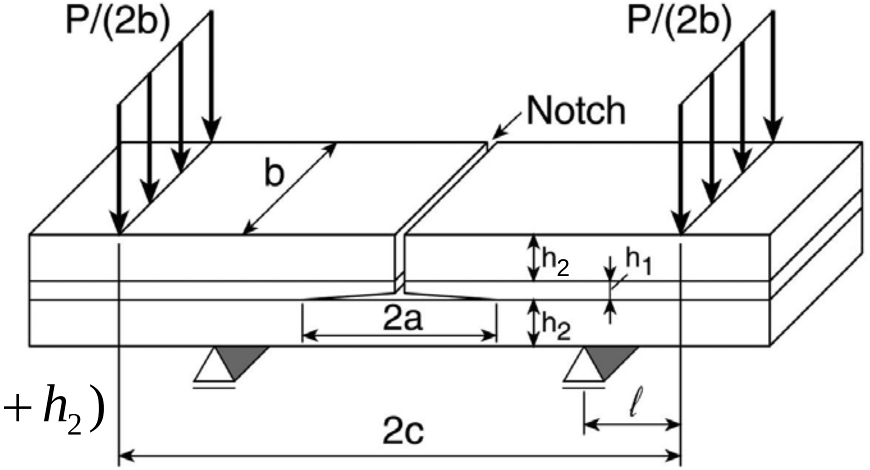
$$G = \frac{(1-\nu^2)M^2}{2E_2}\left(\frac{1}{I_2}-\frac{1}{I_c}\right)$$

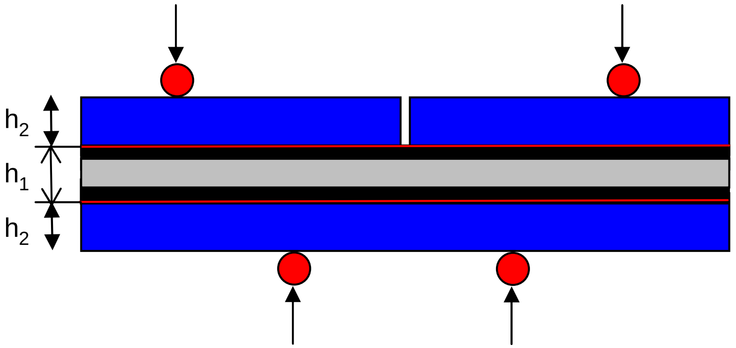
$$M = Pl/2b$$

$$I_c = kh_1^3/12 + 2h_2^3/3 + h_1h_2(h_1/2 + h_2)$$

$$k = \frac{E_1(1-\nu_2^2)}{E_2(1-\nu_1^2)}$$

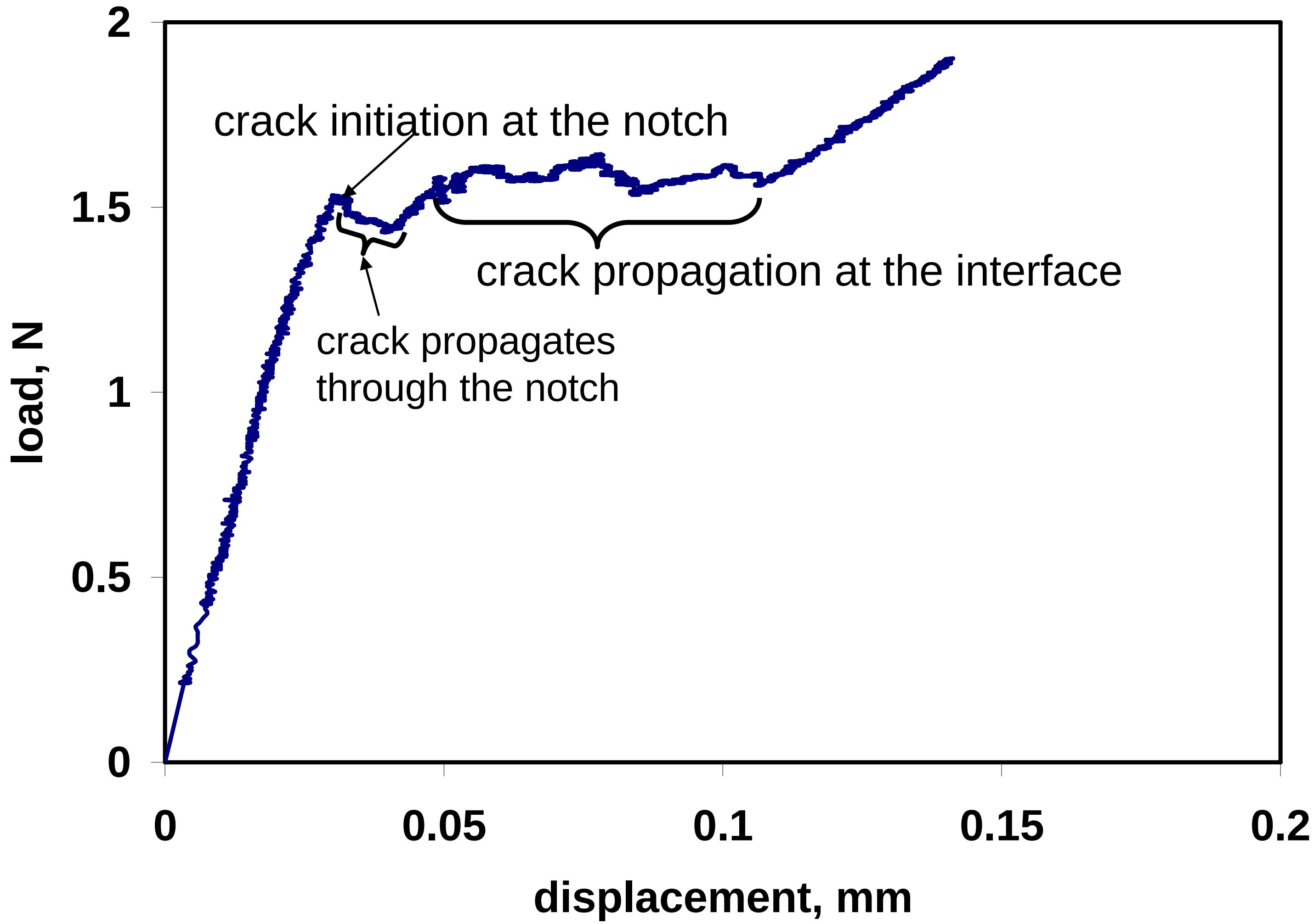
$$I_2 = h_2^3/12$$





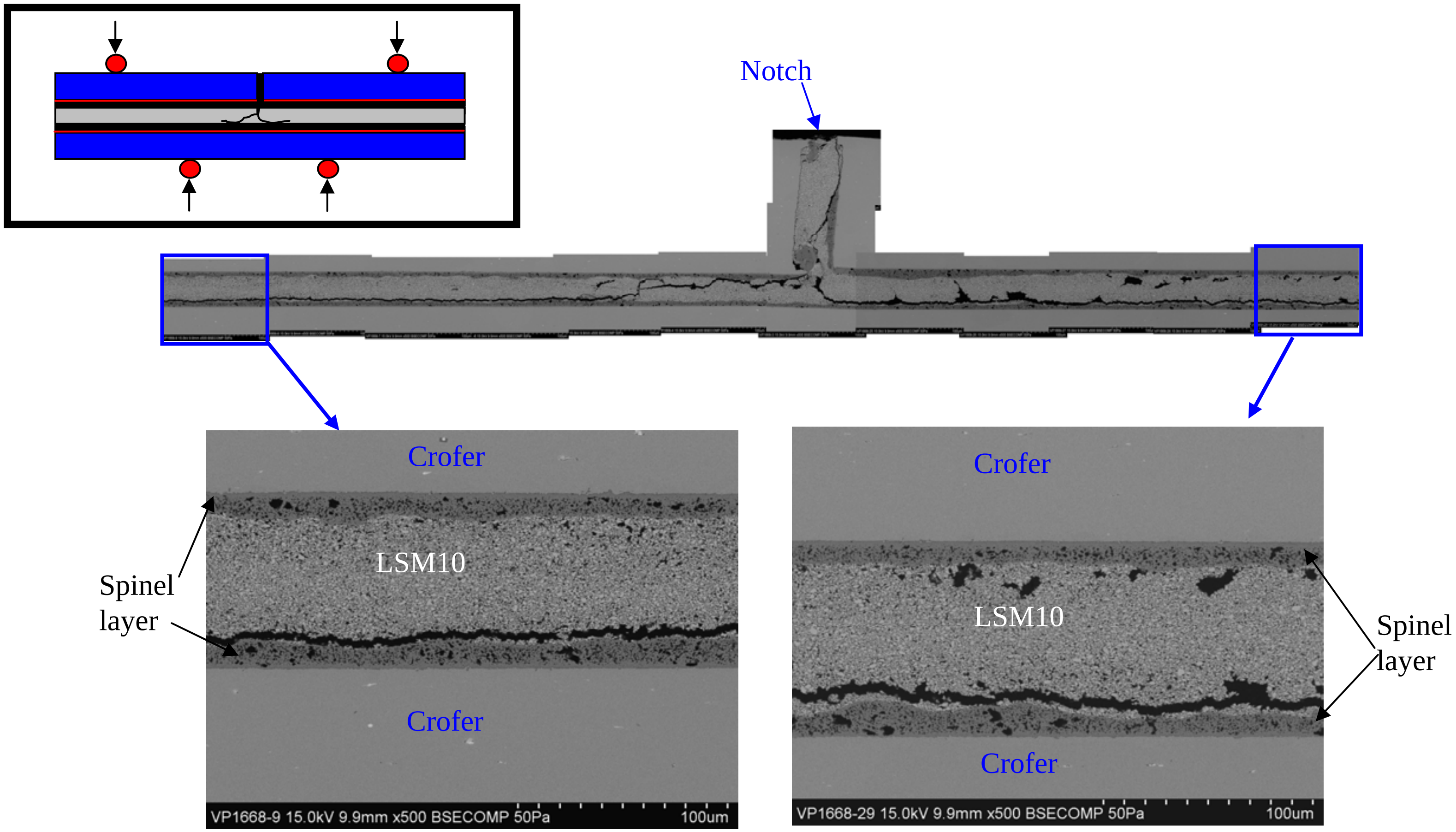
* Hofinger *et al*., International Journal of Fracture **92**: 213-220, 1998.

Example load-displacement behavior



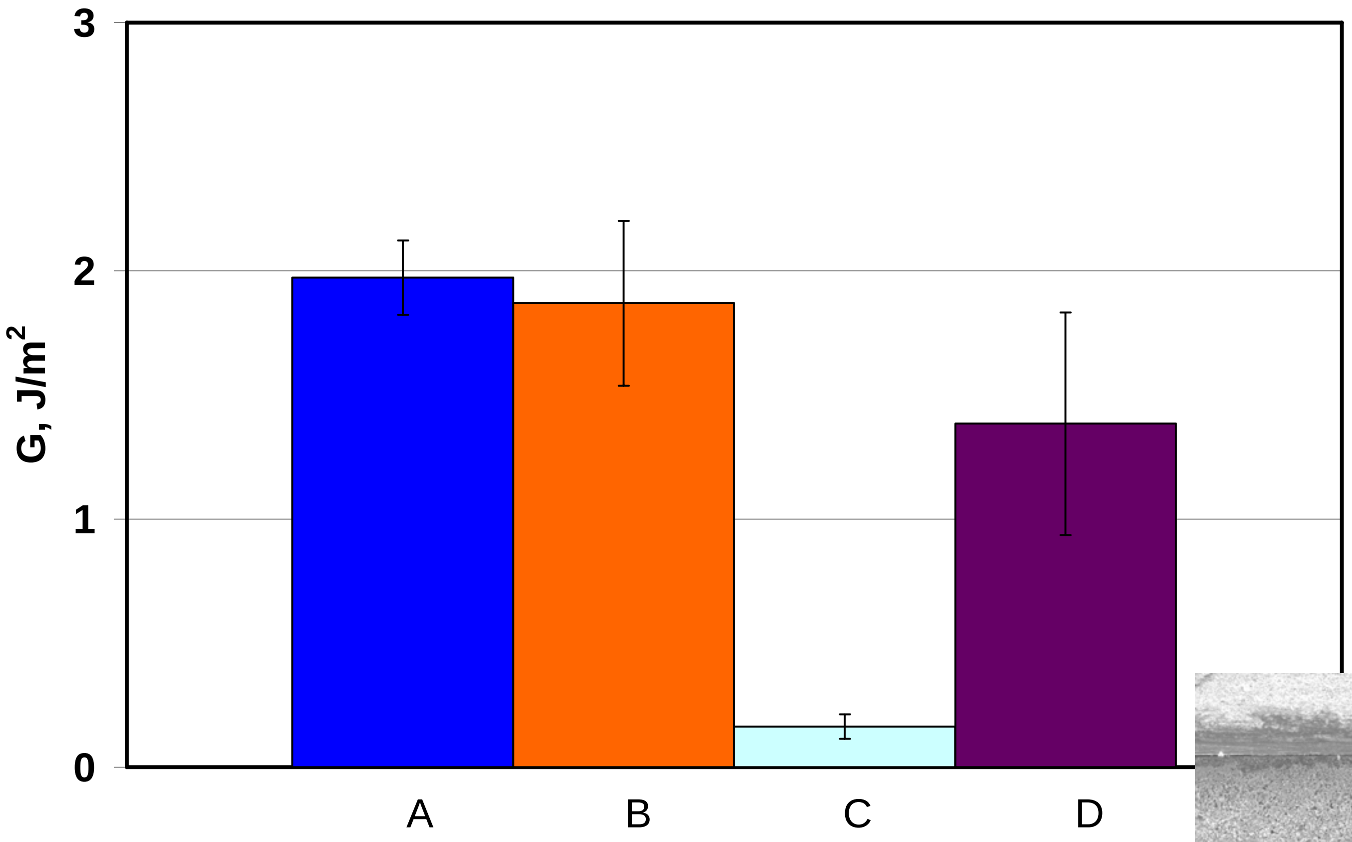
• Steady state load gives a measure of the strain energy release rate of interface

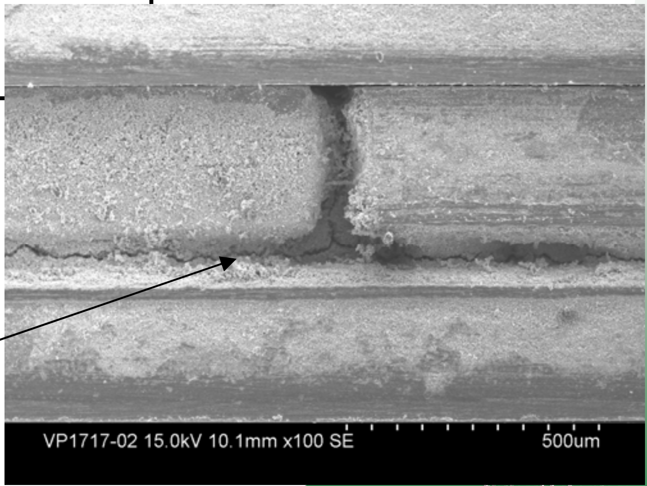
Crack propagation along interface - SEM



- Crack propagation path is the interface between the LSM10 and spinel protective layer or within the LSM10 layer near the interface
- Mechanical behavior is characterized with test method

Strain energy release rate variation





A – 900 °C 4 hours – regular sintering in air (8 tests)
B - 900 °C 4 hours – pO2 cyclic sintering, 12 cycles (10 tests)
C - 900 °C – 12.5 volume % pore former (2 tests)
D - 1000 °C – 12.5 volume % pore former (4 tests)
Debonding in as prepared specimens for <u>22.2 % pore former sintered at 900 and 1000 °C</u>

Lara-Curzio et al. 9th SECA Workshop 2008

Summary – Interfacial Toughness

- A methodology has been established to determine the fracture behavior of metallic interconnects and LSM contact paste interfaces.
- The crack propagation path is identified as the interface between the LSM10 and spinel protective layer or within the LSM10 layer near the interface.
- Preliminary test results show that pO_2 cycling sintering does not influence the interfacial toughness (t-test at the 95% confidence level indicates the difference between the mean values is not significant).

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Summary

- Phase evolution in the screen printed spinel protective layer and its implications for the mechanical behavior were identified.
- Interfacial toughness testing methodology was developed and implemented.

Acknowledgments

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James Rakowski – Allegheny Ludlum

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