Interconnect-Coating Interactions: Mn-Co Spinel Oxides

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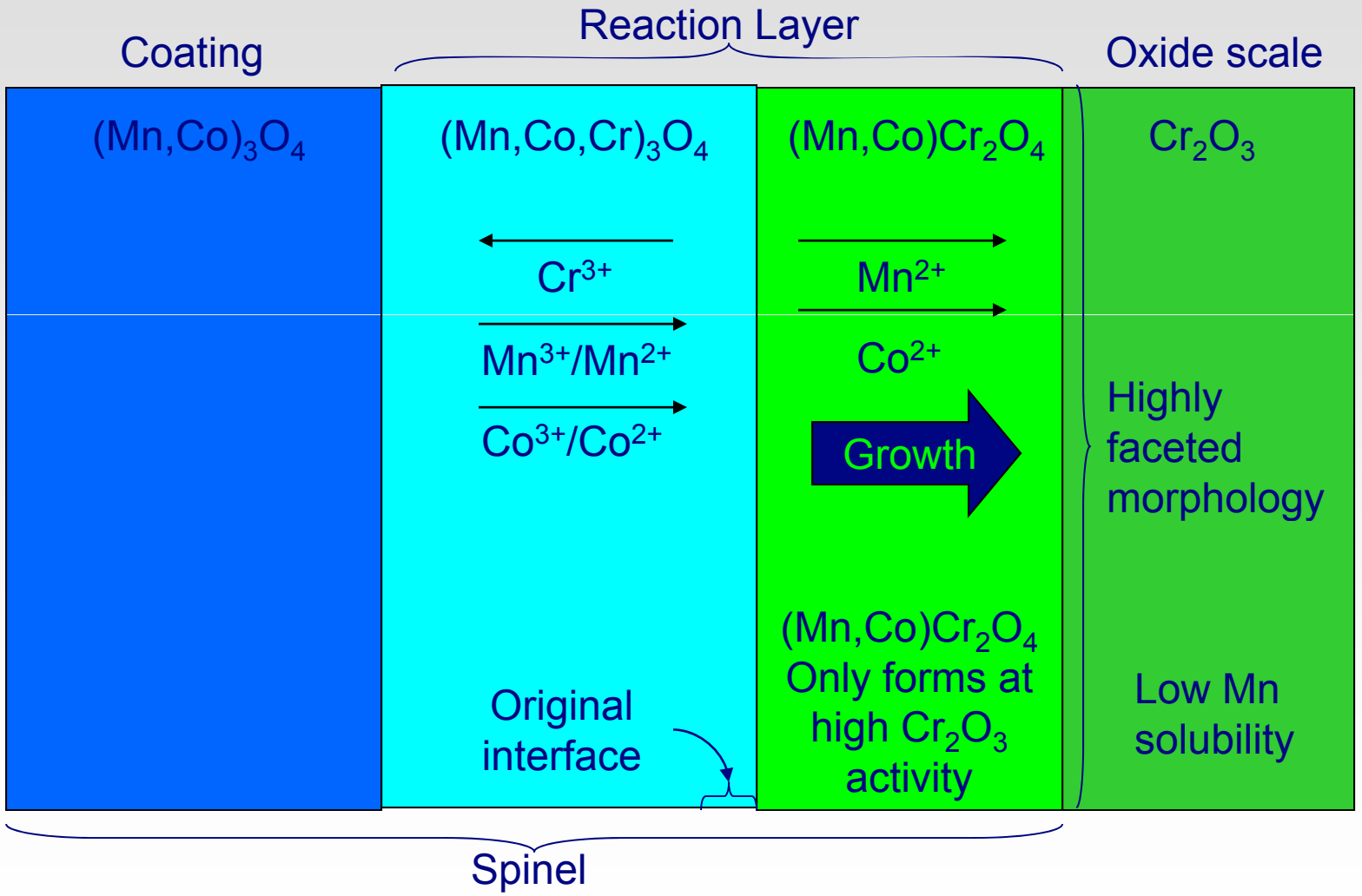
    - Division of Materials Research (DMR)
    - Complementary project on interconnect oxidation in dual atmospheres

Coating-Alloy Reaction Interface



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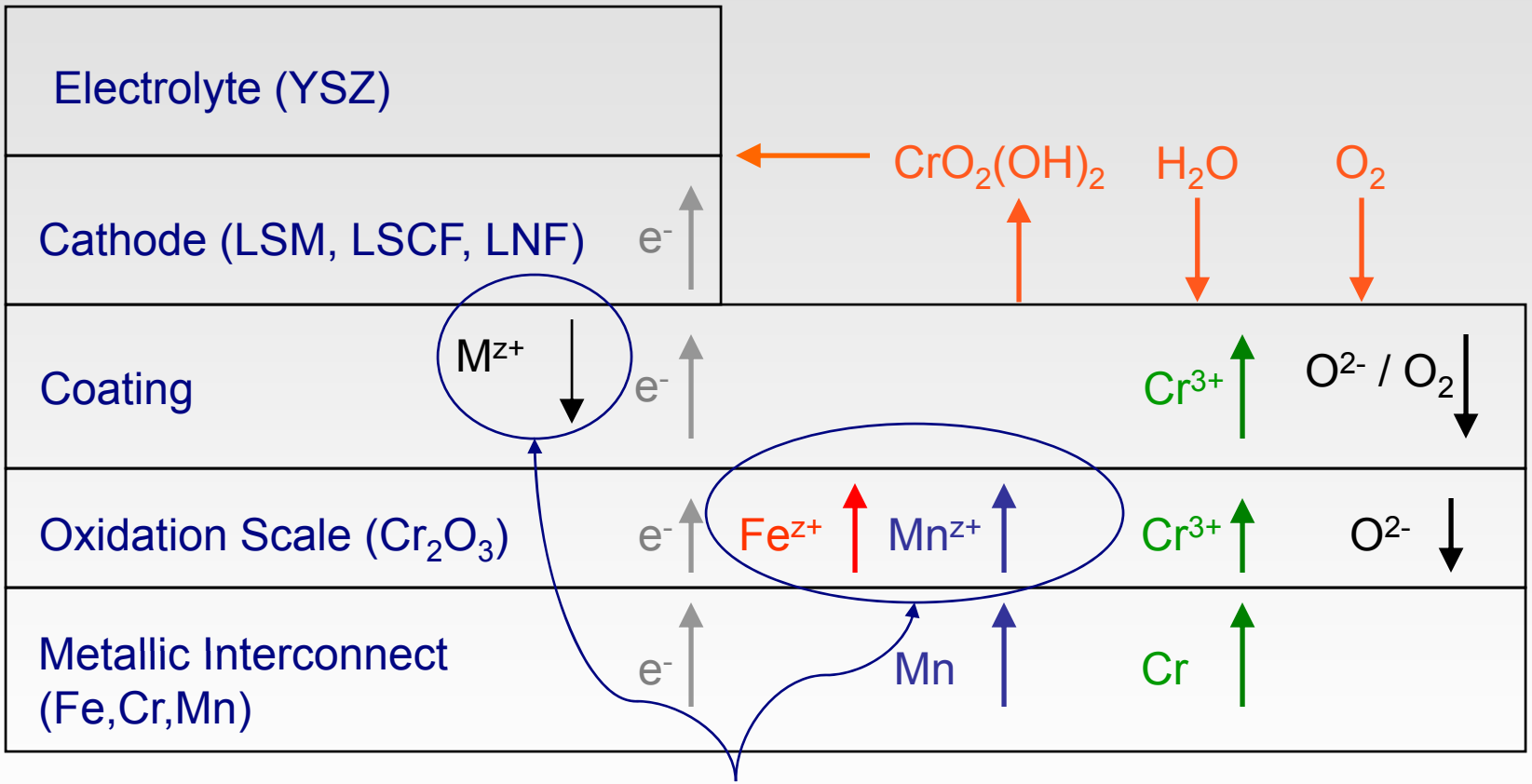
Coatings for Interconnects

- Combine advantages of metallic and ceramic interconnects
  - Low-cost easily fabricated metal
  - Ceramic coating to reduce vaporization
- Coating requirements
  - High electronic conductivity
  - Low oxygen ion conductivity
  - Low chromium solubility/diffusivity

Transport in Ceramic Coatings

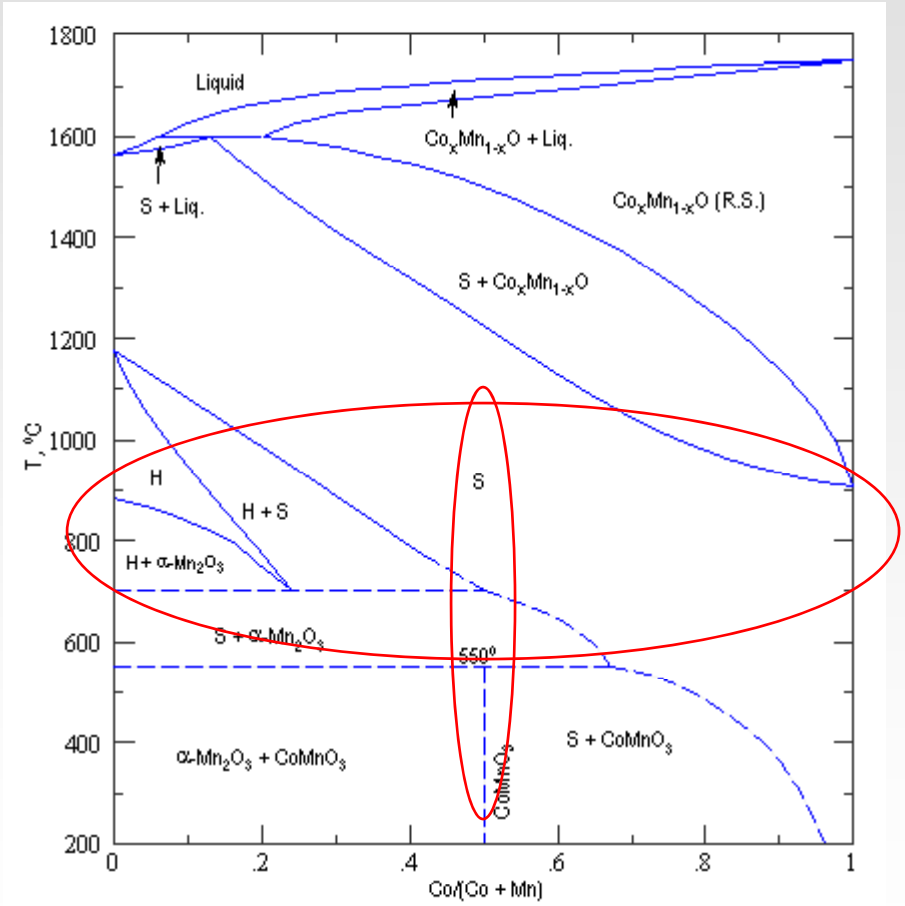


Changes in coating composition can affect performance

Coatings Using SOFC Materials

- Ceramic interconnect materials
  - Doped lanthanum chromite
  - Contains chromia, but at low activity
- Cathode materials
  - Electrical conductors, stable/compatible in SOFC
- Transition-metal oxides
  - Spinel structure
    - Lower chromium activity
    - High electrical conductivity

$(Mn,Co)_3O_4$ Phase Diagram



- IT-SOFC range
- Spinel solid solution
- Phase change at lower temperatures

Figure 9570, *Phase Diagrams for Ceramists*

Spinel Structure

- Sites per M_3O_4 unit
  - Two octahedral, one tetrahedral
- Valence
  - Two M^{3+} and one M^{2+} ("normal" - M^{3+} octahedral)
- Site preference
  - Octahedral: Cr > Mn > Co
  - $(Mn,Co)_3O_4$: Mn^{3+} prefers octahedral sites
  - $(Mn,Co,Cr)_3O_4$: Mn,Co reduce valence with Cr^{3+} addition
  - $(Mn,Co)Cr_2O_4$: Cr^{3+} occupies octahedral sites

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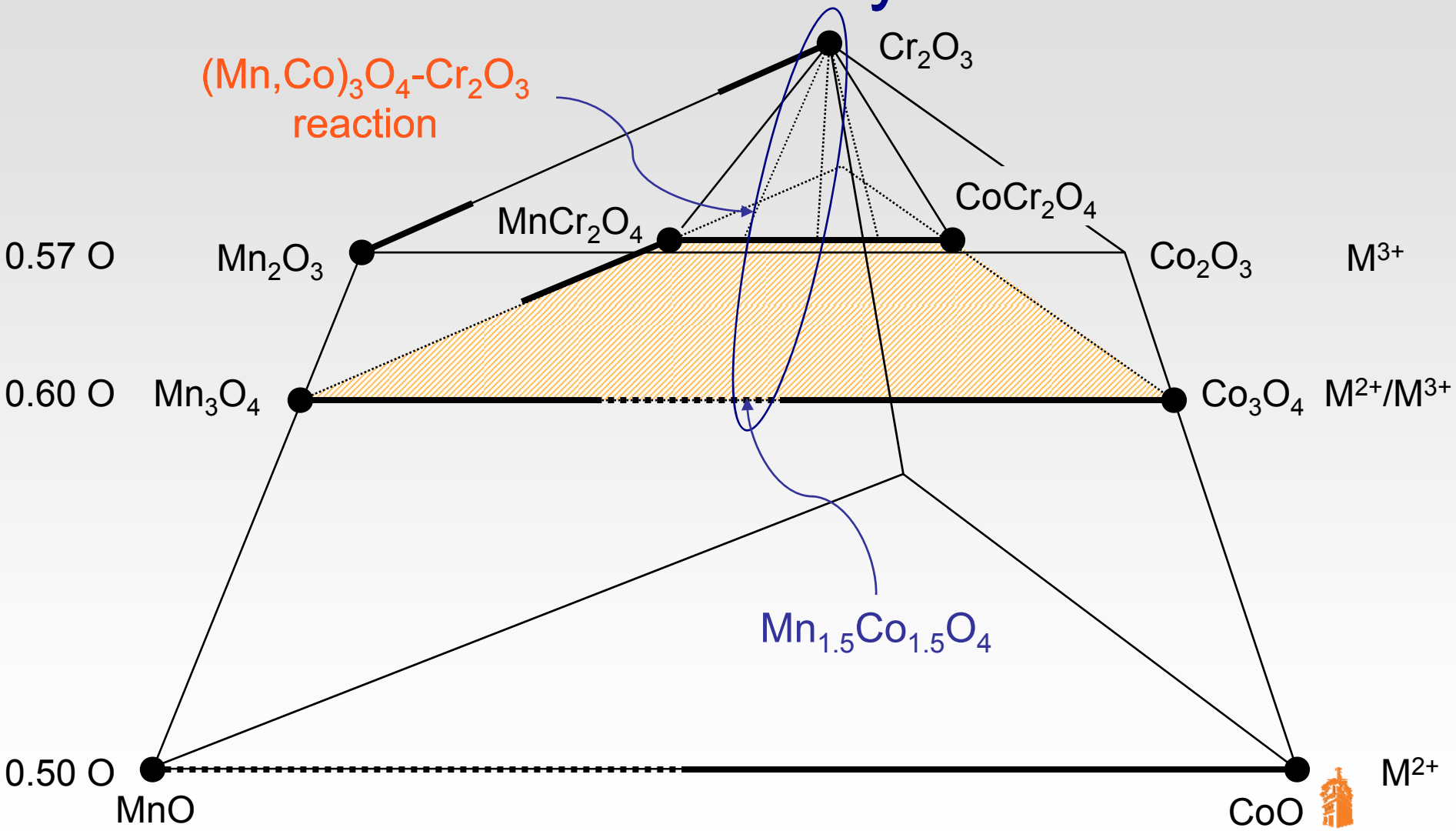
Mn-Co-Cr-O System



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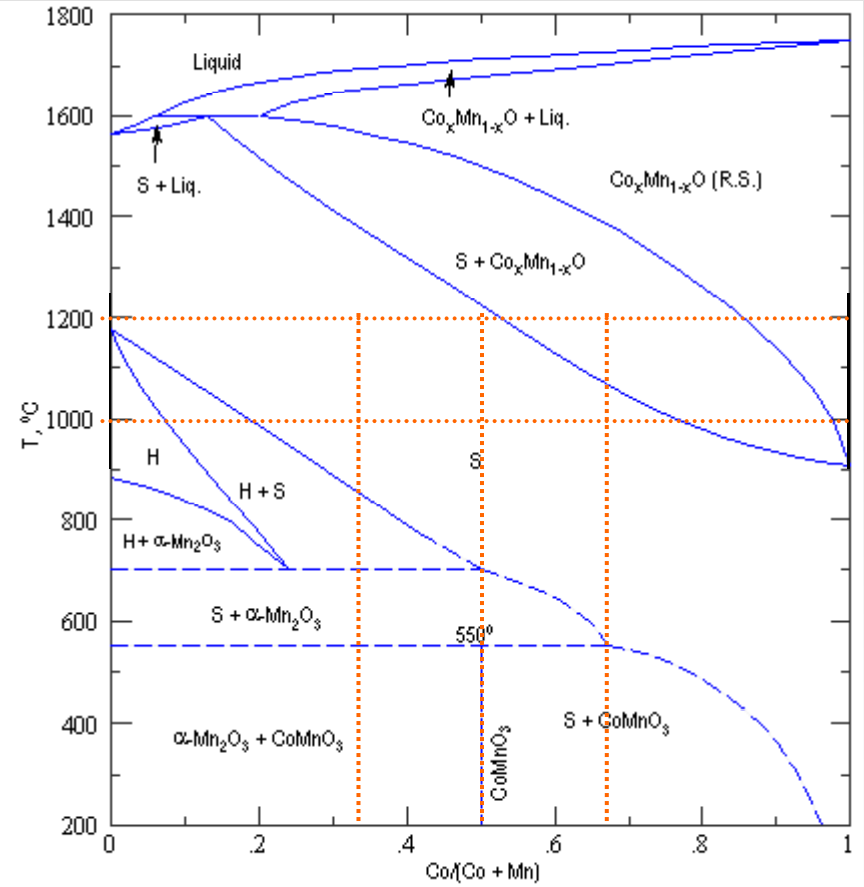
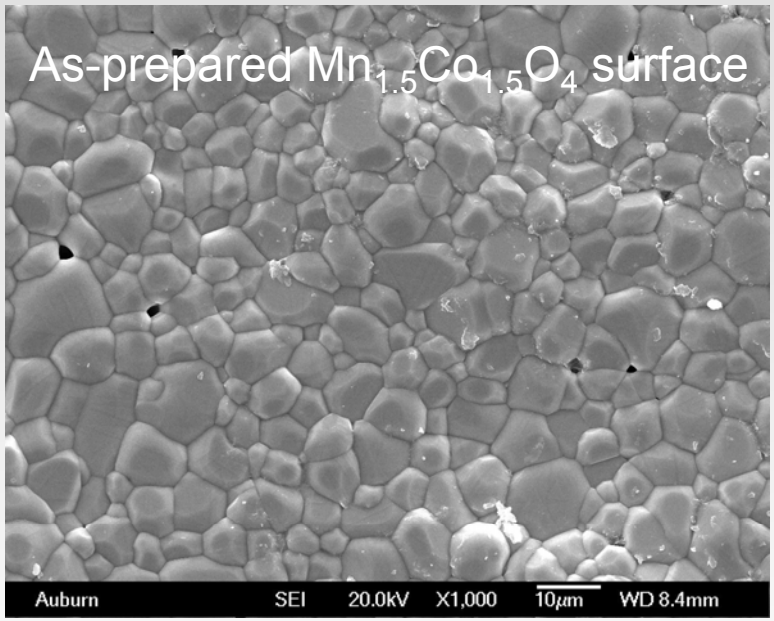
Compositions / Temperatures

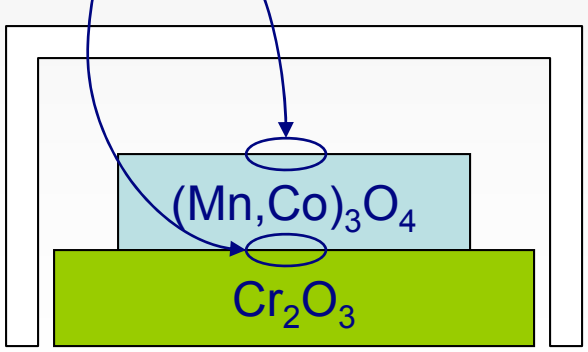
- Compositions
  - Mn_2CoO_4
  - $Mn_{1.5}Co_{1.5}O_4$
  - $MnCo_2O_4$
- Temperatures
  - 1200°C
  - 1000°C

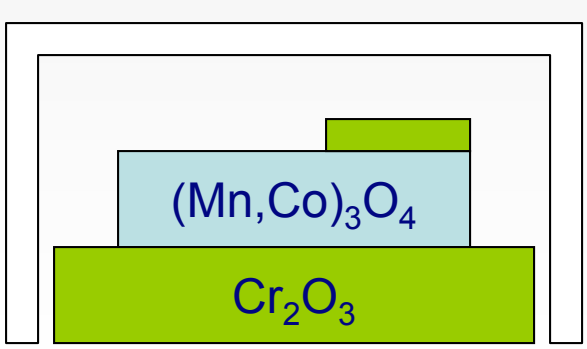


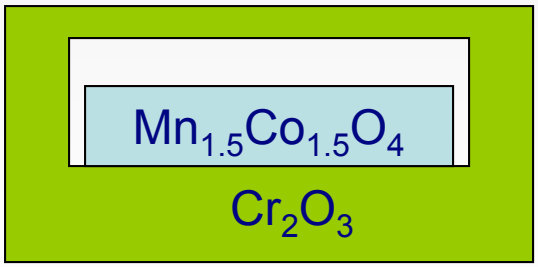
Interaction of $(Mn,Co)_3O_4$ with Cr_2O_3

- $(Mn,Co)_3O_4$ synthesis
  - Powder processing
  - 24 hrs in air
- Reaction with Cr_2O_3
  - Solid contact
  - Vapor transport

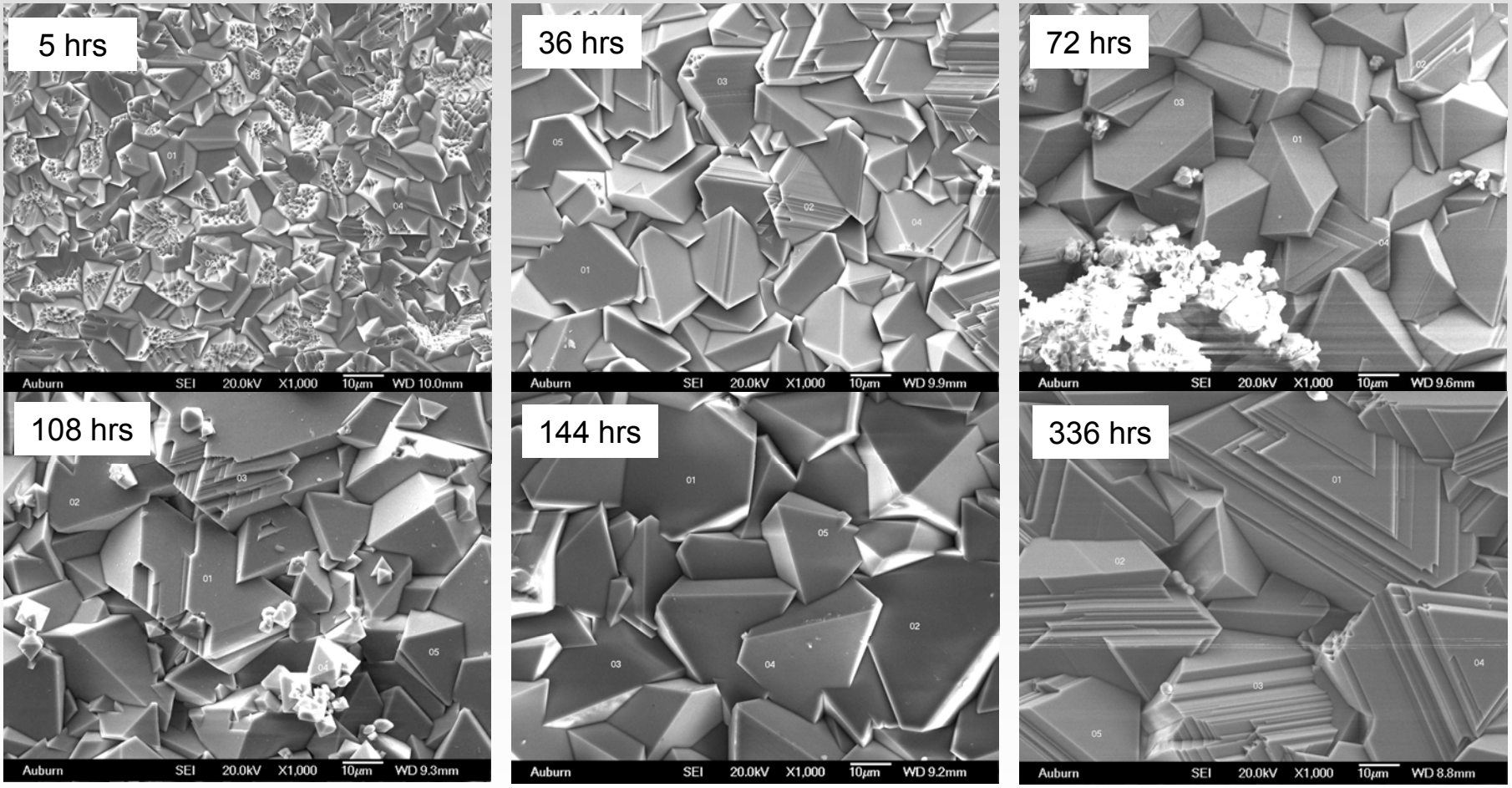






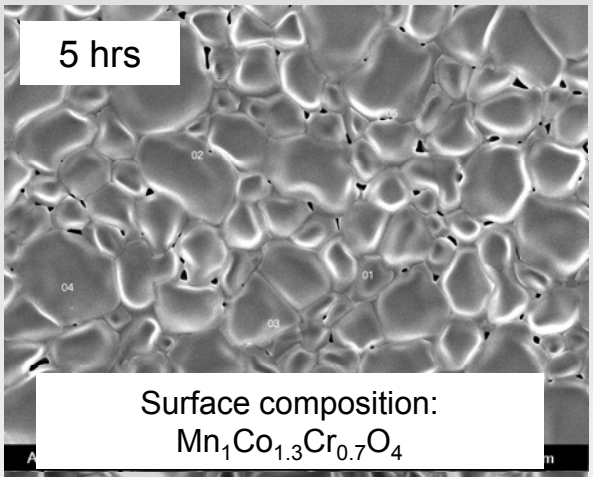


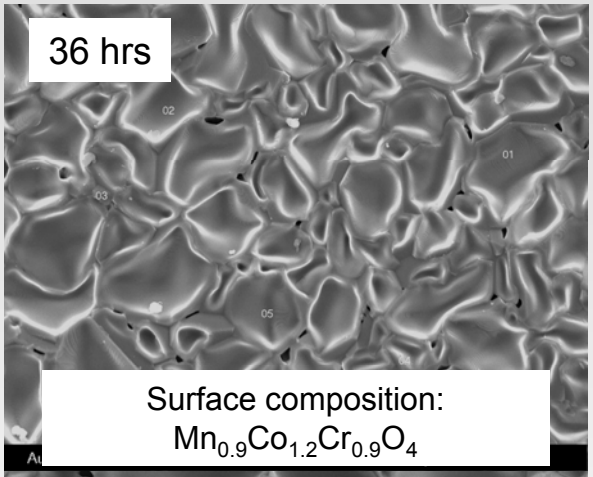
$Mn_{1.5}Co_{1.5}O_4$ (1200°C, solid contact)

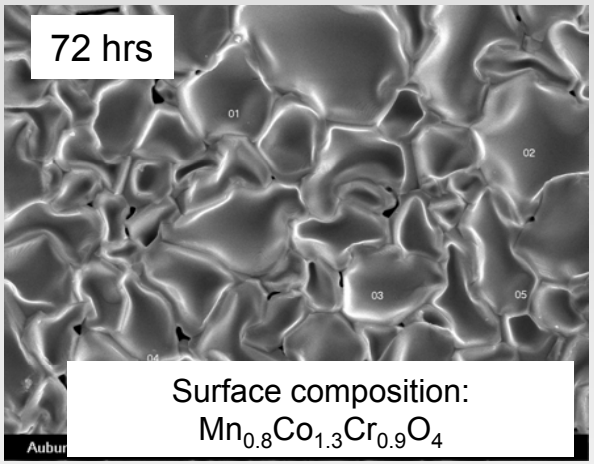


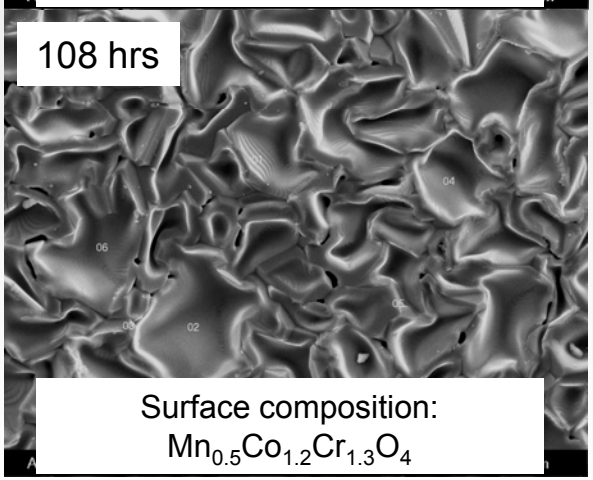
Surface composition (from 36 hrs): $Mn_{0.4}Co_{0.6}Cr_2O_4$

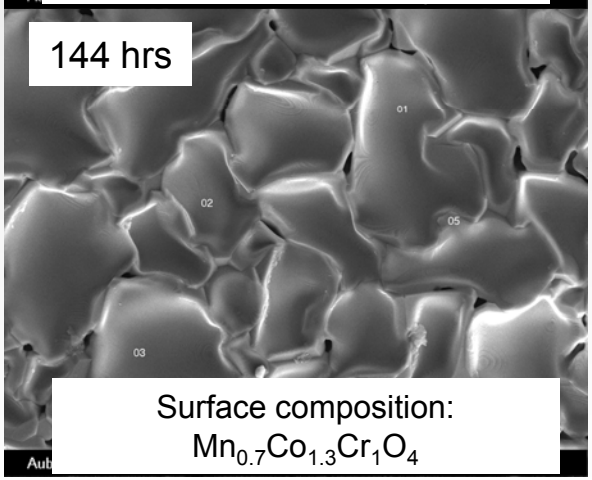
$Mn_{1.5}Co_{1.5}O_4$ (1200°C, vapor transport)

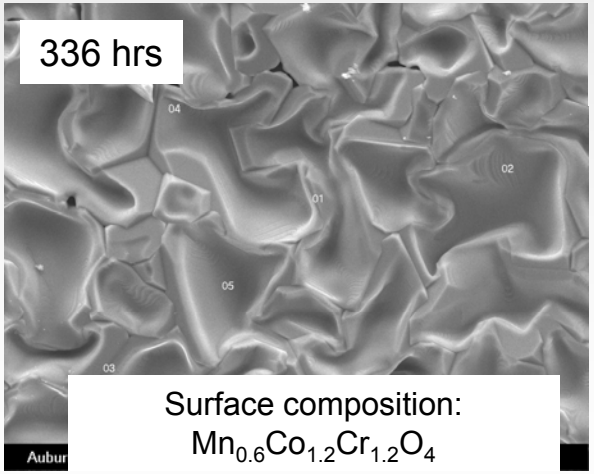






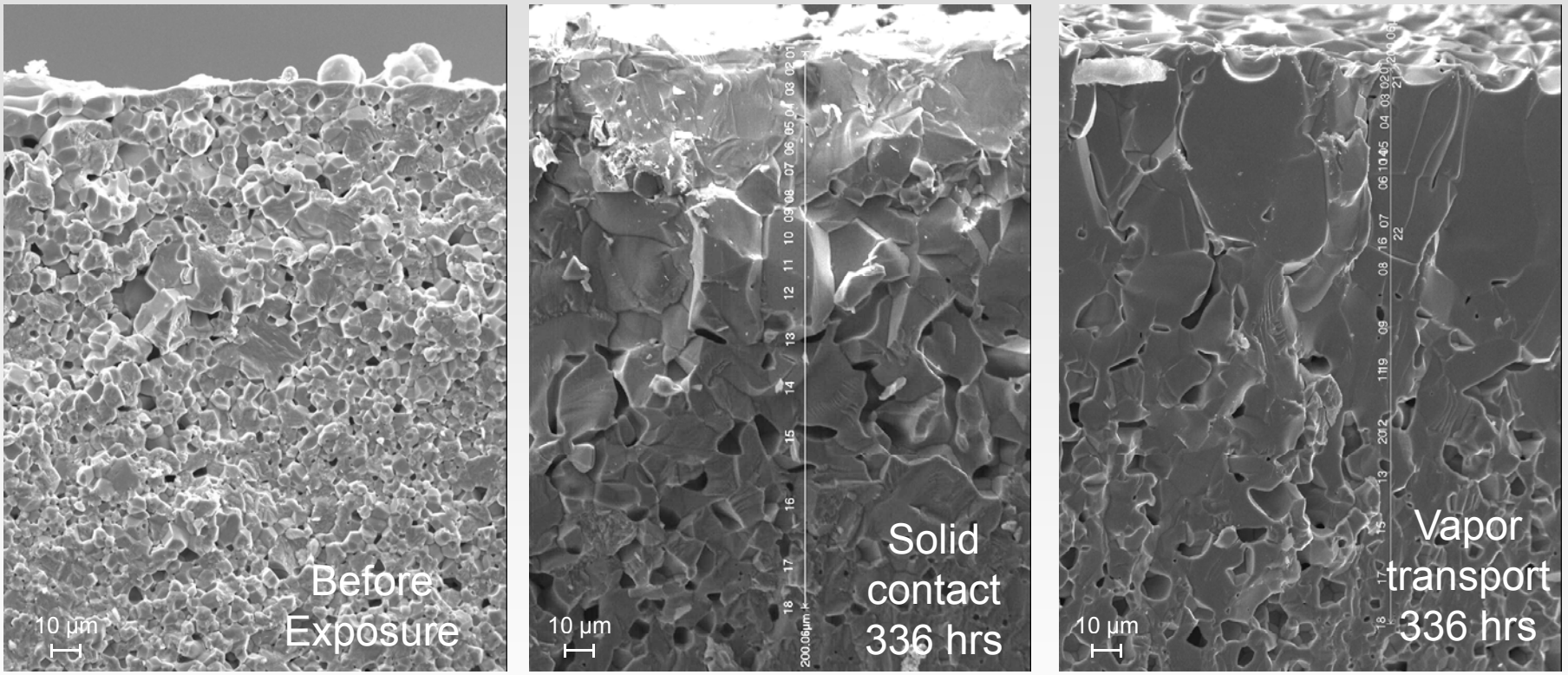






No facets – faster growth at grain boundaries.

$Mn_{1.5}Co_{1.5}O_4$ (1200°C, Cross section)



Dense outer layer – similar thickness for solid contact vs. vapor transport

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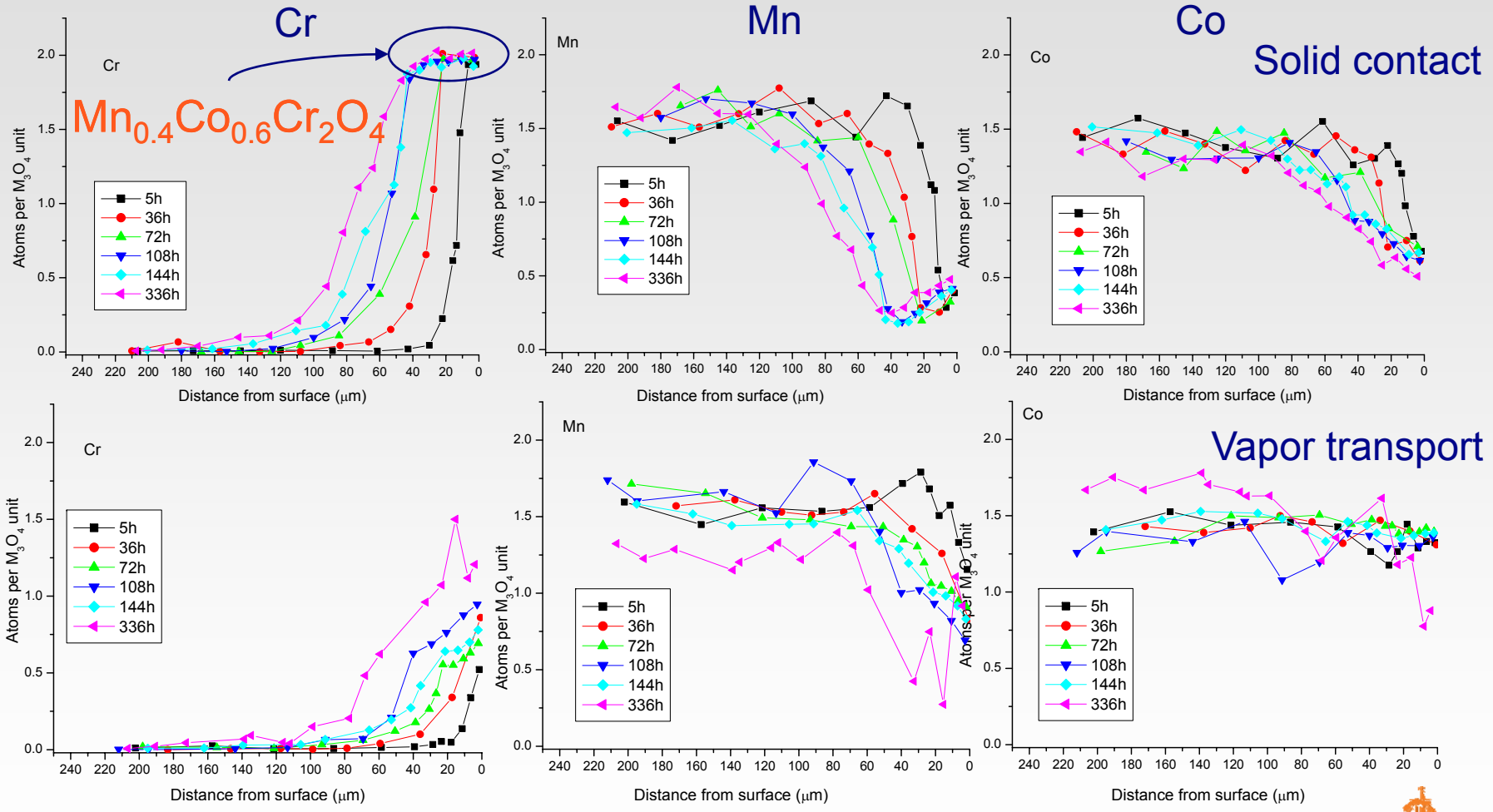
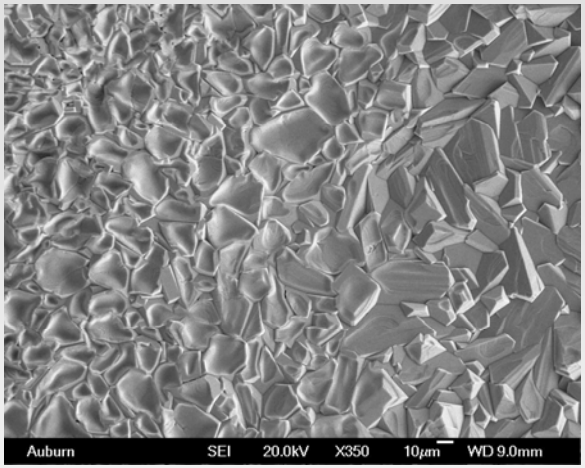
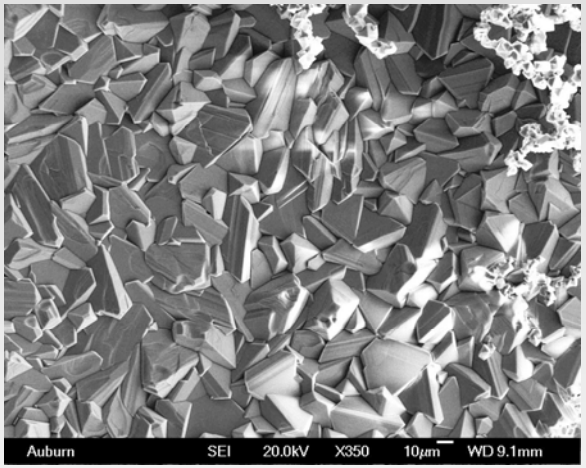
$Mn_{1.5}Co_{1.5}O_4$ (1200°C, Composition)

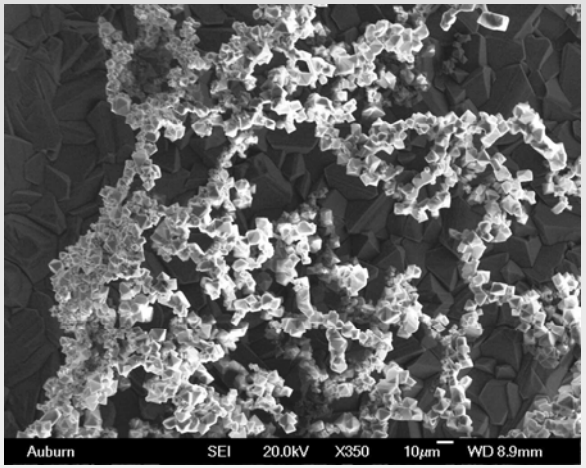


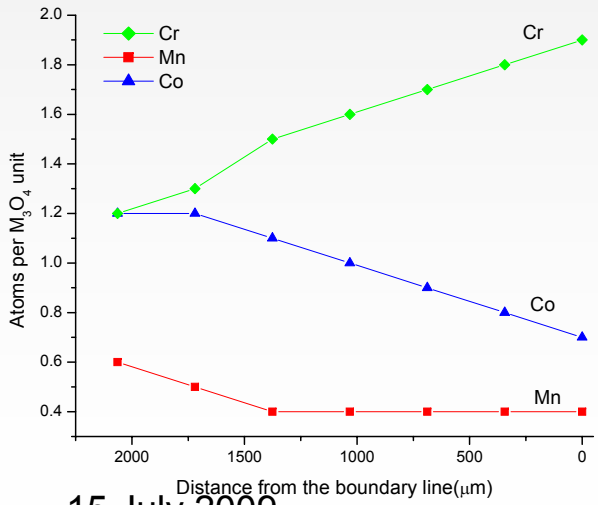
Co: higher surface composition, smaller gradient

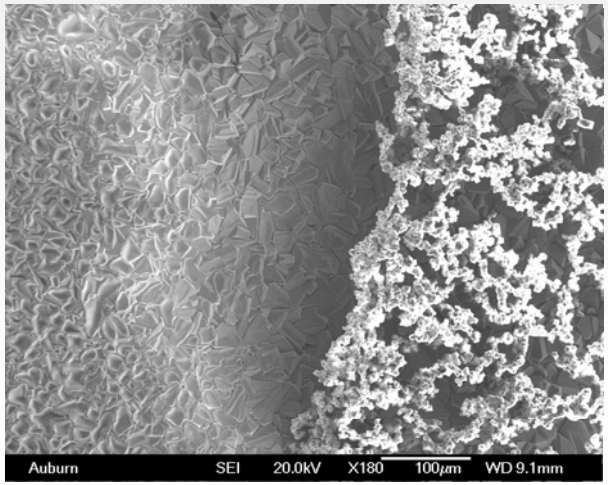
Vapor-Solid Transition (1200°C, 144 hrs)





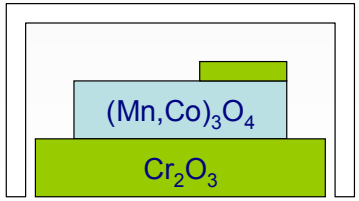






Gradient in Cr_2O_3 activity

$4CrO_3 = 2Cr_2O_3 + 3O_2$



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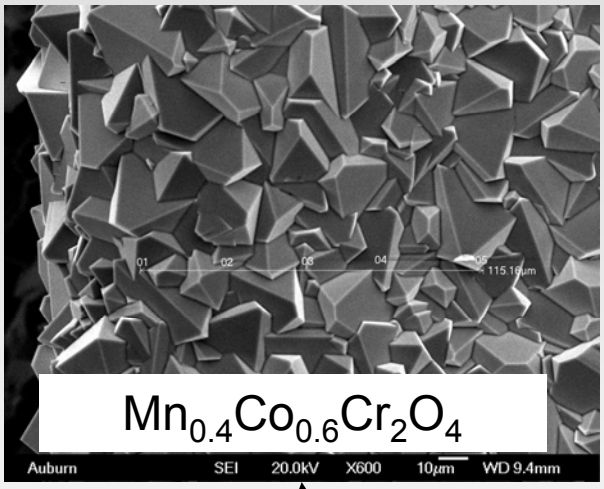
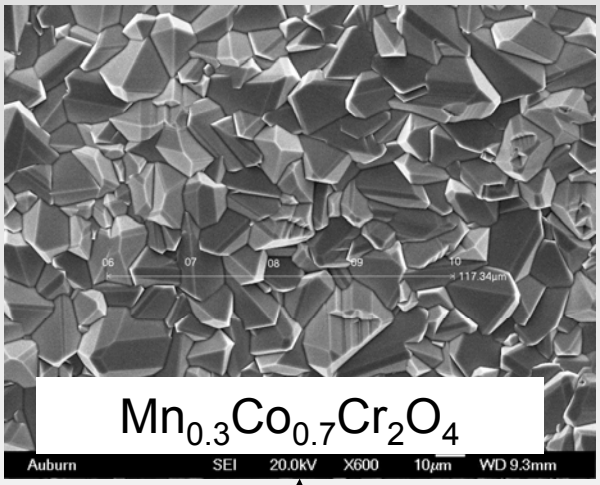
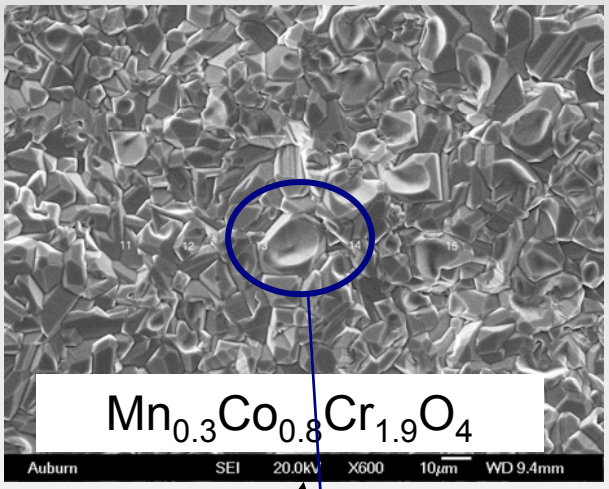
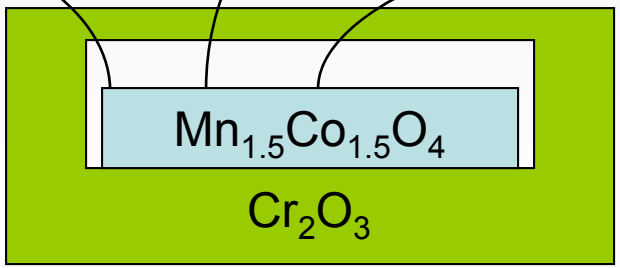
Vapor-Solid Transition (1200°C, 72 hrs)

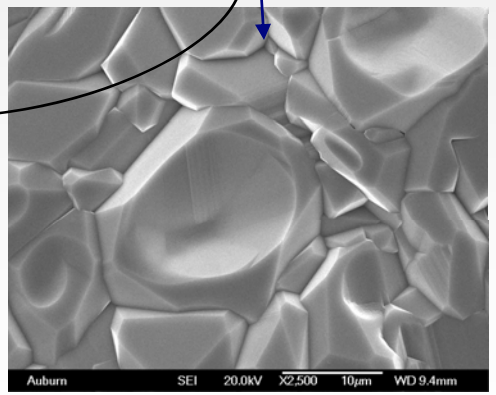






$Mn_{0.4}Co_{0.6}Cr_2O_4$ can form from vapor





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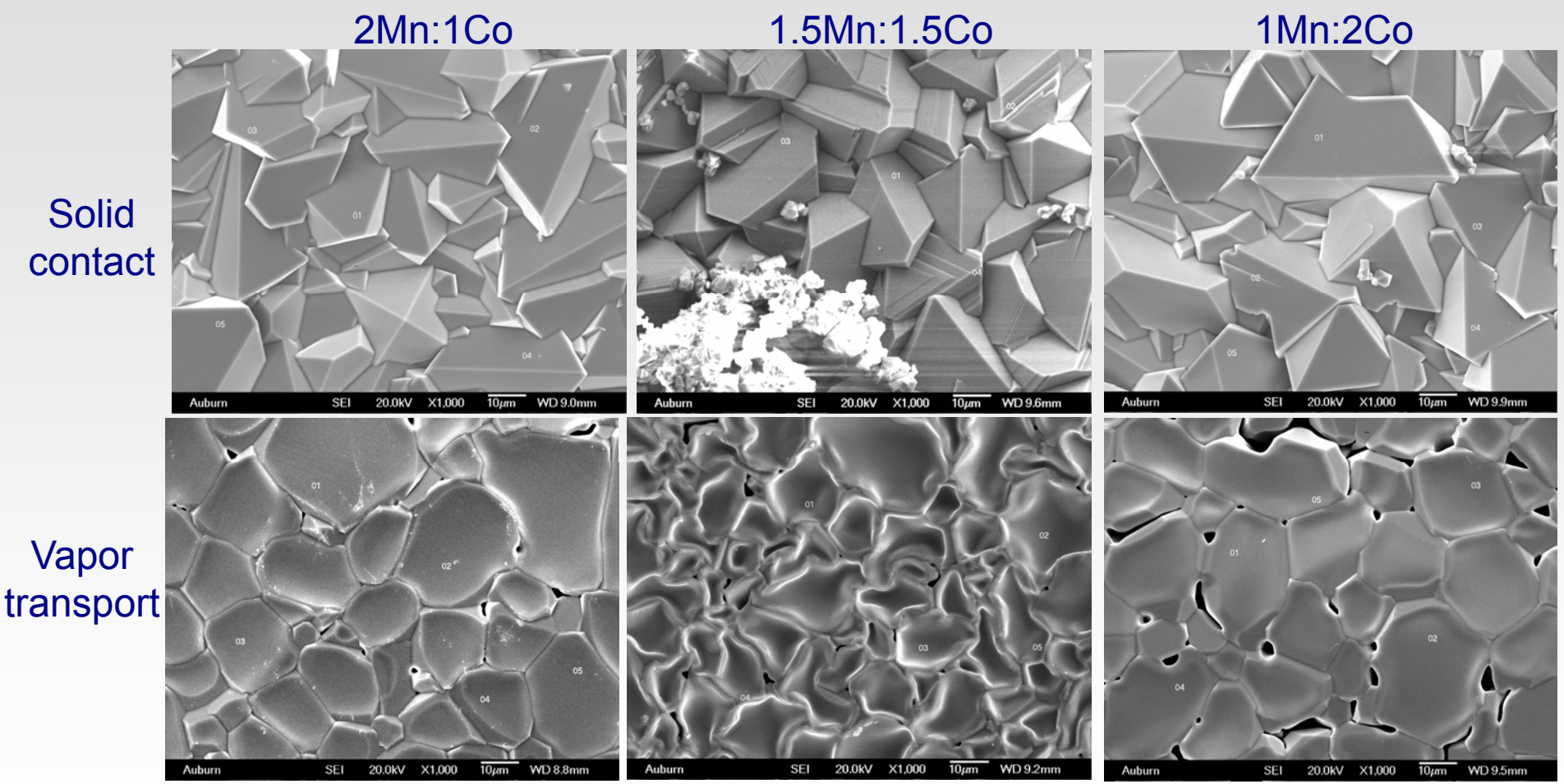
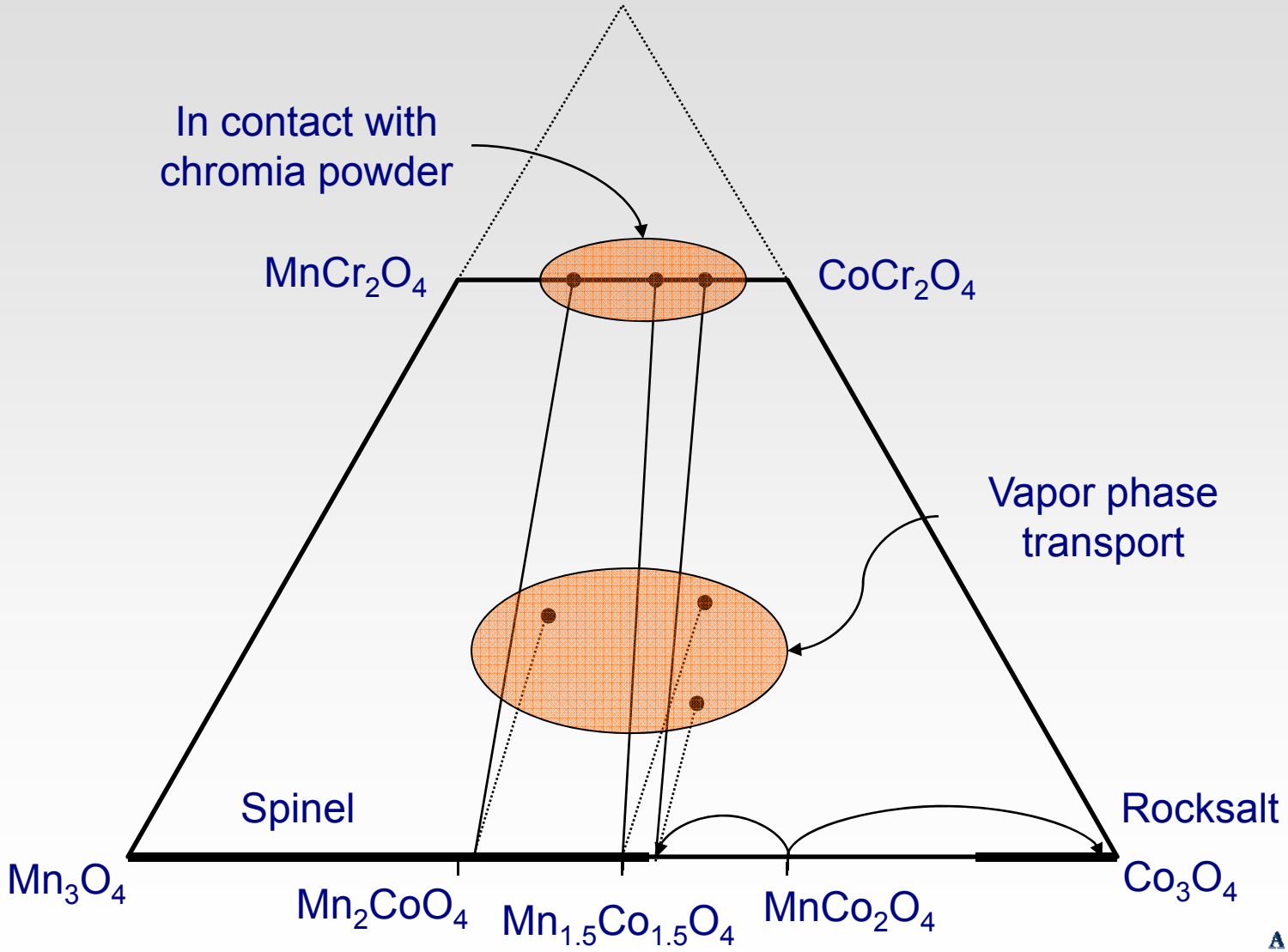
Effect of Mn/Co Ratio (1200°C, 72 hrs)

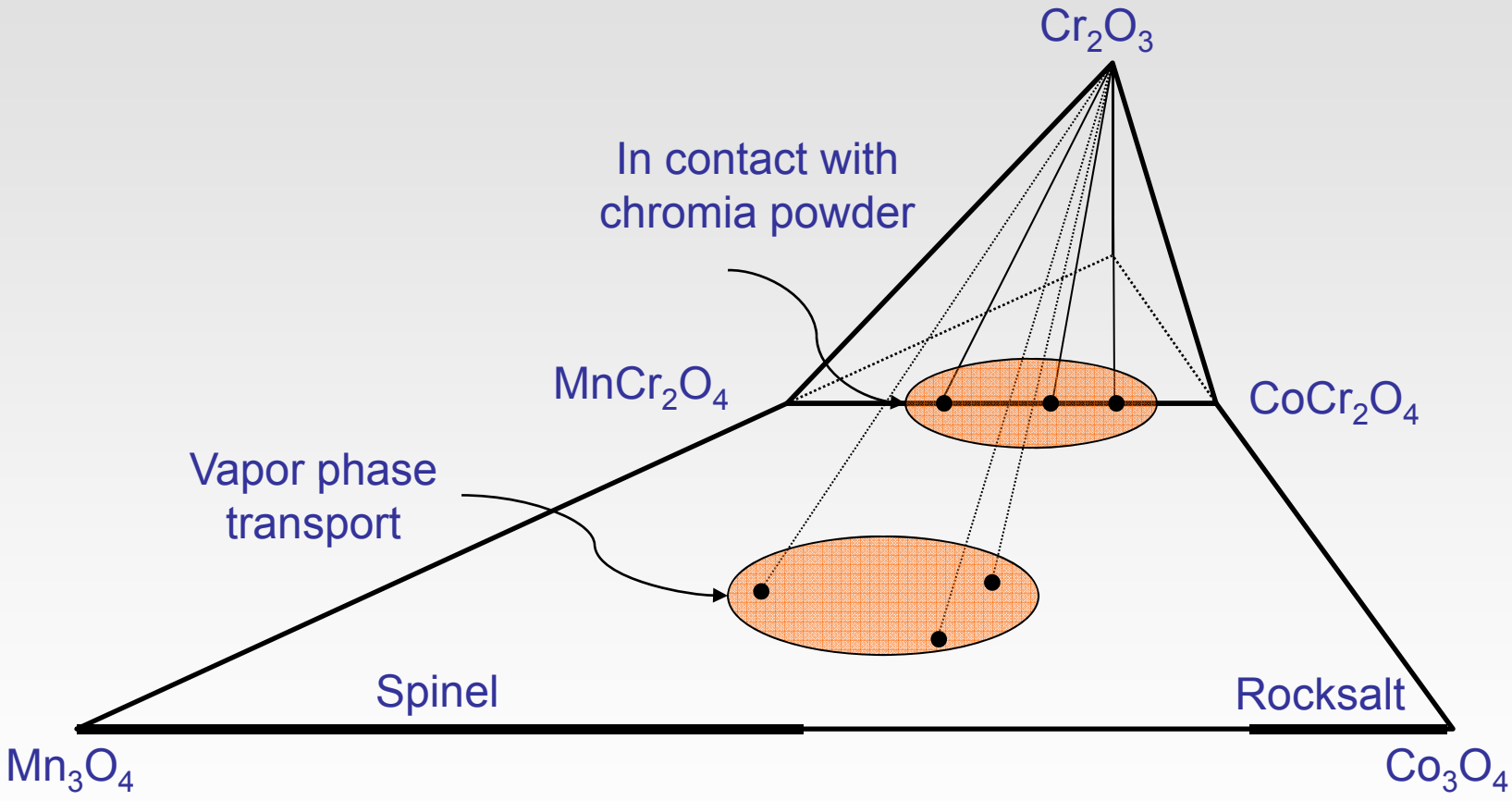


$MnCo_2O_4$: Less preferential grain boundary growth

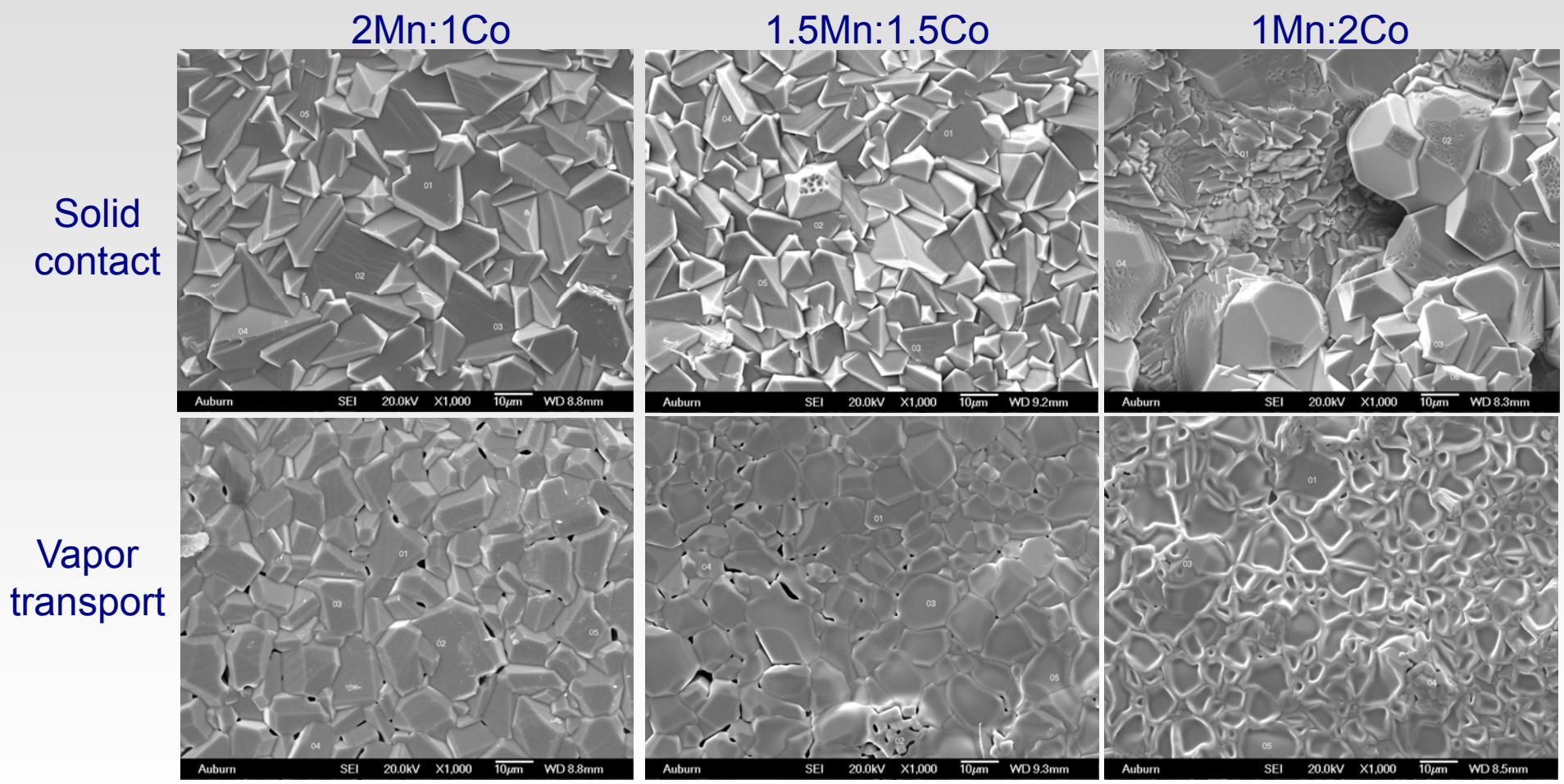
Surface Compositions (1200°C, 72 hrs)



Surface Compositions (1200°C, 72 hrs)



Effect of Mn/Co Ratio (1000°C, 72 hrs)



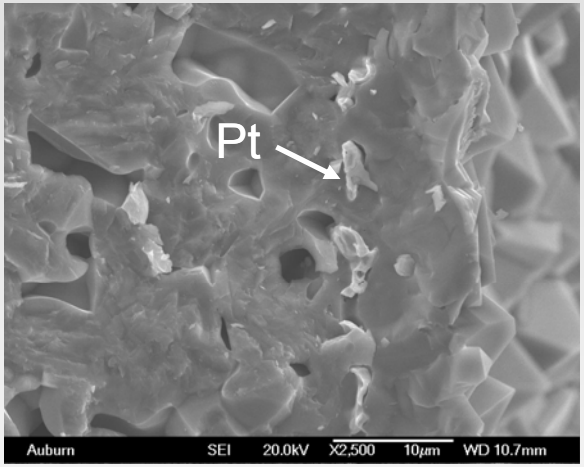
$MnCo_2O_4$: 2-phase from synthesis at 1200°C

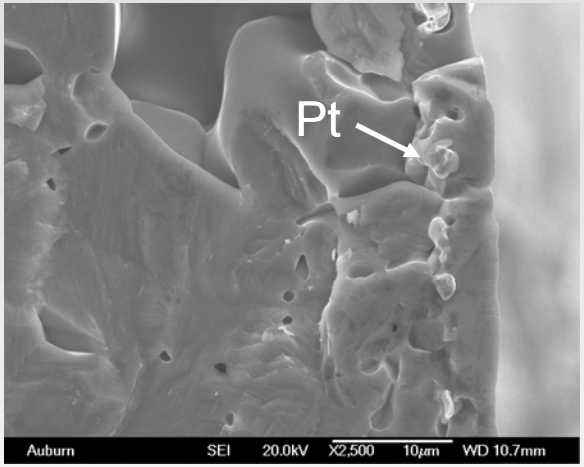
Pt Marker Experiments

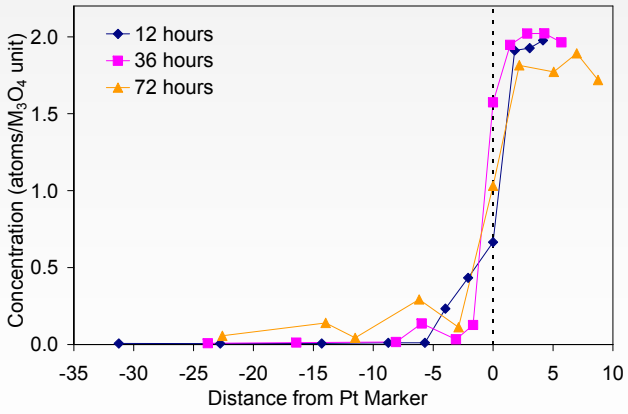
Solid contact

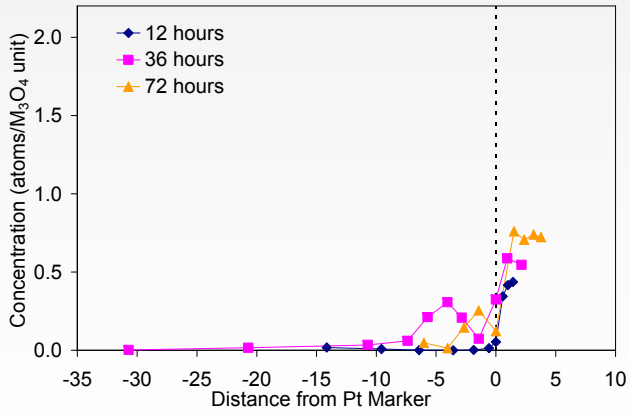
Vapor transport

36 hours
1000°C

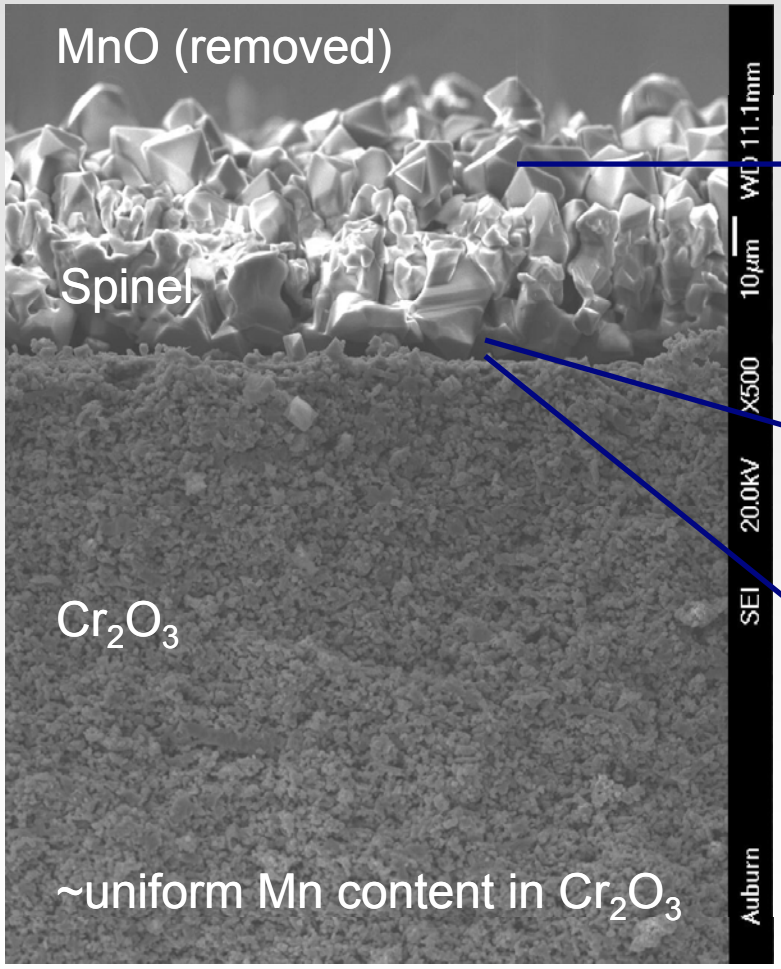


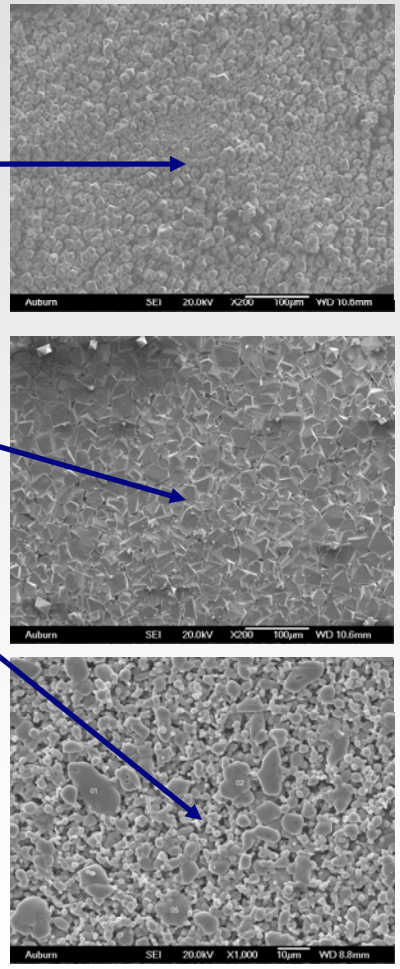






$MnO + Cr_2O_3$ (1200°C for 72 hours)



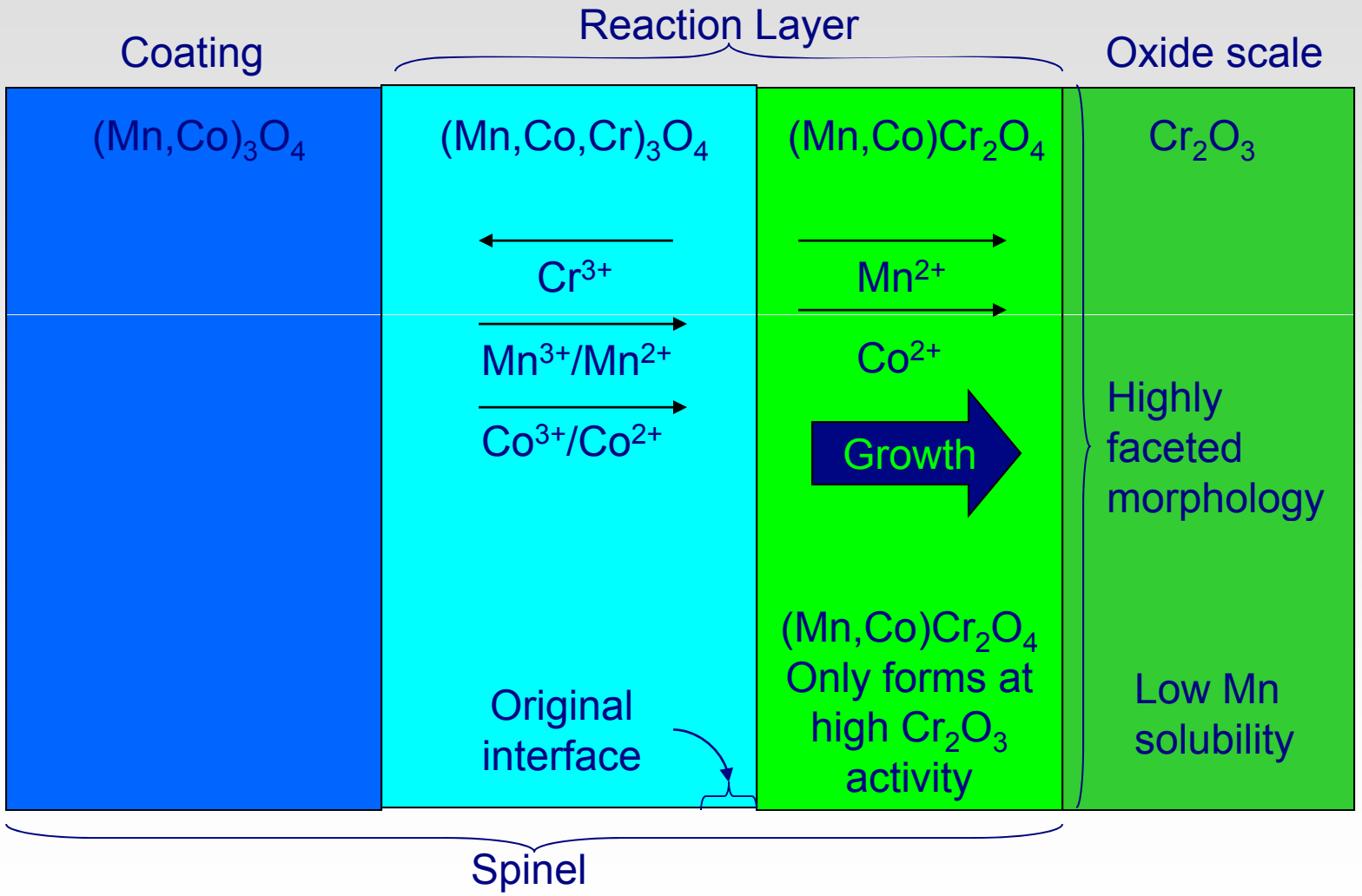


$Mn_{1.1}Cr_{1.9}O_4$

$Mn_{1.02}Cr_{1.98}O_4$

Cr_2O_3 (~0.6% Mn)

Coating-Alloy Reaction Interface



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Future Plans

- Lower temperature (IT-SOFC)
  - Phase formation and growth mechanism
  - Predict performance at long time through extrapolation
- Effects of reaction on coating performance
  - Prepare bulk analogues of reaction products
  - Characterize properties
    - -*e.g*. electrical conductivity (cell resistance), structure (site occupancy / transport), CTE (thermal stresses)