Interconnect-Coating Interactions: Transition Metal Spinel Oxides

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COLLEGE OF ENGINEERING

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- Researchers
  - Postdocs: Kangli Wang (now at MIT), Jason Ganley, Dileep Kumar
  - Ph.D. Students: Yingjia Liu, Yu (Joey) Zhao
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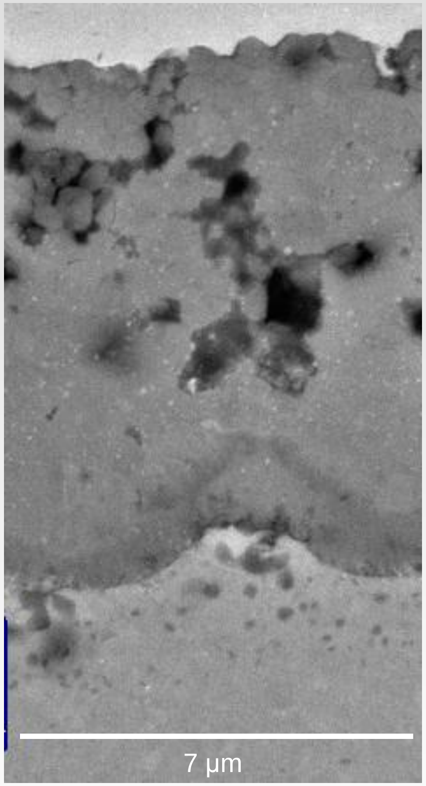
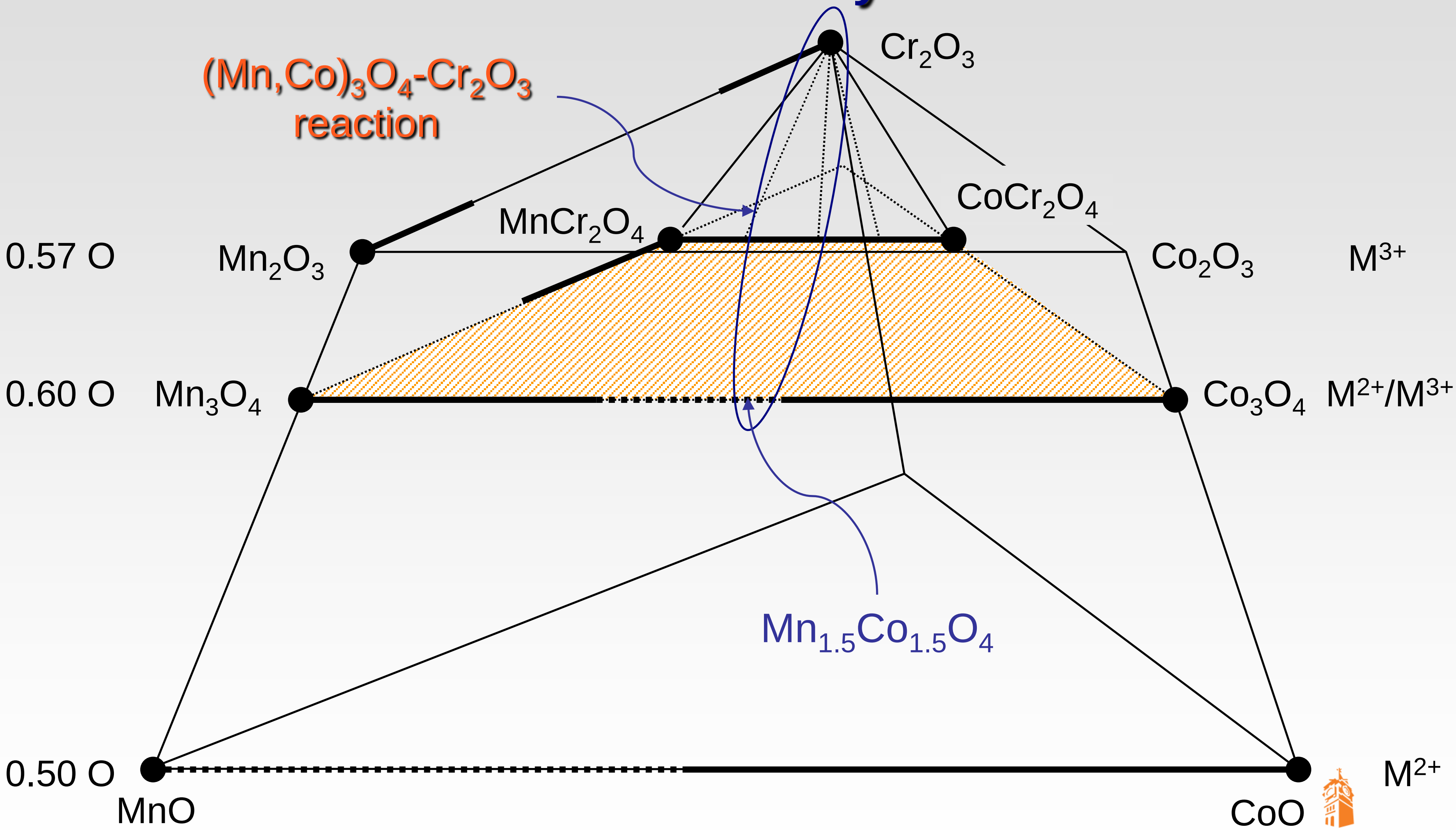
  - Pacific Northwest National Laboratory (Jeff Stevenson)

Reducing Cr Poisoning in SOFCs

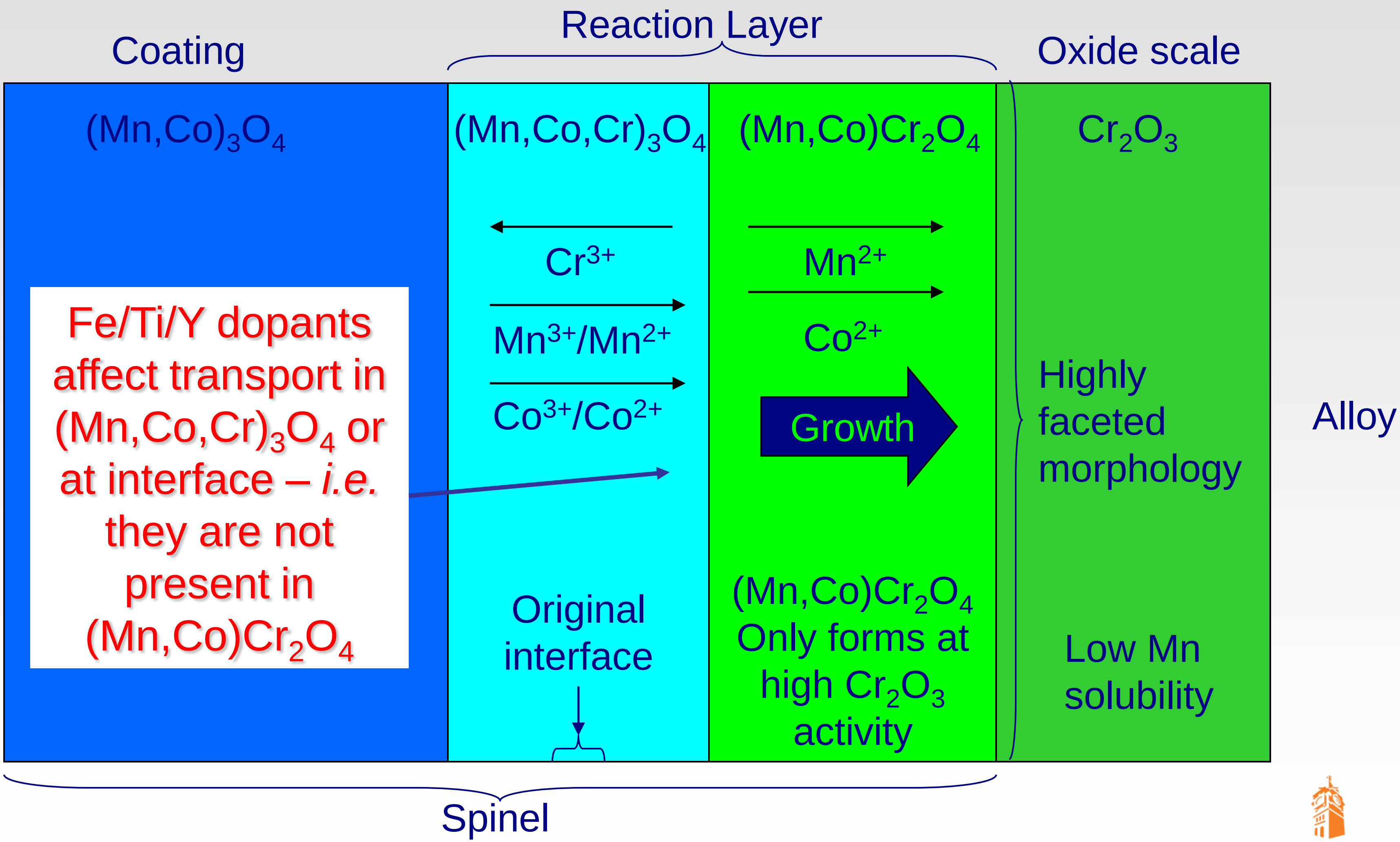
- Chromium poisoning
  - Oxidation of Cr_2O_3 to Cr^{6+} species ($CrO_2(OH)_2$ or CrO_3)
  - Deposition of Cr_2O_3 on cathode
  - Occurs even at IT-SOFC temperatures
- Cr-poisoning reduced with coating
- Alloy-coating interaction
  - Forms modified scale
  - $(Mn,Co)_3O_4$: Transition from chromia to spinel
- Can lower chromium contents be used in coated alloys?



Mn-Co-Cr-O System



Interconnect Alloy-Coating Interaction



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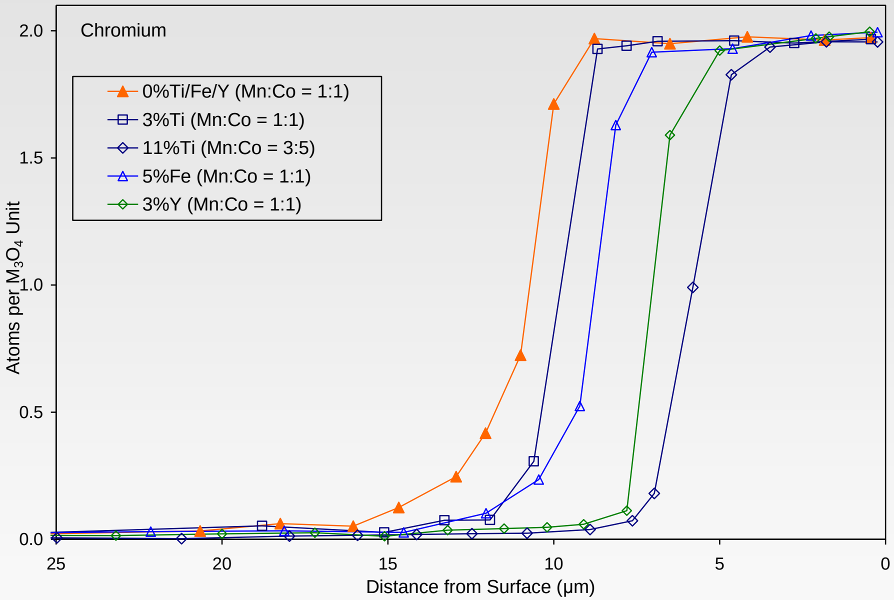
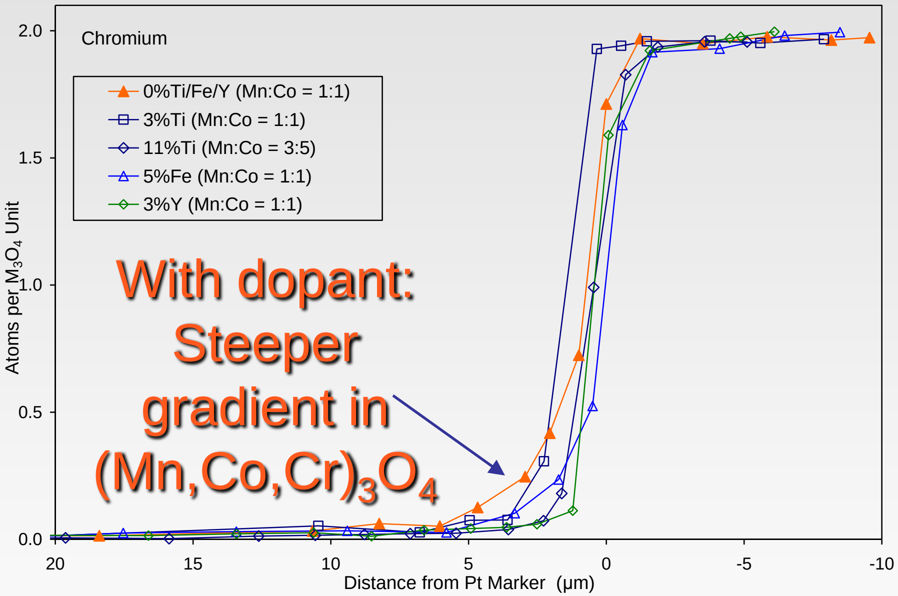
Doped $(Mn,Co)_3O_4$ – 1000°C / 72 hr

Chromium





Distance from sample surface

Distance from Pt marker

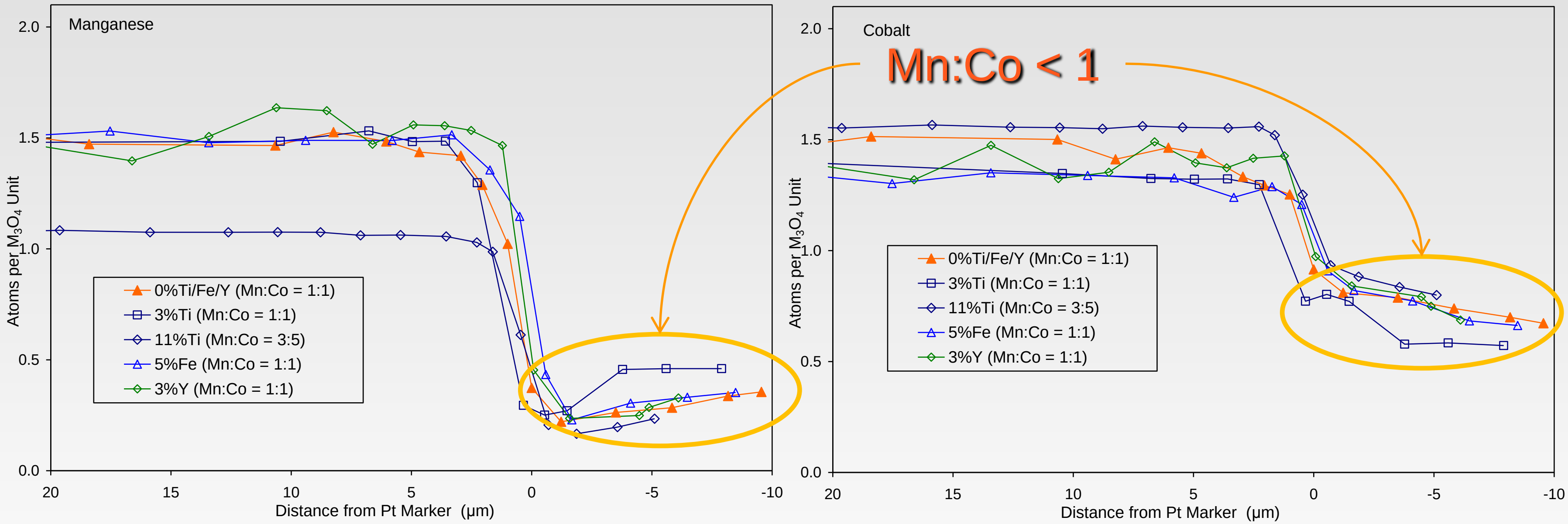
3% Ti: $Mn_{1.455}Co_{1.455}Ti_{0.09}O_4$ **5% Fe: $Mn_{1.425}Co_{1.425}Fe_{0.15}O_4$**

11% Ti: $MnCo_{1.66}Ti_{0.34}O_4$ **3% Y: $Mn_{1.455}Co_{1.455}Y_{0.09}O_4$**

Doped $(Mn,Co)_3O_4$ – 1000°C / 72 hr

Manganese

Cobalt



Distance from Pt marker

3% Ti: $Mn_{1.455}Co_{1.455}Ti_{0.09}O_4$

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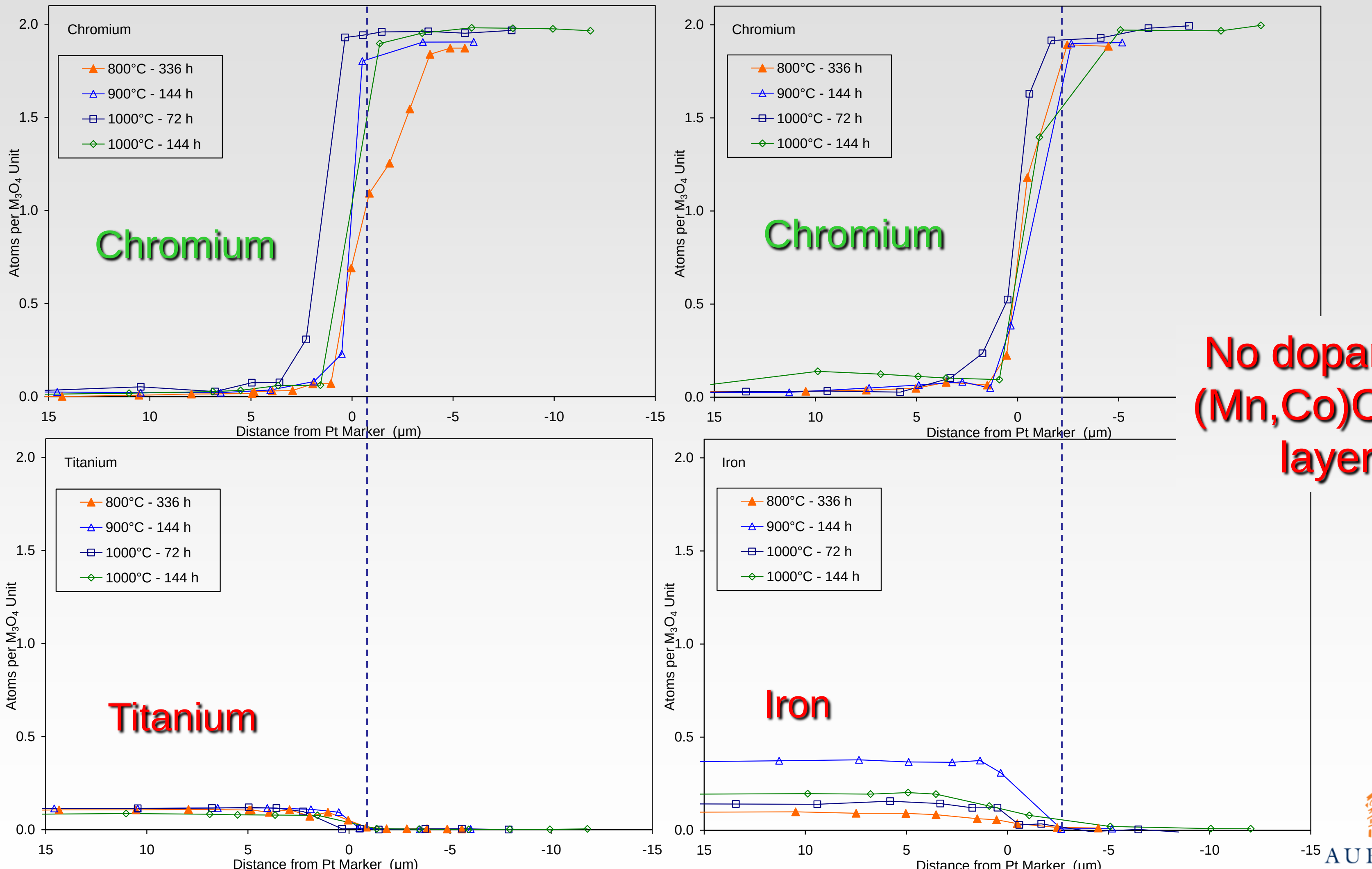
11% Ti: $MnCo_{1.66}Ti_{0.34}O_4$

3% Y: $Mn_{1.455}Co_{1.455}Y_{0.09}O_4$

Dopant Location

3%Ti

5%Fe



No dopant in $(Mn,Co)Cr_2O_4$ layer

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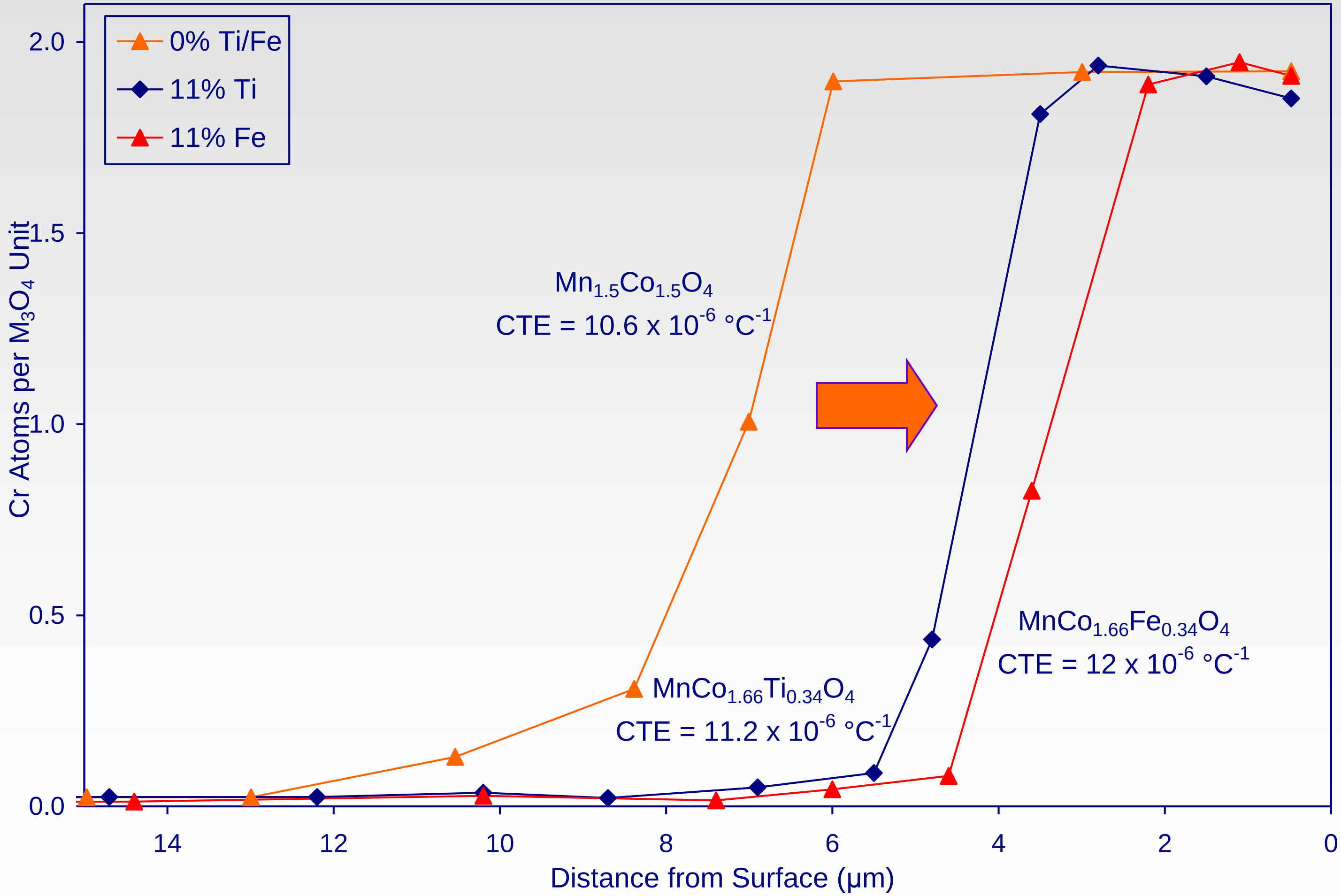
Reaction Layer Thickness (900°C for 144 hrs)



Ti and Fe additions significantly decrease the thickness of the reaction layer – small increase in CTE

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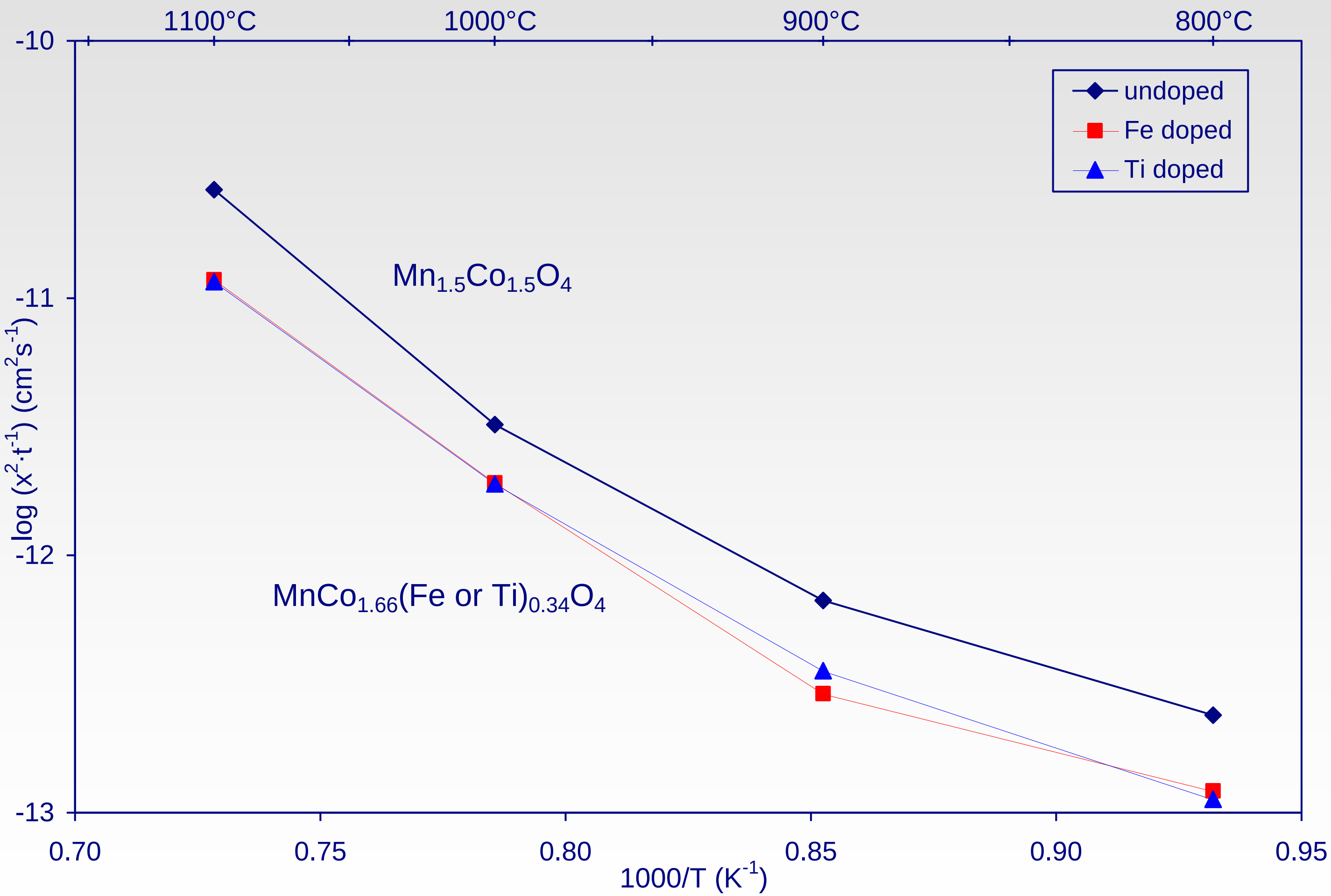
Reaction Layer Thickness – Temperature Dependence



Activations Energy:

- Decreases with decreasing temperature
- Similar for doped and undoped

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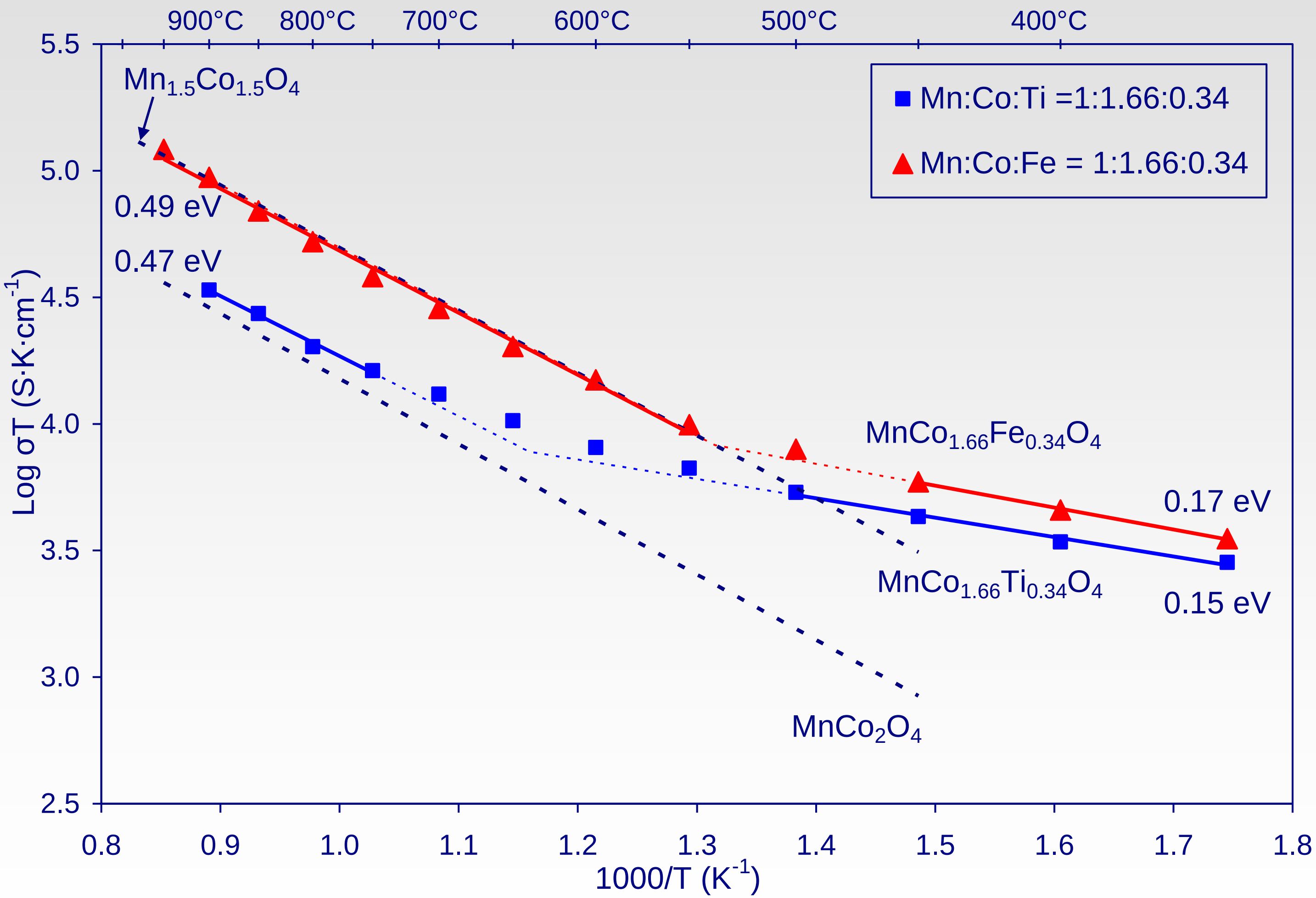
Conductivity of Fe- and Ti-doped $(Mn,Co)_3O_4$



Fe-doped: Conductivity same as $Mn_{1.5}Co_{1.5}O_4$

Ti-doped: Conductivity lower than $Mn_{1.5}Co_{1.5}O_4$ but higher than $MnCo_2O_4$

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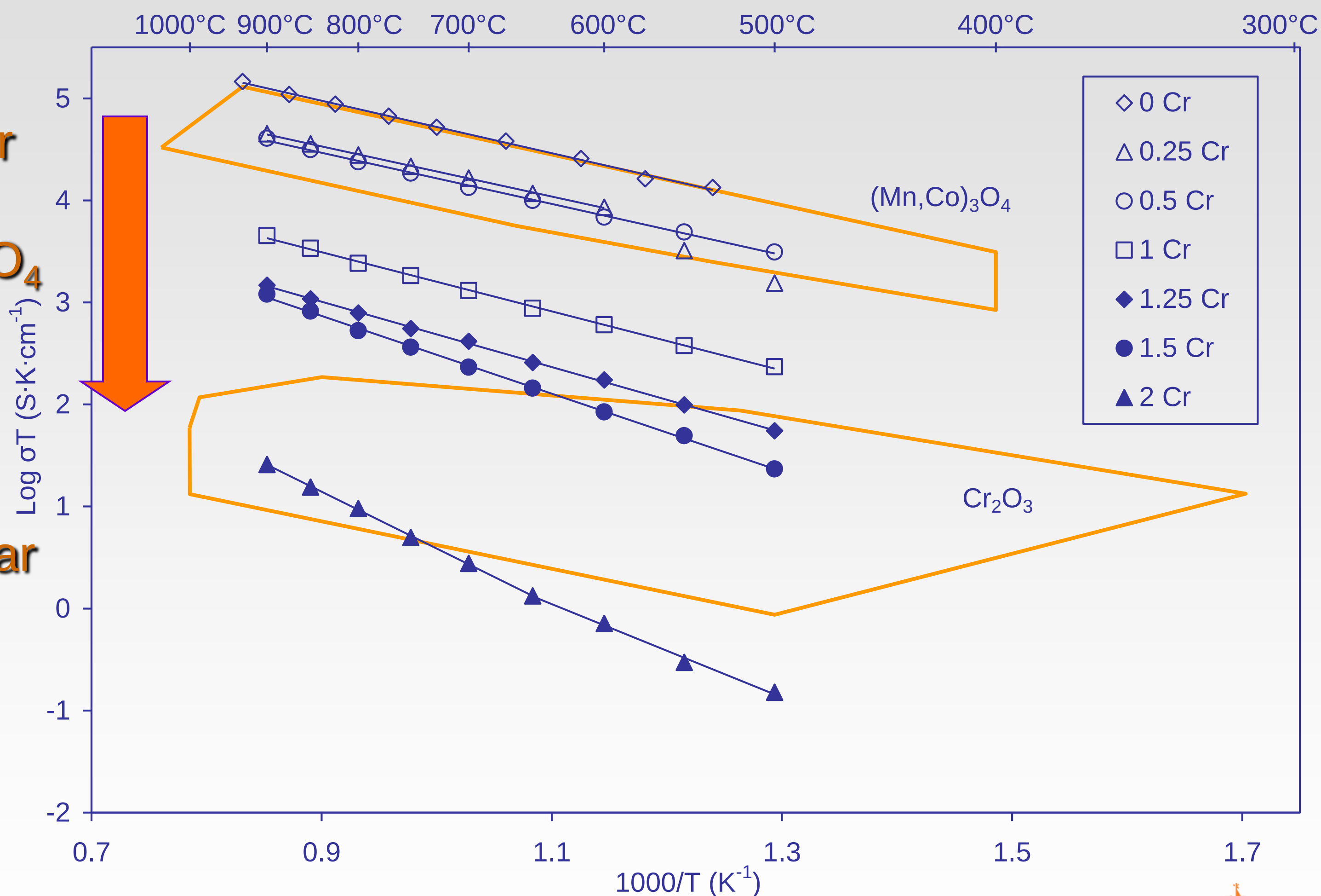
Conductivity of $(Mn,Co,Cr)_3O_4$

Increasing Cr content in $(Mn,Co)_{3-x}Cr_xO_4$

High Cr similar to Cr_2O_3



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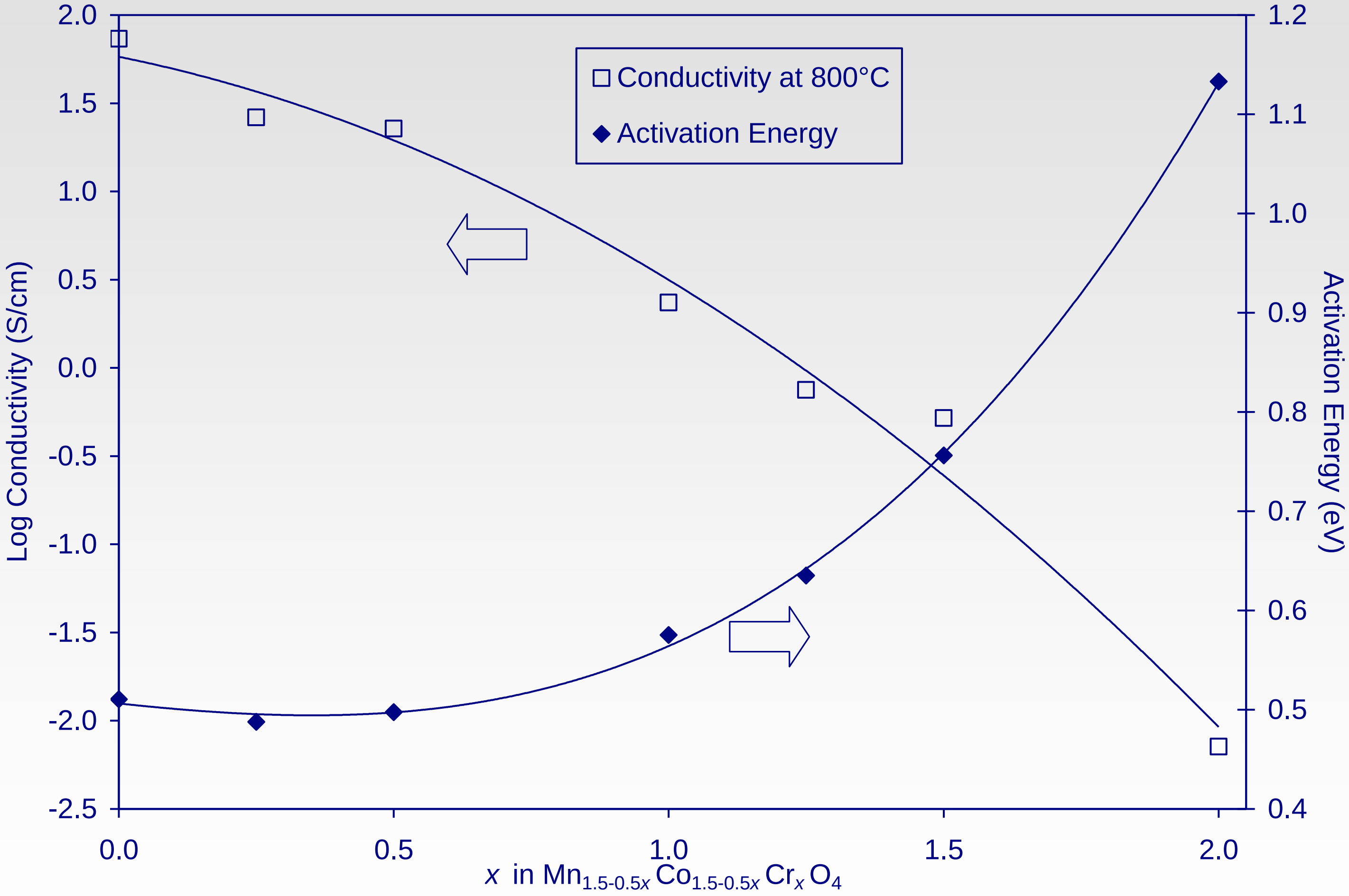
Conductivity of $(Mn,Co,Cr)_3O_4$



Increase in activation energy occurs for 0.5-1.0 Cr

Experimental Alloys

Alloy	Concentration (wt%)					
	Fe	Cr	Mn	Si	Ti	Nb
H52	Bal.	13	0.3	0.4	0.2	0.4
H53	Bal.	15	0.3	0.4	0.2	0.4
H54	Bal.	17	0.3	0.4	0.2	0.4
H55	Bal.	18	0.3	0.4	0.2	0.4
AISI 441	Bal.	18	0.4	0.3	0.2	0.5

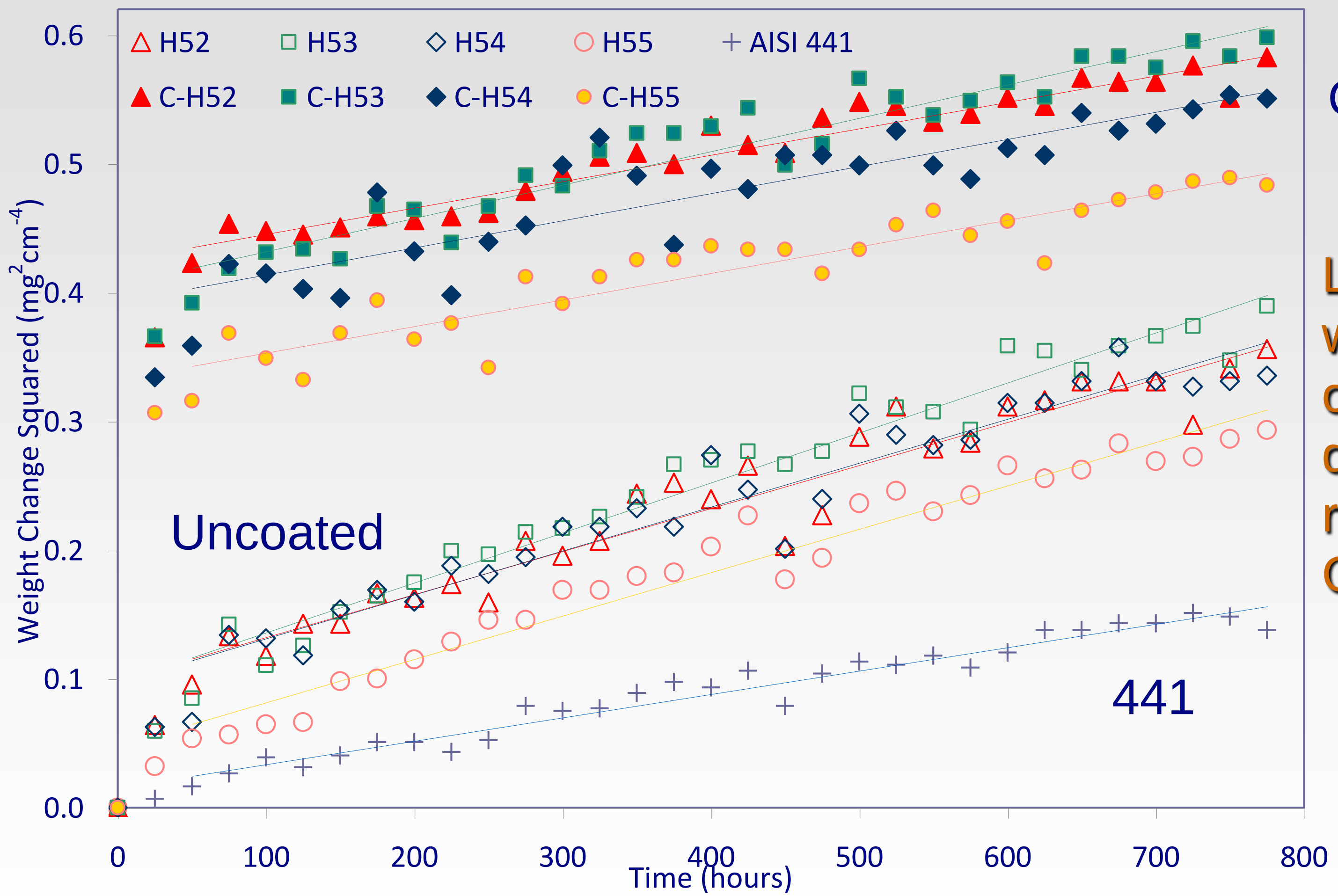
Composition of 441 with similar and lower Cr contents

Alloys were supplied by Allegheny Technologies, Inc. (ATI) (Matthew Bender)

Experimental Alloy Evaluation

- Coatings
  - Some samples coated with $Mn_{1.5}Co_{1.5}O_4$ by Pacific Northwest National Laboratory (PNNL) (Jeffry Stevenson) using slurry coating process
- Oxidation Exposure
  - Cyclic oxidation at 800 C
  - Isothermal oxidation for 800 and 1600 hours at 800 C
- Characterization
  - Scanning electron microscopy (SEM) with energy dispersive x-ray spectroscoy (EDS)
  - X-ray diffraction (XRD)

Cyclic Oxidation at 800°C



Coated

Large initial weight gain in coated samples due to reoxidation of Co in coating

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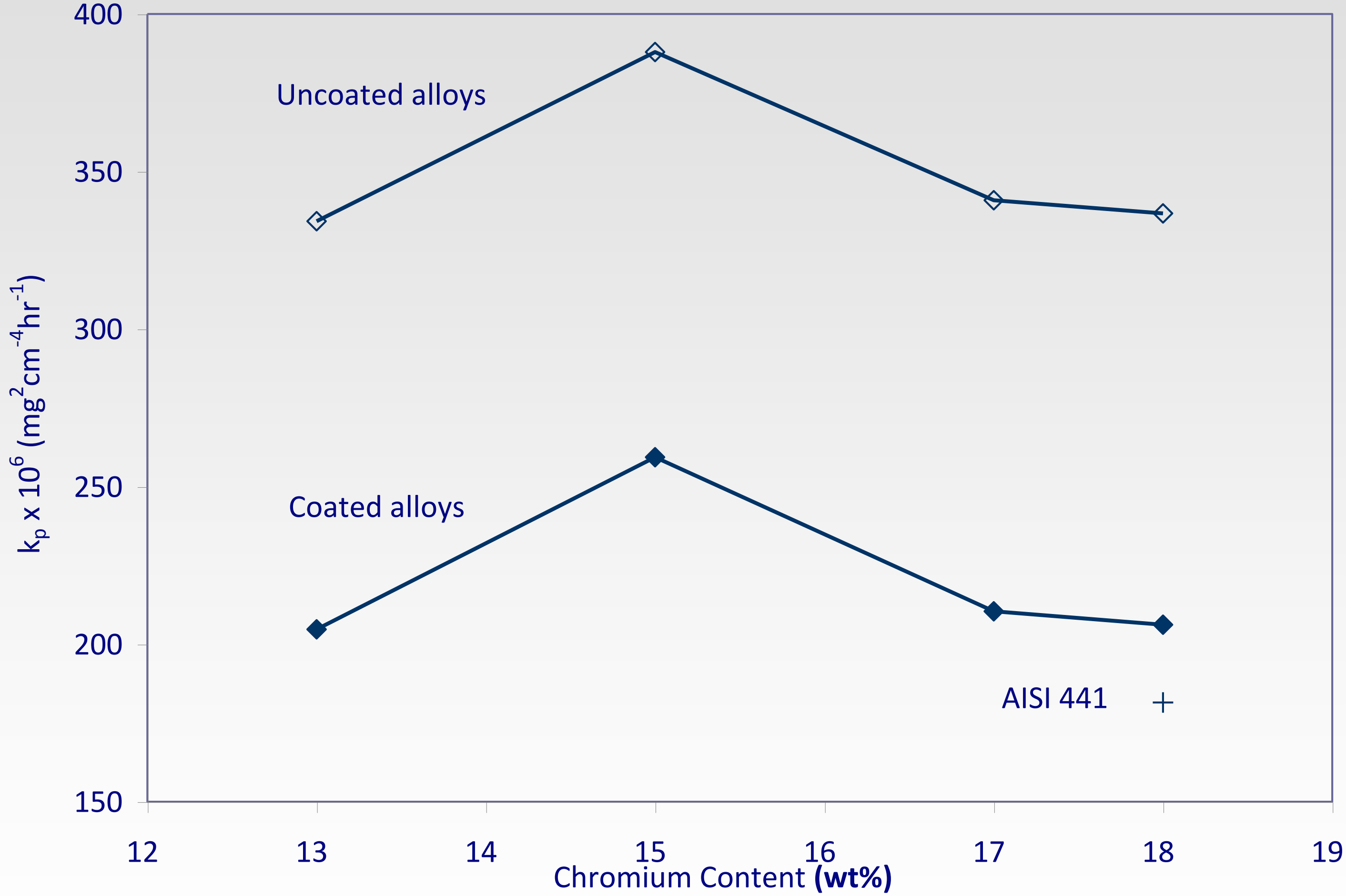
Parabolic Rate Constants – Cr Content

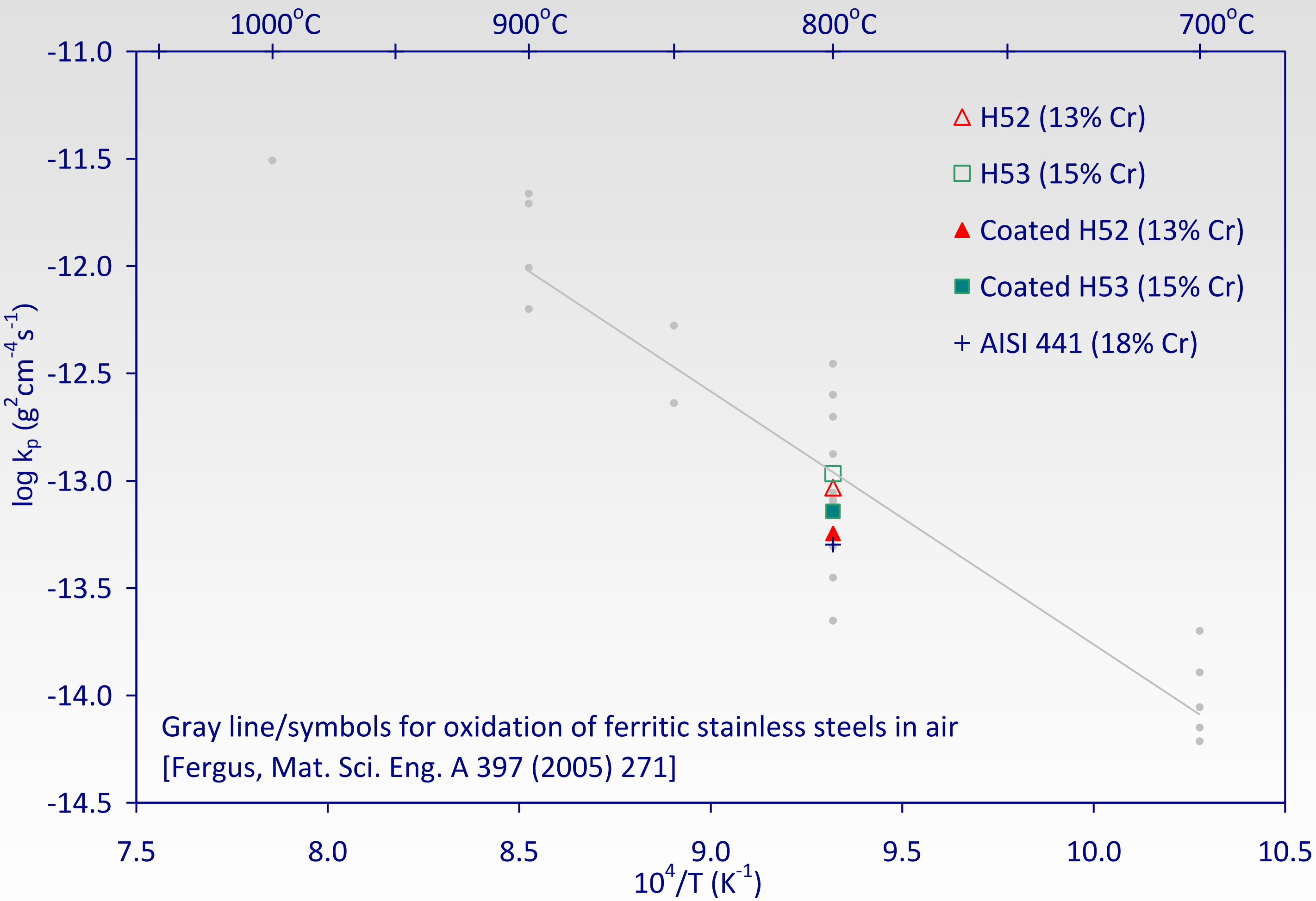


k_p of coated alloys lower than uncoated

No strong Cr dependence

Experimental alloys high k_p than 441

Parabolic Rate Constants - Literature



Values of k_p of similar to those found in the literature

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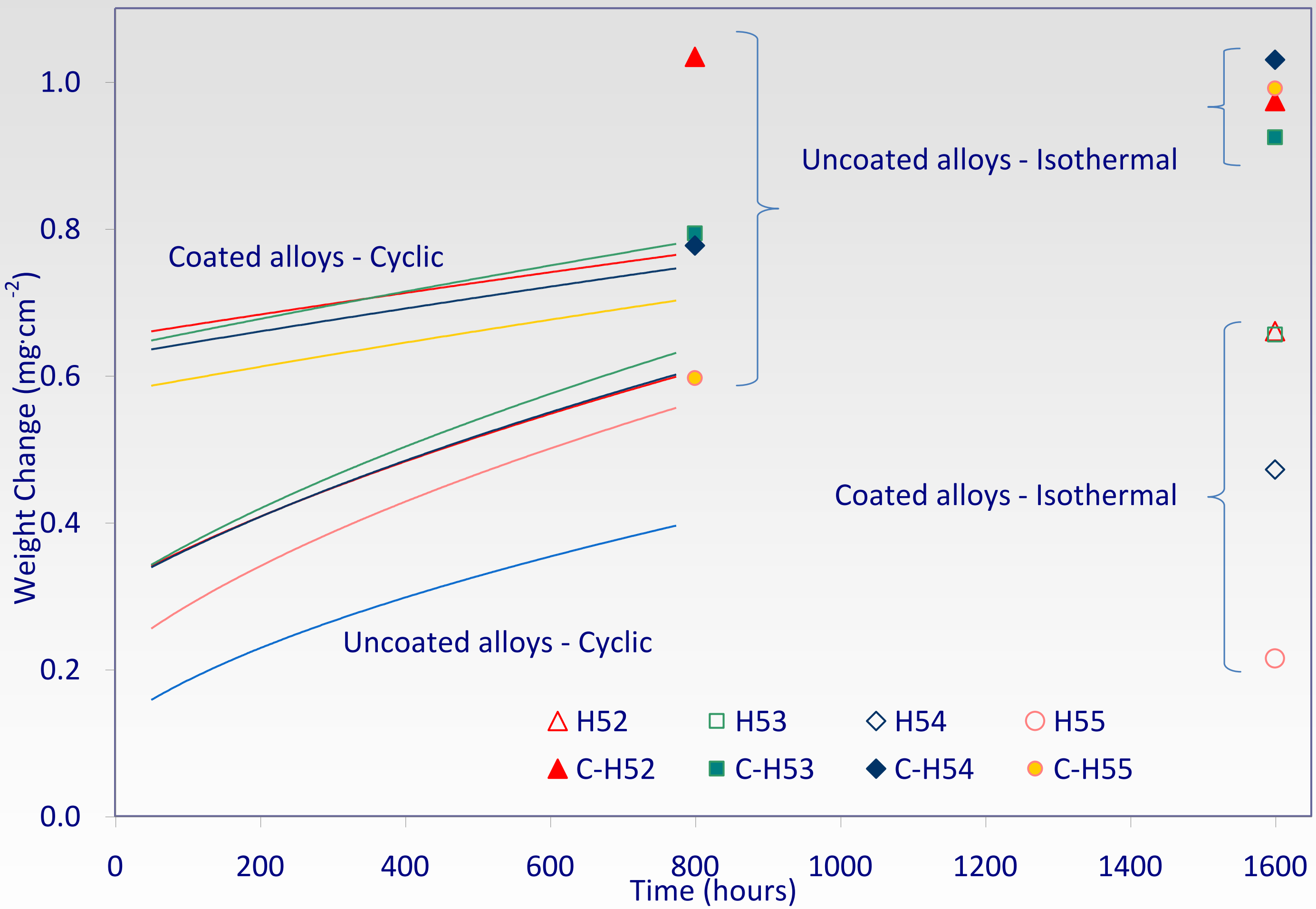
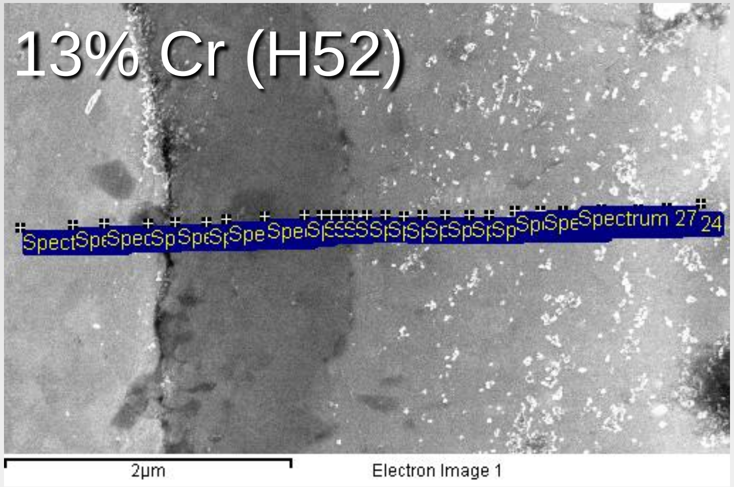
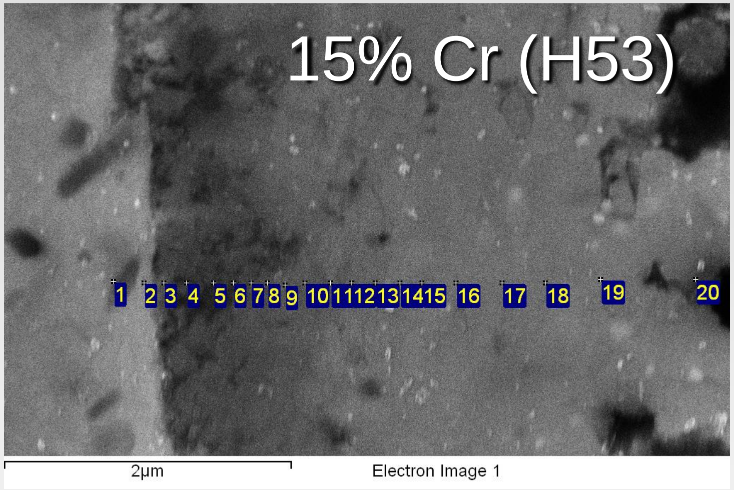
Isothermal Oxidation at 800°C

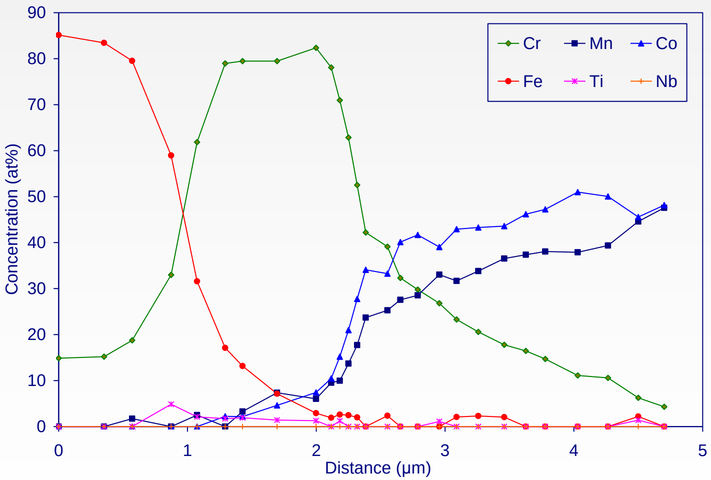


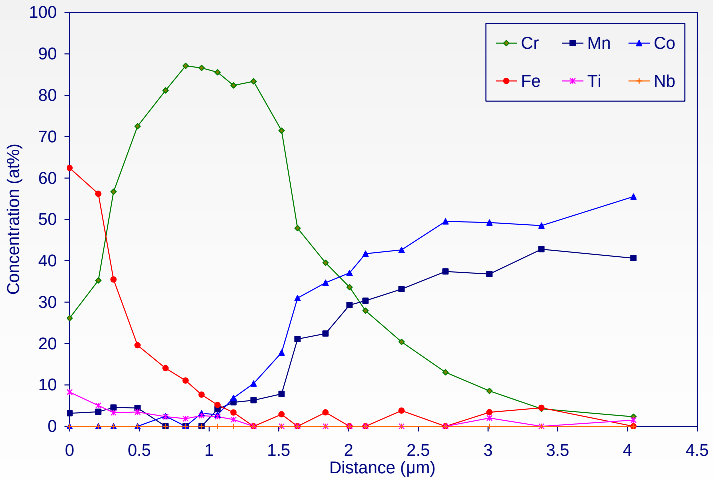
Isothermal weight gains similar to cyclic

Cross-Sections: 13-15%Cr – 800°C/800 h

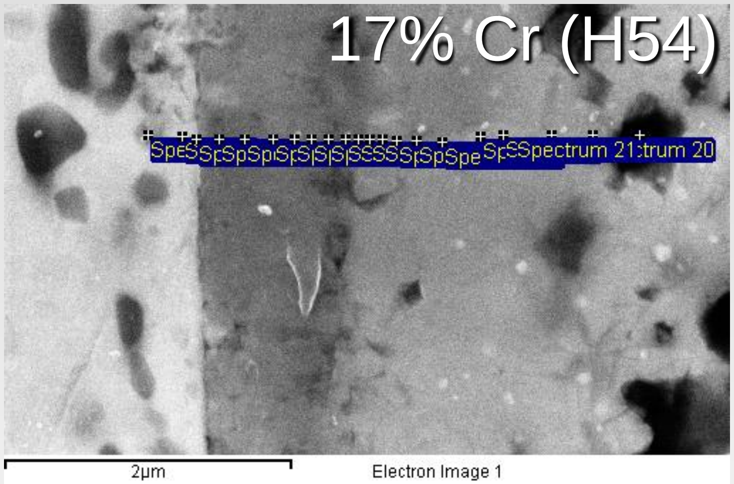


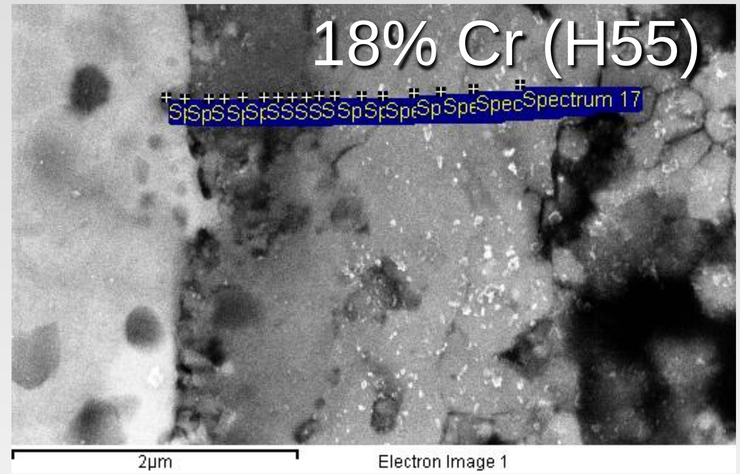


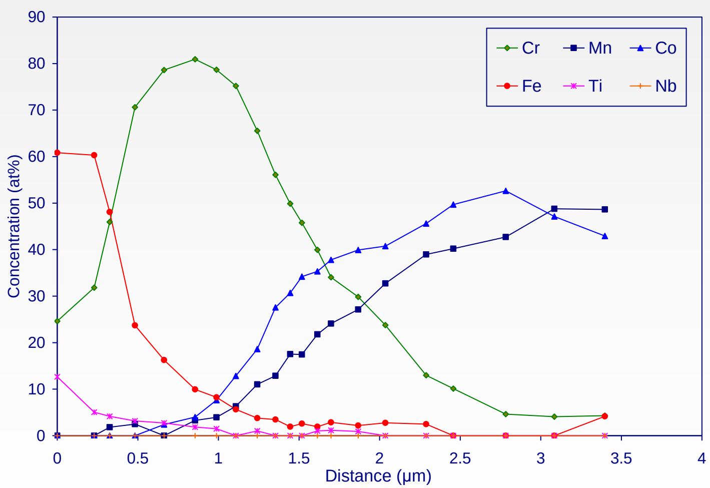


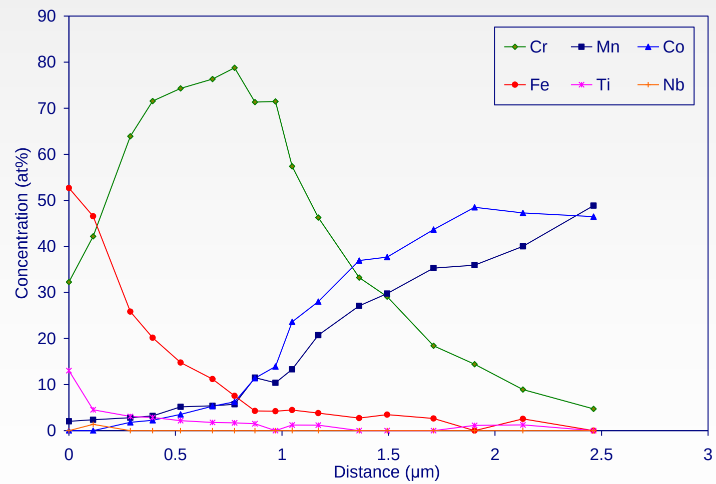


Cross-Sections: 17-18%Cr – 800°C/800 h

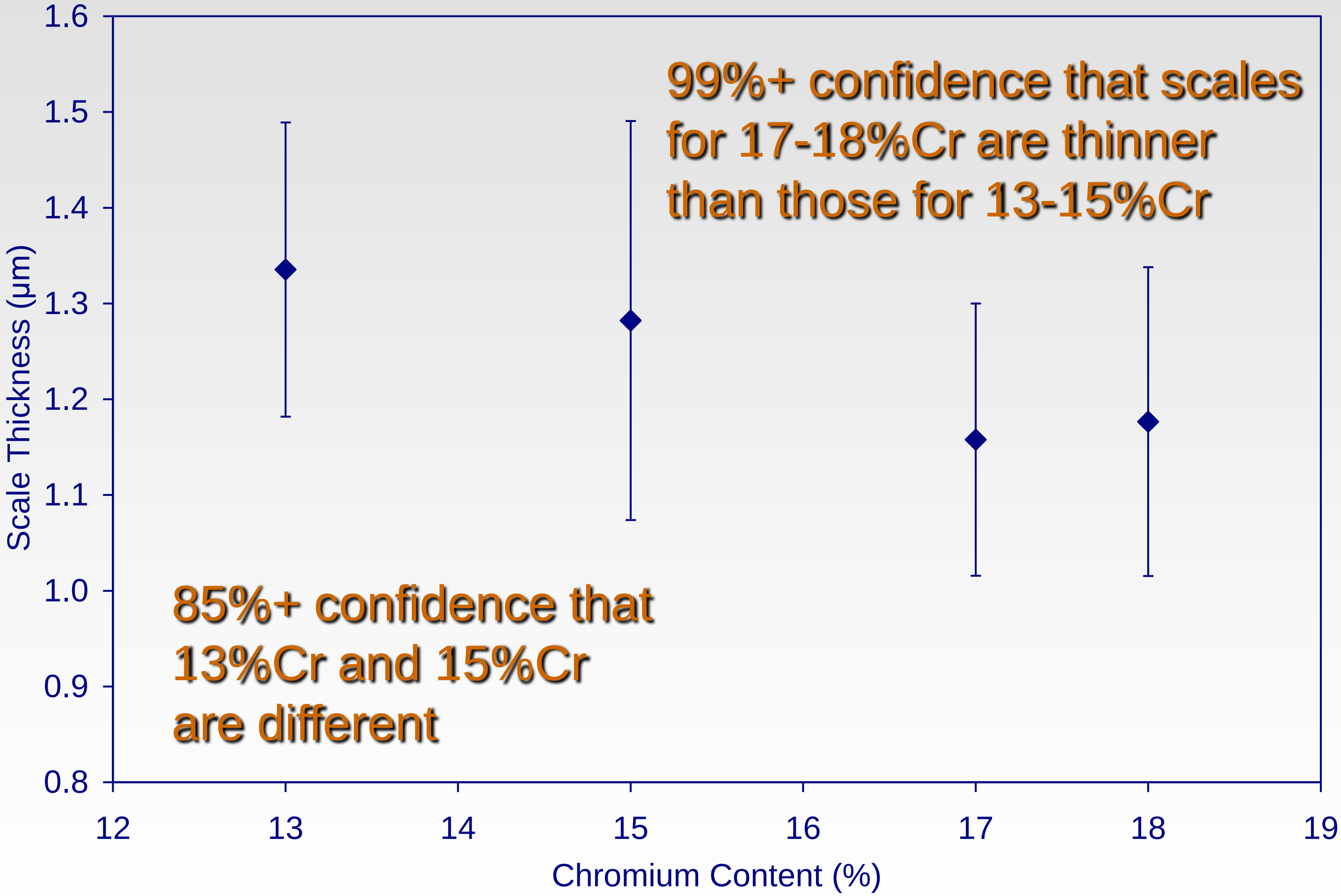








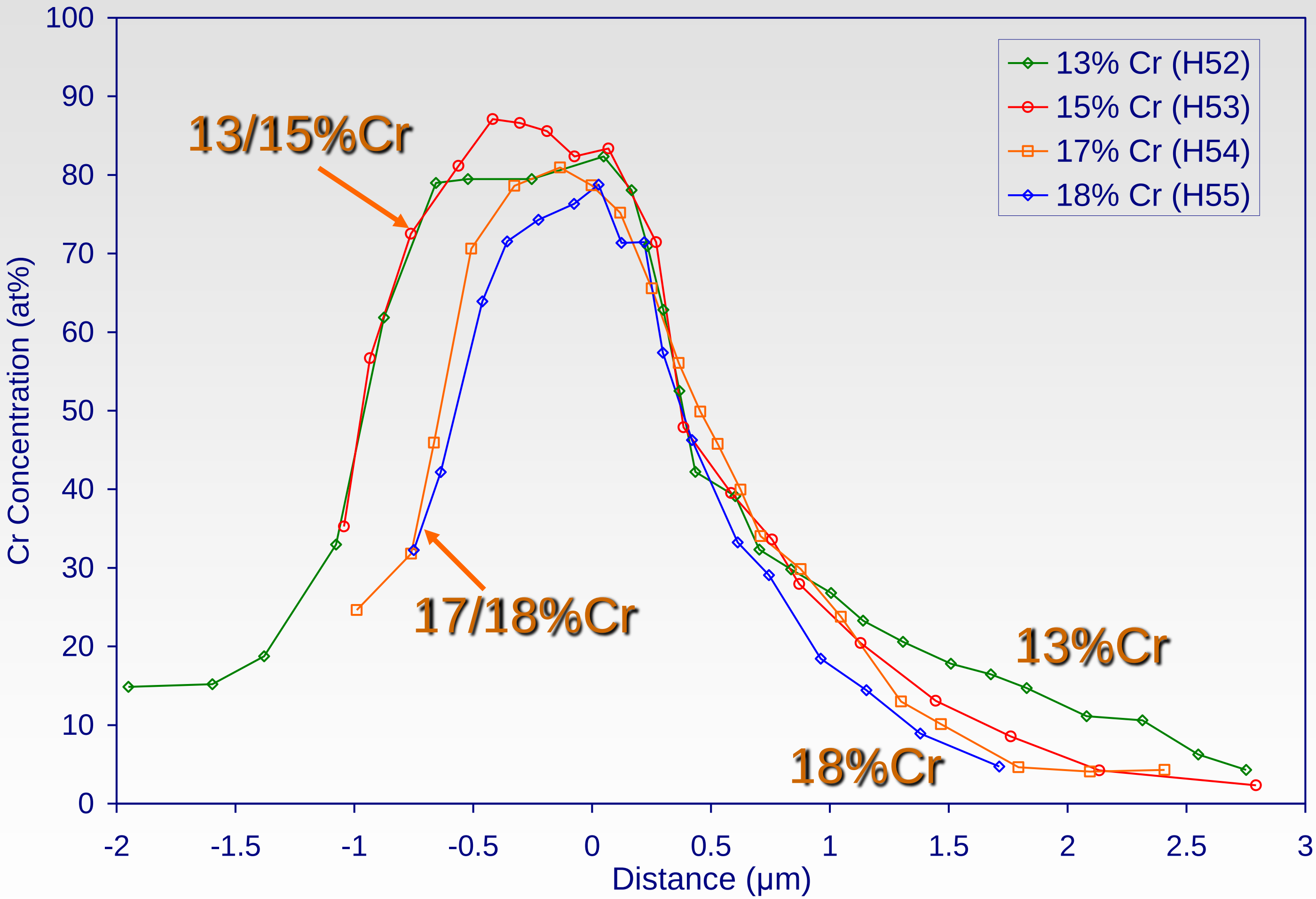
Scale Thickness – Coated Alloys after 800 hours at 800°C



50 thickness measurements from SEM micrographs

Error bars represent 1 standard deviation

Reaction Layer – 800°C/800 h



Distance referenced to original interface

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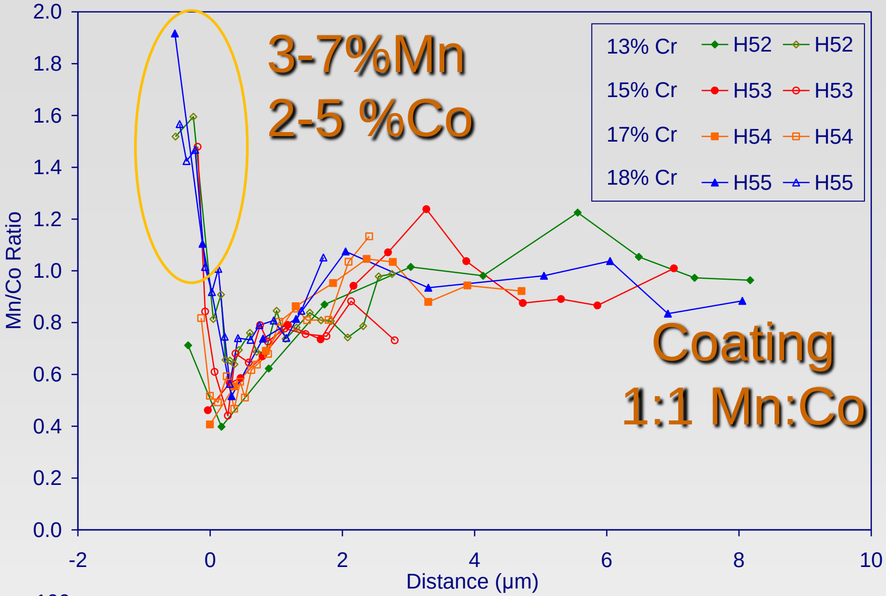

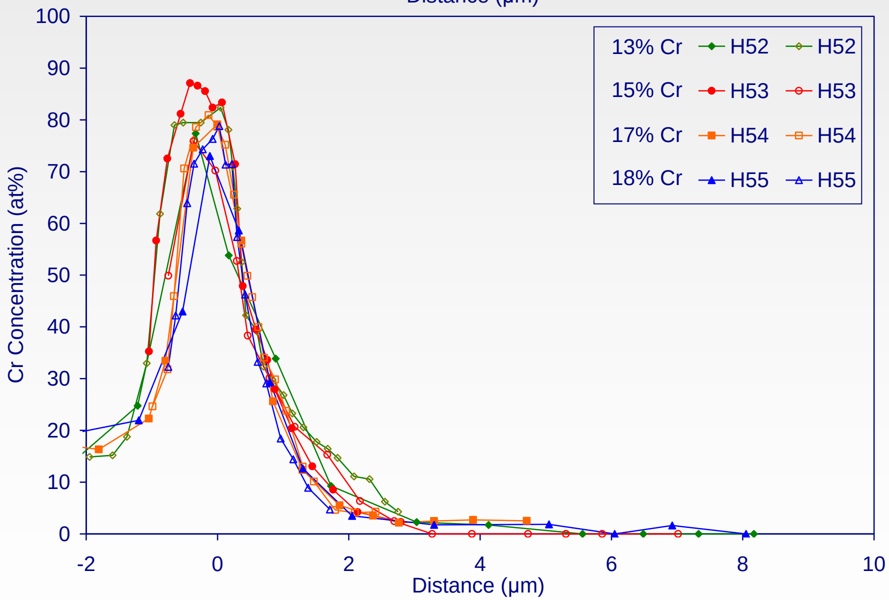

Mn/Co Ratio – 800°C/800 h

Low Mn / High Co in Cr-containing spinel

Cr^{3+} strongest preference for octahedral site

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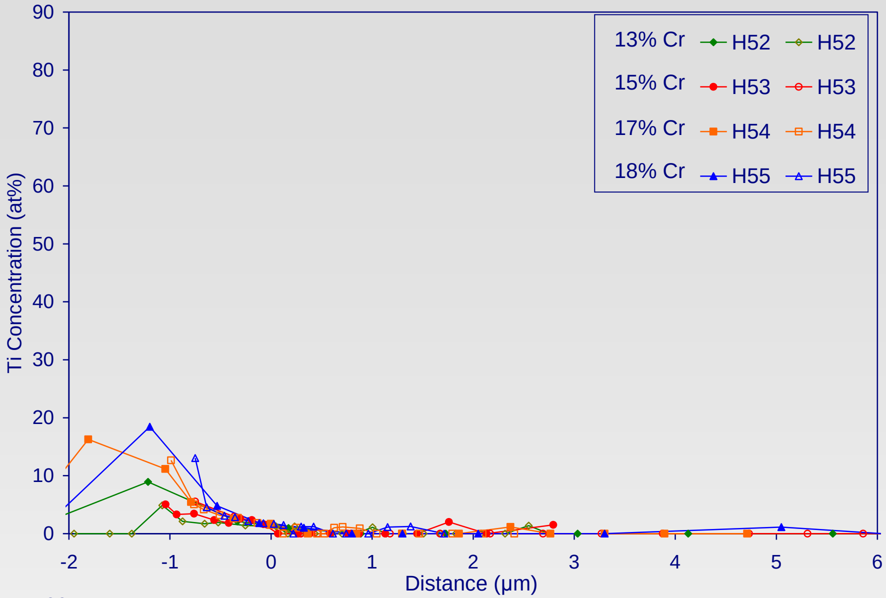

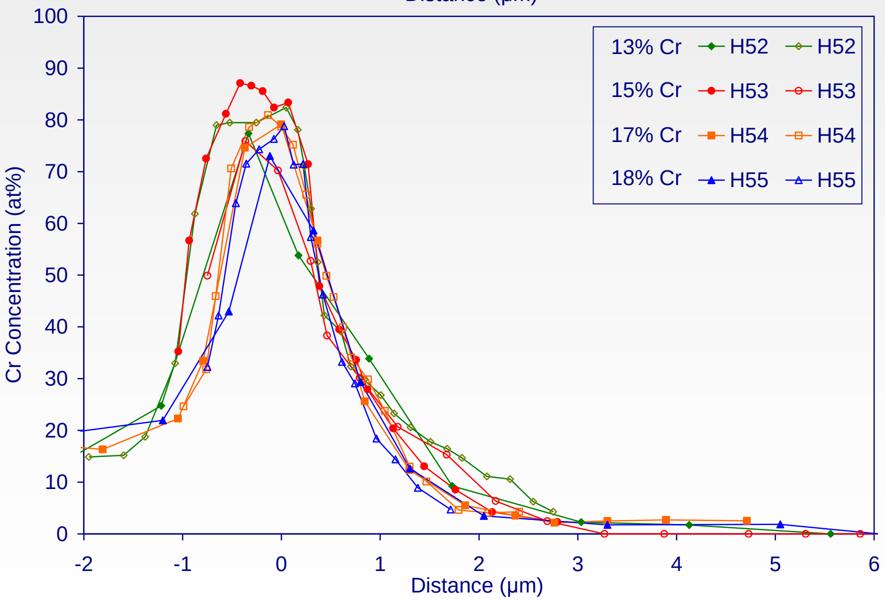

Titanium
800°C/800 h

Ti present at alloy-scale interface

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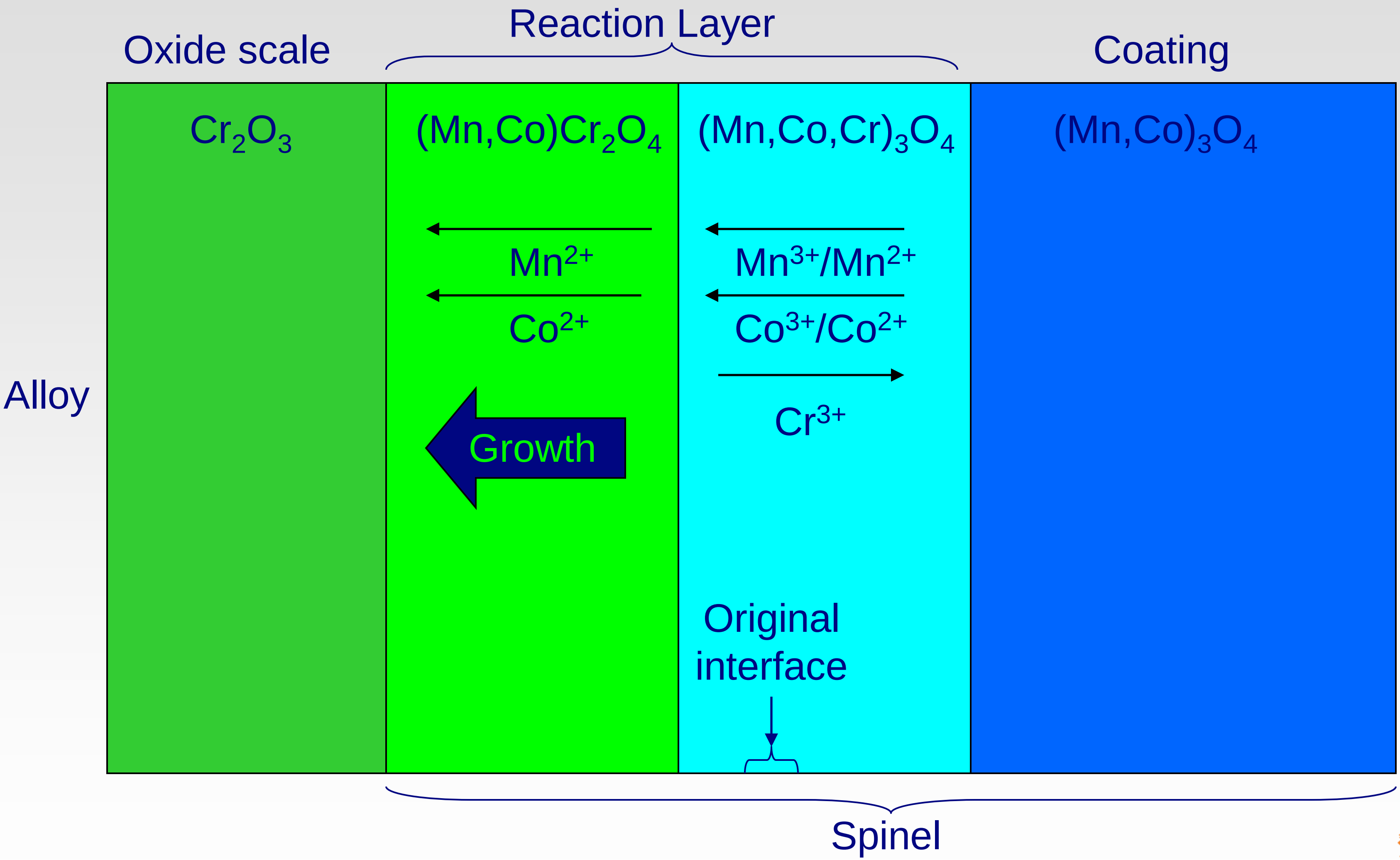
Interconnect Alloy-Coating Interaction



Conclusions

- Conductivity of spinel decreases with increasing Cr content
  - Decrease thickness / increase conductivity of Cr_2O_3 or Cr-rich spinel
- Low-chromium alloys with alloy additions present in 441
  - Uncoated alloys
    - Difference between Cr contents in experimental alloys less than that between experimental alloys and 441
  - Coated alloys
    - Composition gradients / phase formation similar among alloys
    - Reaction layer thicker for alloys with low Cr content
    - 17-18 %Cr better than 13-15 %Cr