Interconnect-Coating Interactions: Transition Metal Spinel Oxides

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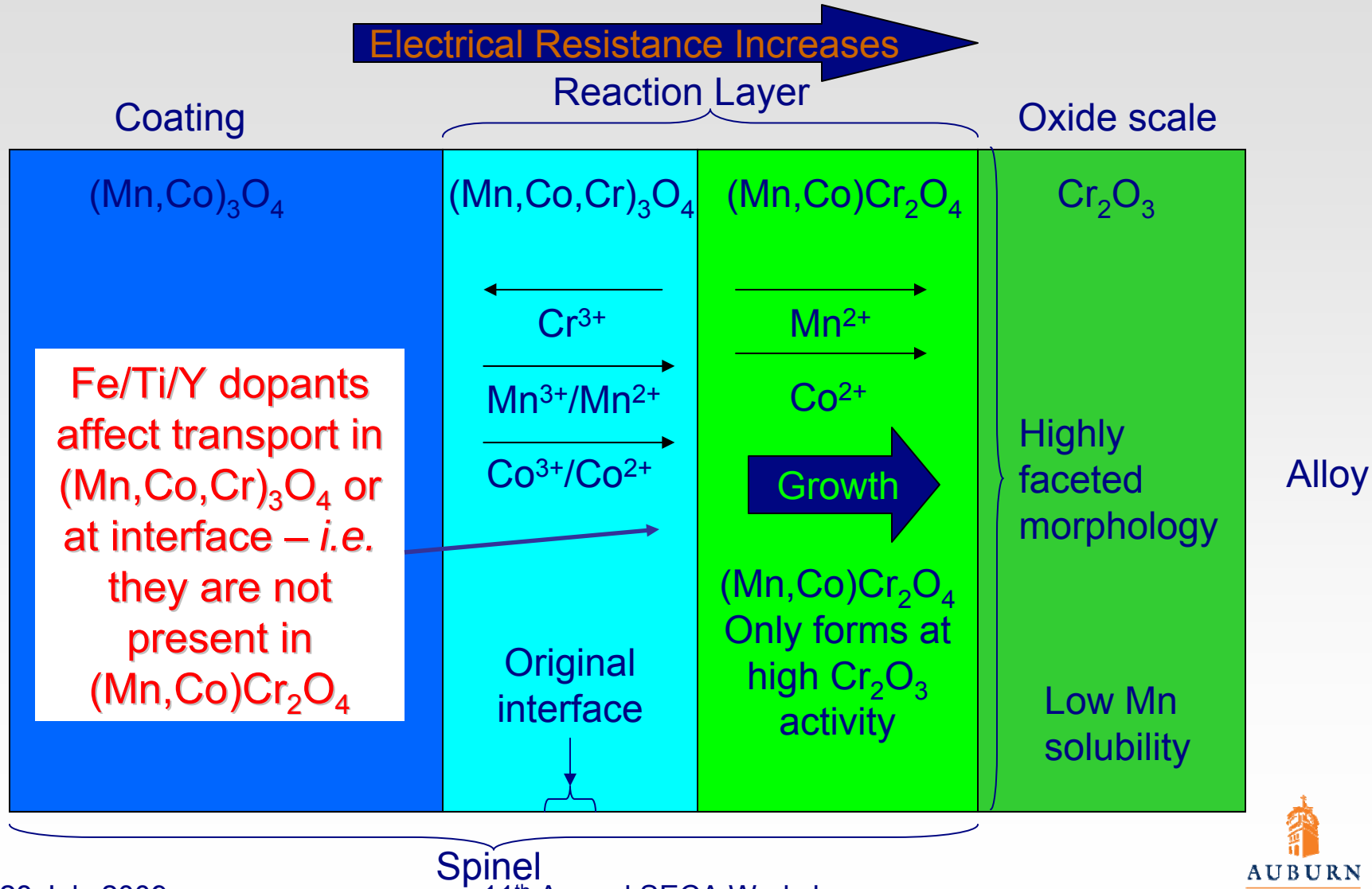
Interconnect Alloy-Coating Interaction



$(Mn,Co)_3O_4$ Spinel

- 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
  - Maximum Cr: Cr^{3+} on all octahedral sites

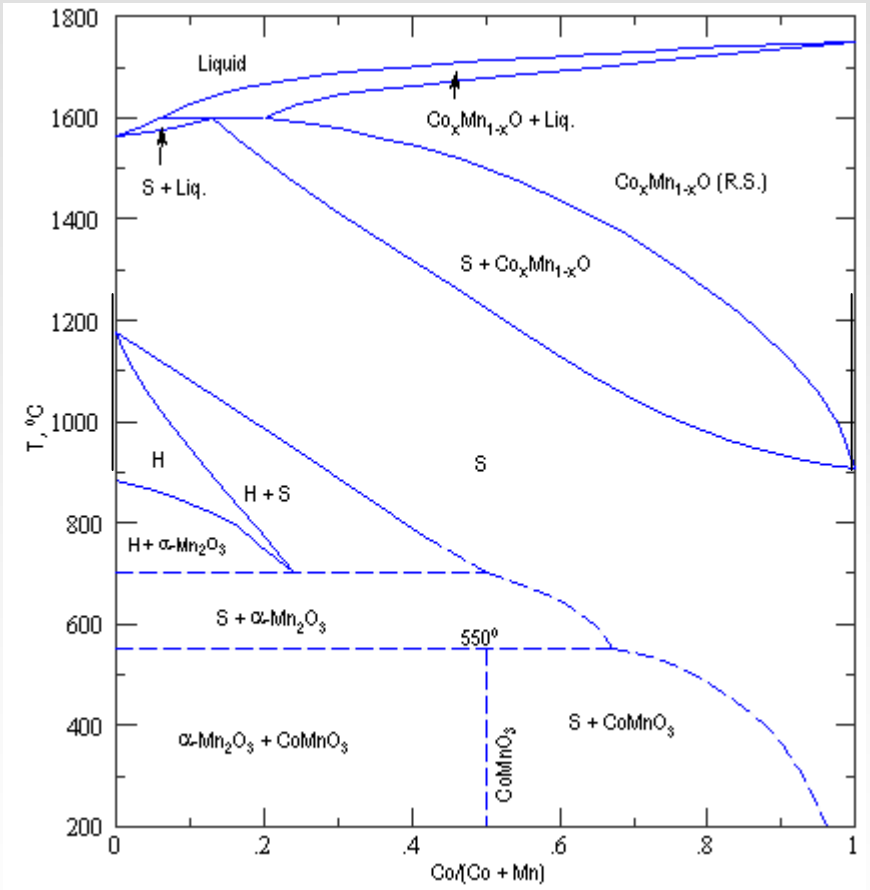
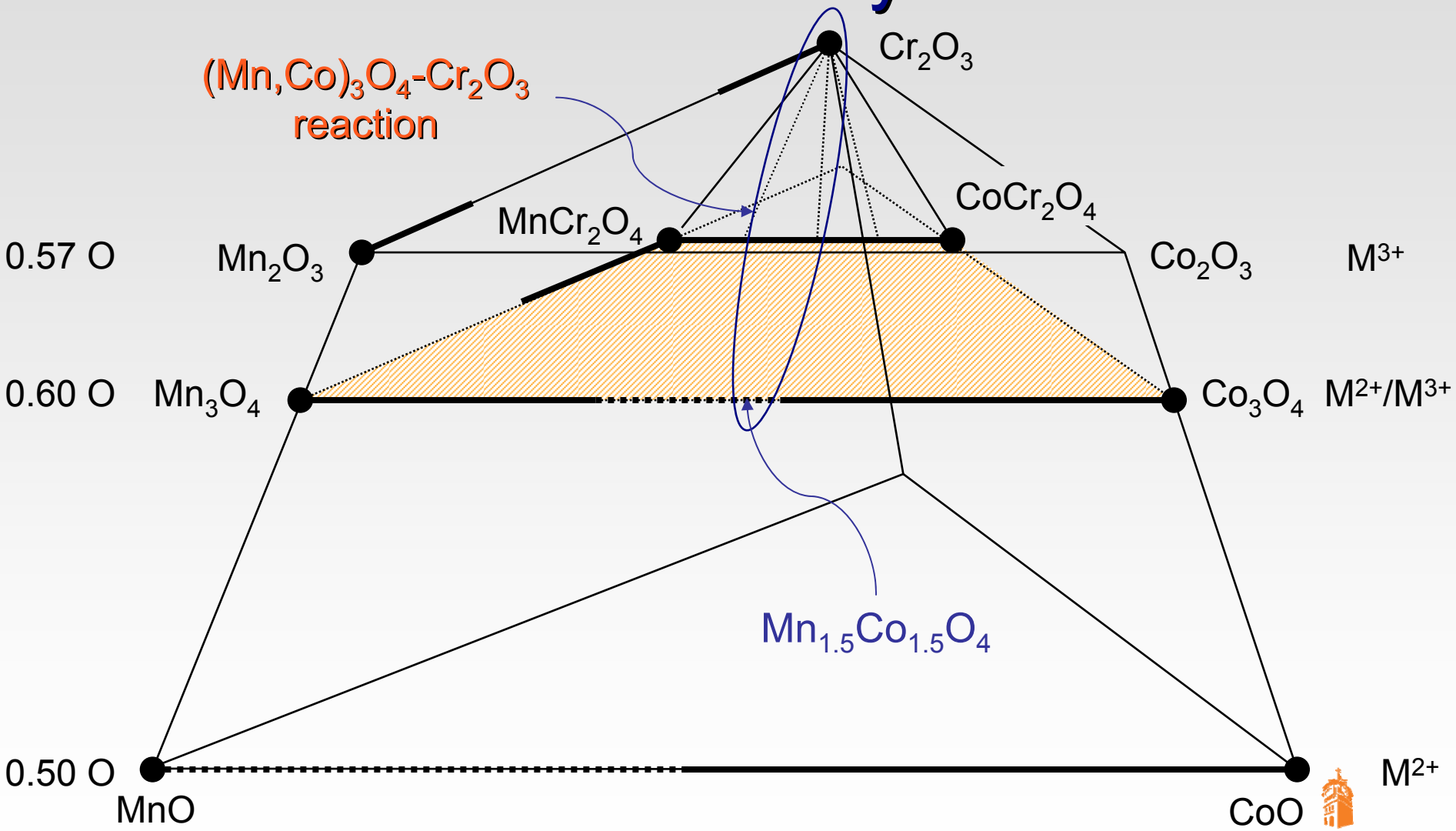


Figure 9570, *Phase Diagrams for Ceramists*

Mn-Co-Cr-O System



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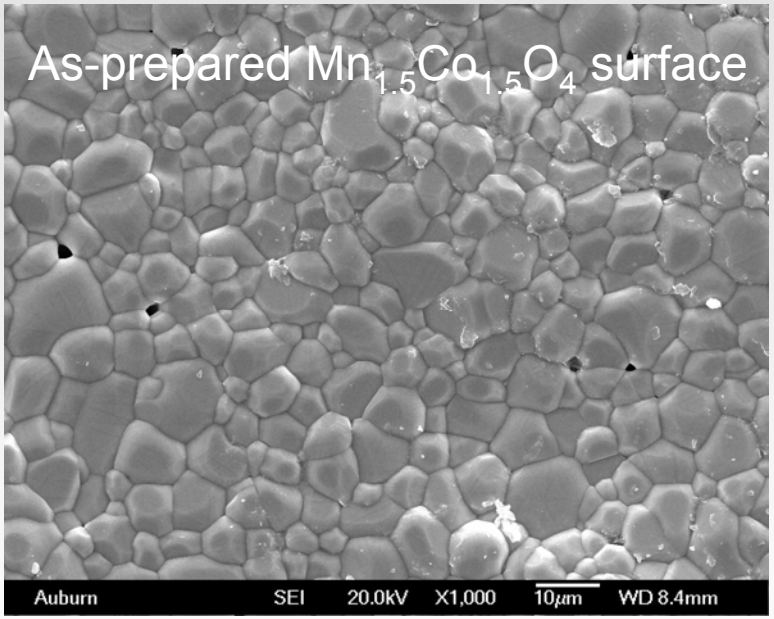
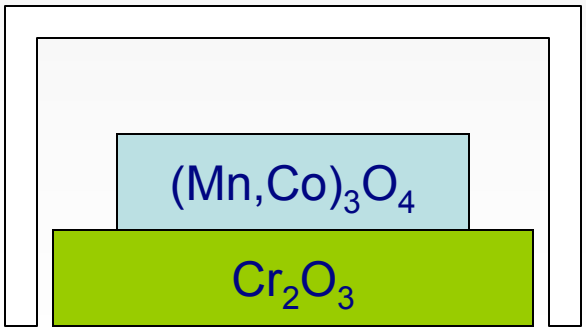
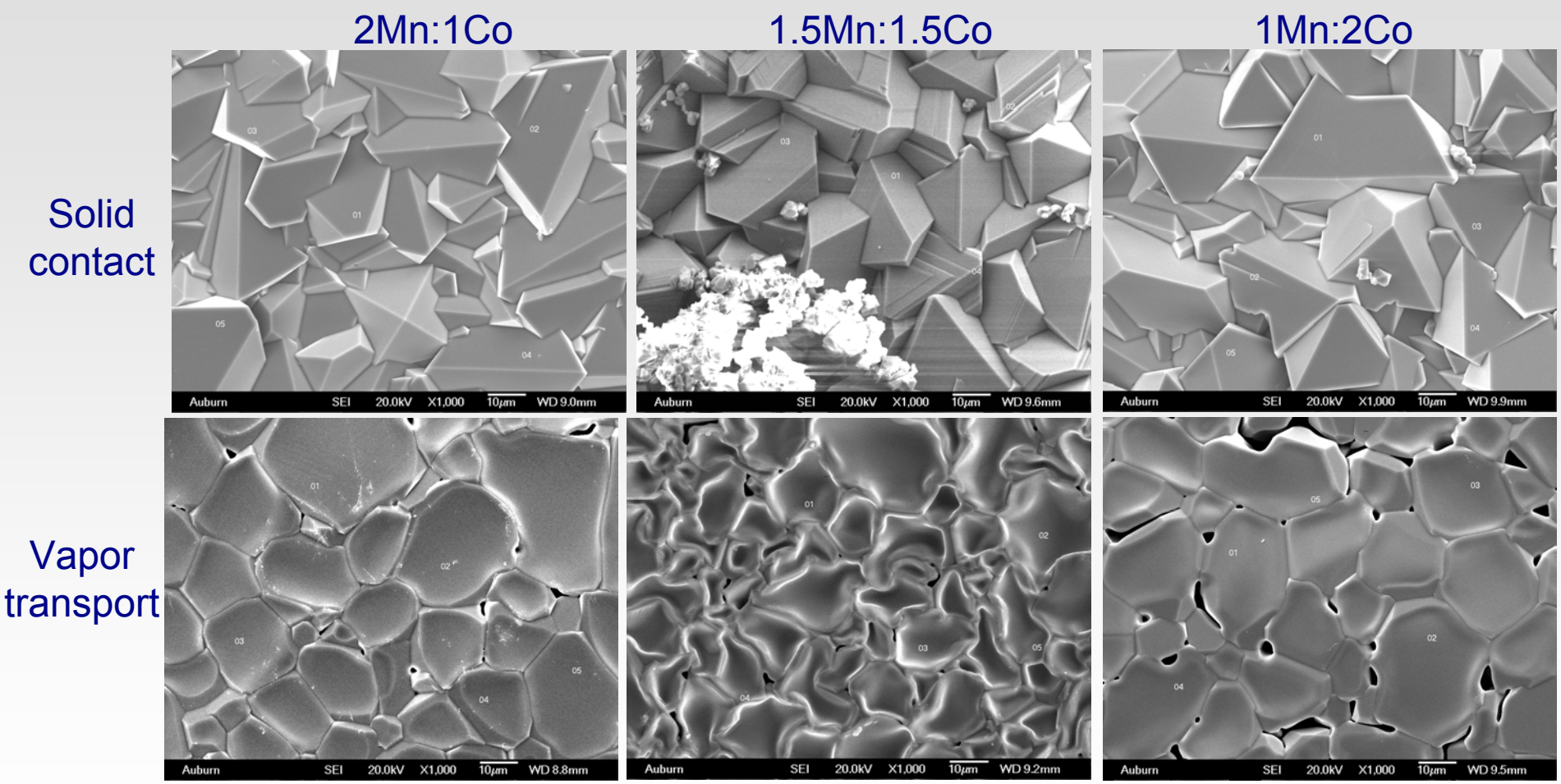
Interaction of $(Mn,Co)_3O_4$ with Cr_2O_3

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



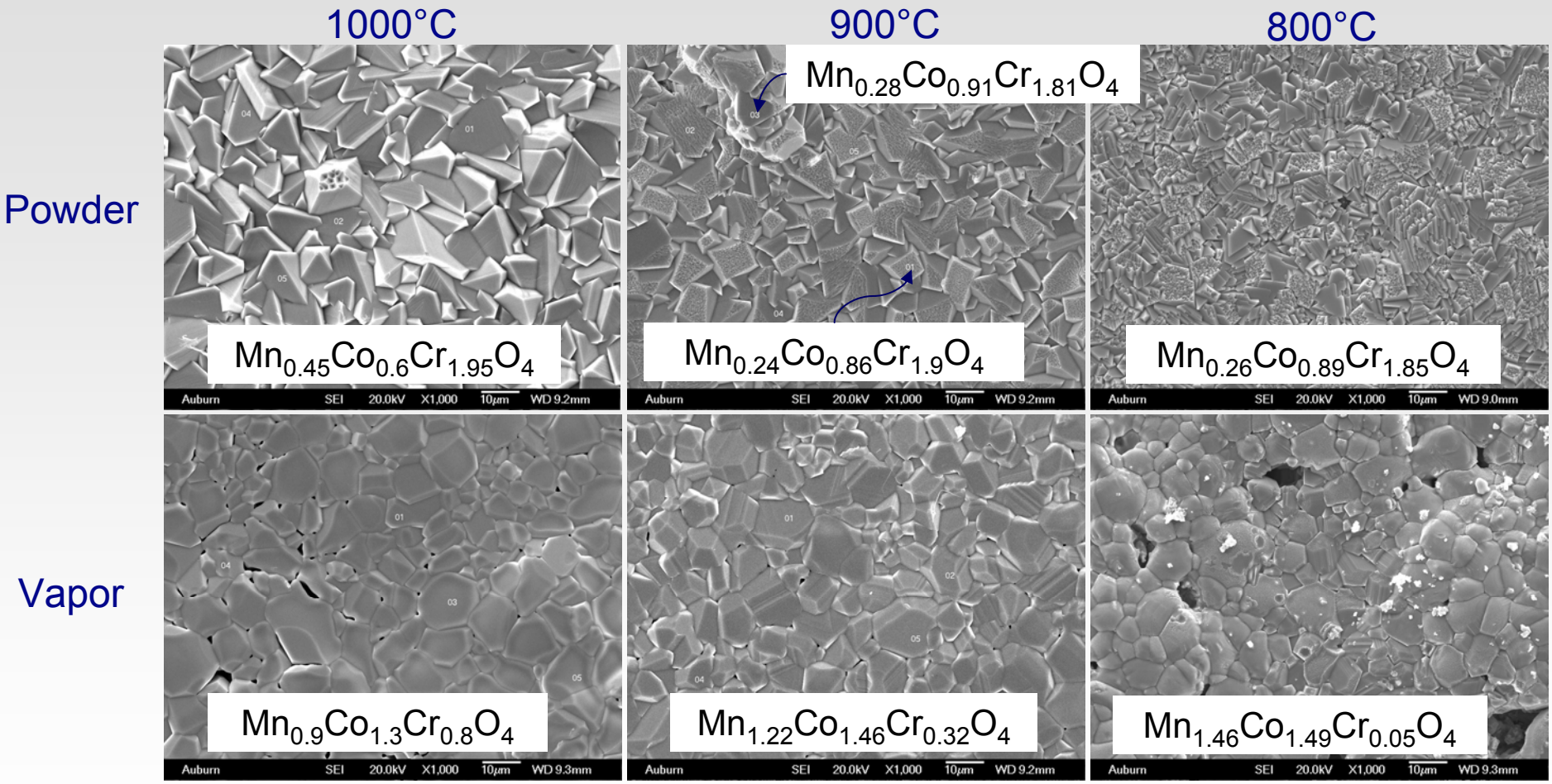


Effect of Mn/Co Ratio (1200°C, 72 hrs)



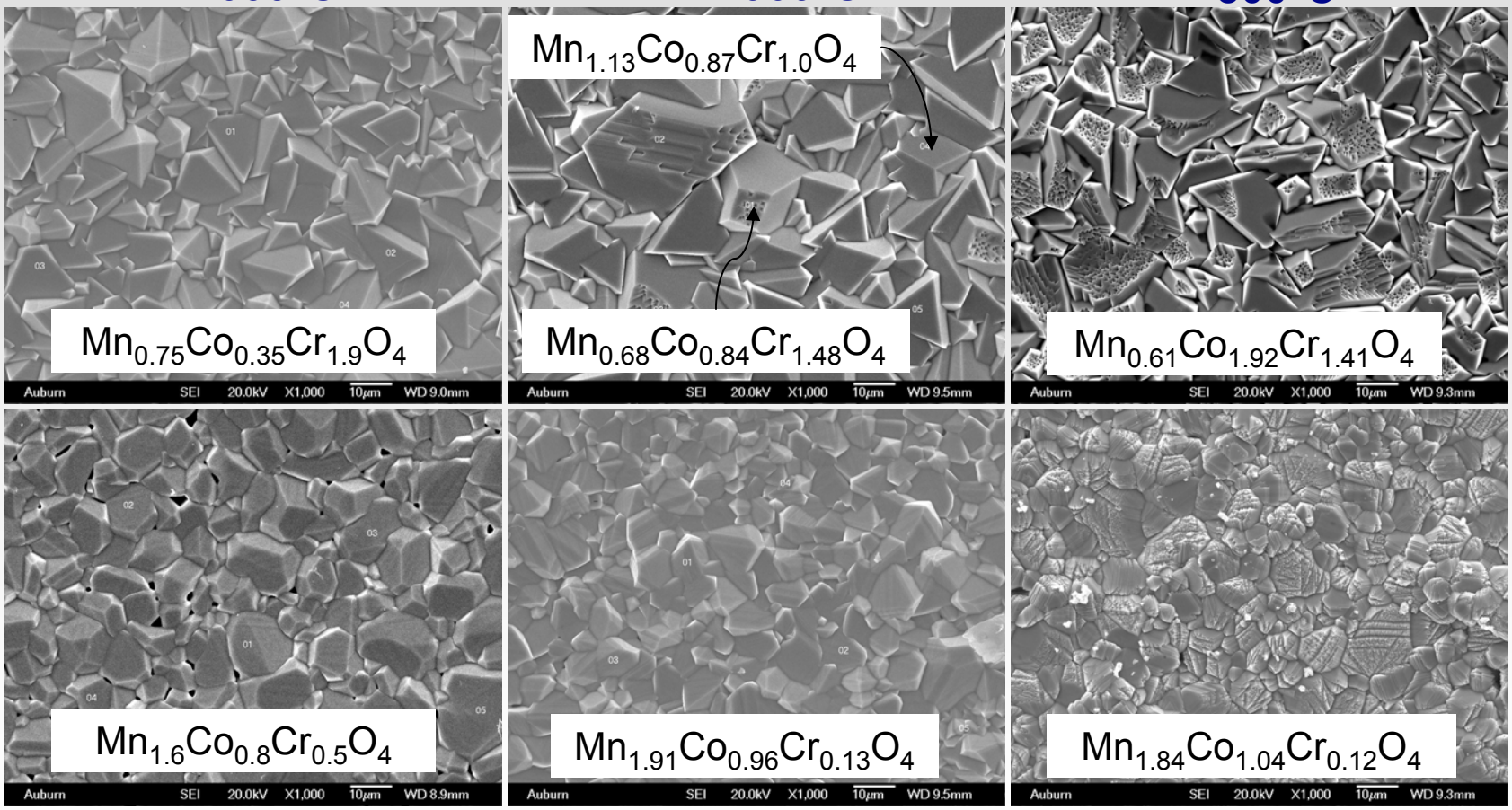
$MnCo_2O_4$: Less preferential grain boundary growth

$Mn_{1.5}Co_{1.5}O_4 + Cr_2O_3$ (72 hrs)



800°C: Faceted morphology for lower Cr

$Mn_2CoO_4 + Cr_2O_3$ (72 hrs)

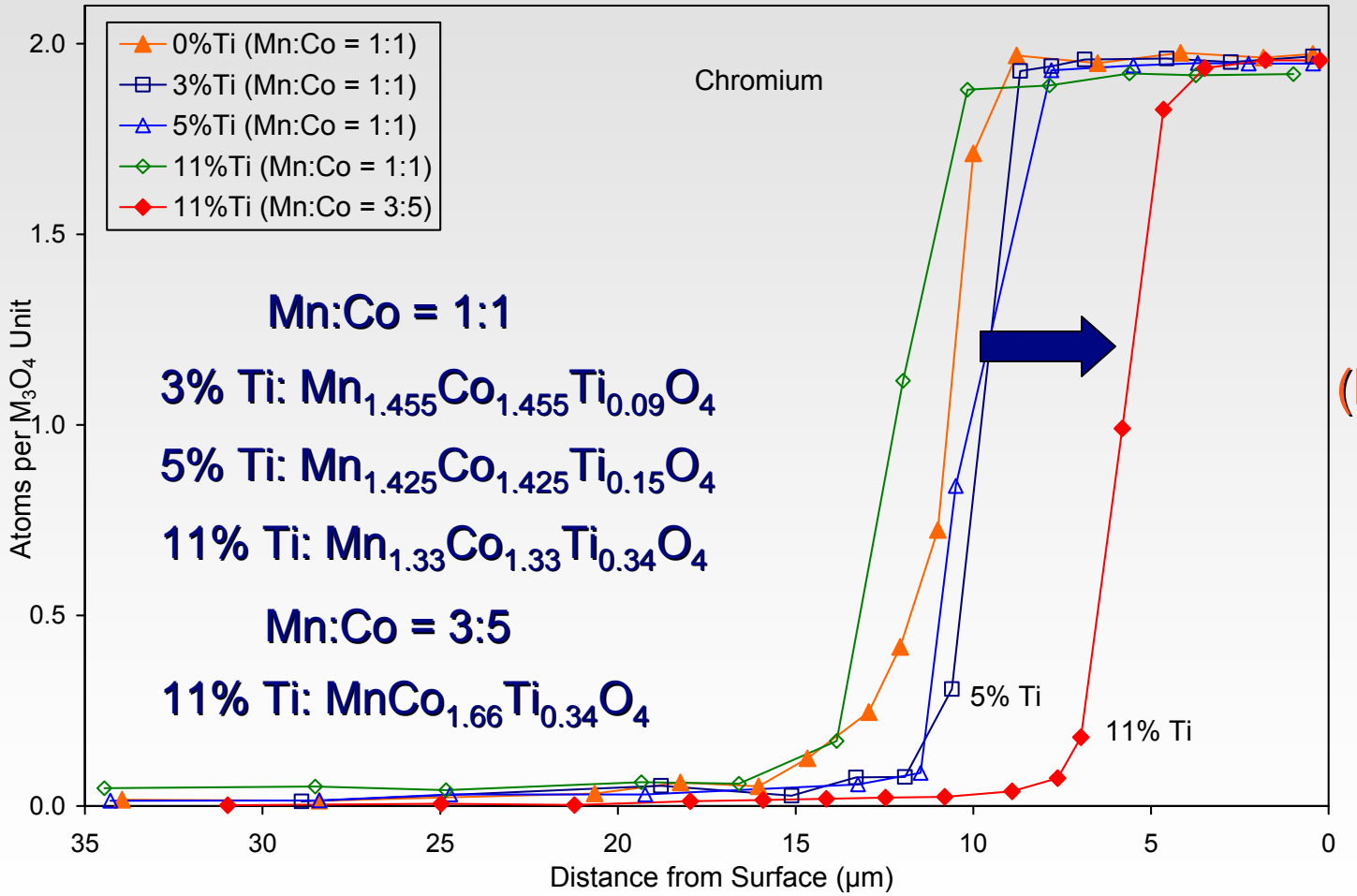


Facets form at lower Cr at lower temperatures

$(Mn,Co)_3O_4$-Cr_2O_3 Reaction

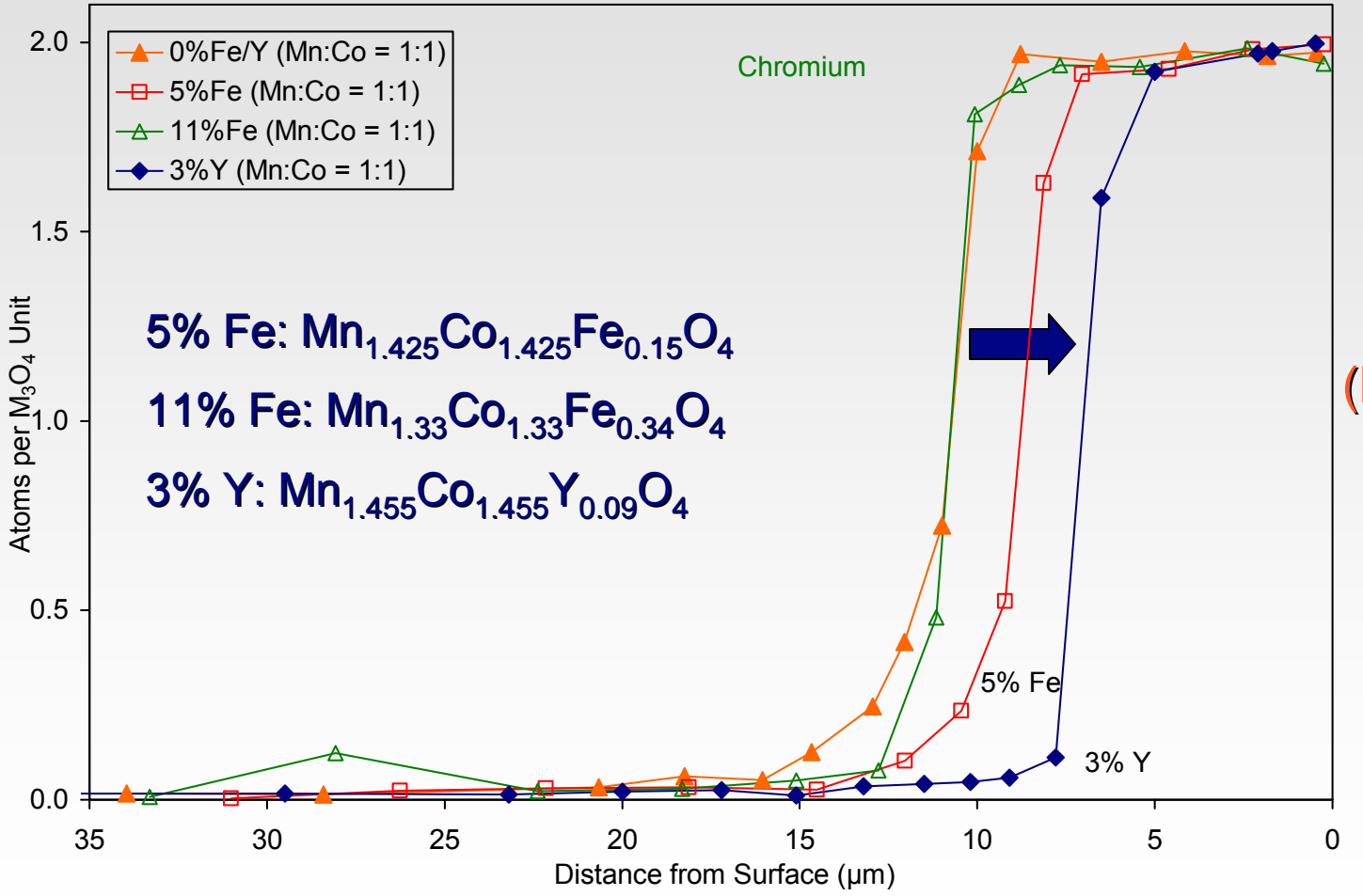
- Faceted morphology forms at lower Cr content at lower temperatures
  - Similar mechanism
  - Dominance of Co^{n+}/Mn^{n+} diffusion reaction control increases with decreasing temperature
- Dopants (Fe, Ti, Y) added to decrease reaction rate

Ti-doped $(Mn,Co)_3O_4$ – 1000°C / 72 hr



Decreased thickness of $(Mn,Co)Cr_2O_4$ layer

Fe/Y-doped $(Mn,Co)_3O_4$ – 1000°C / 72 hr



Decreased thickness of $(Mn,Co)Cr_2O_4$ layer

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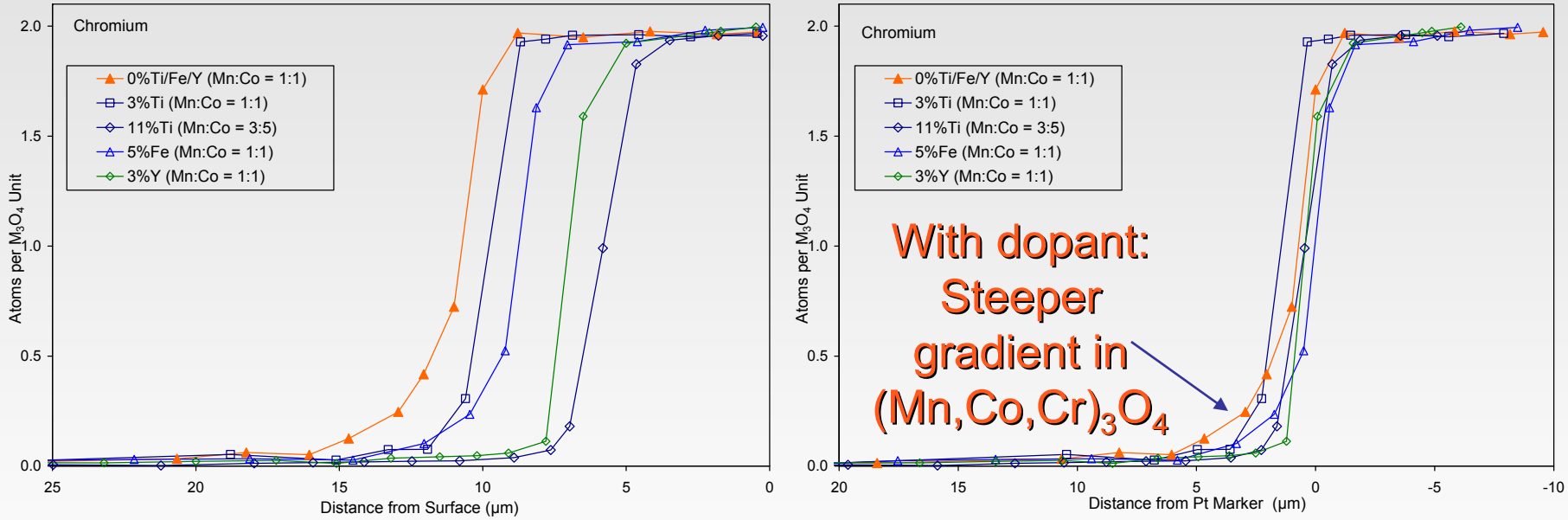
Doped $(Mn,Co)_3O_4$ – 1000°C / 72 hr

Chromium



Distance from sample surface

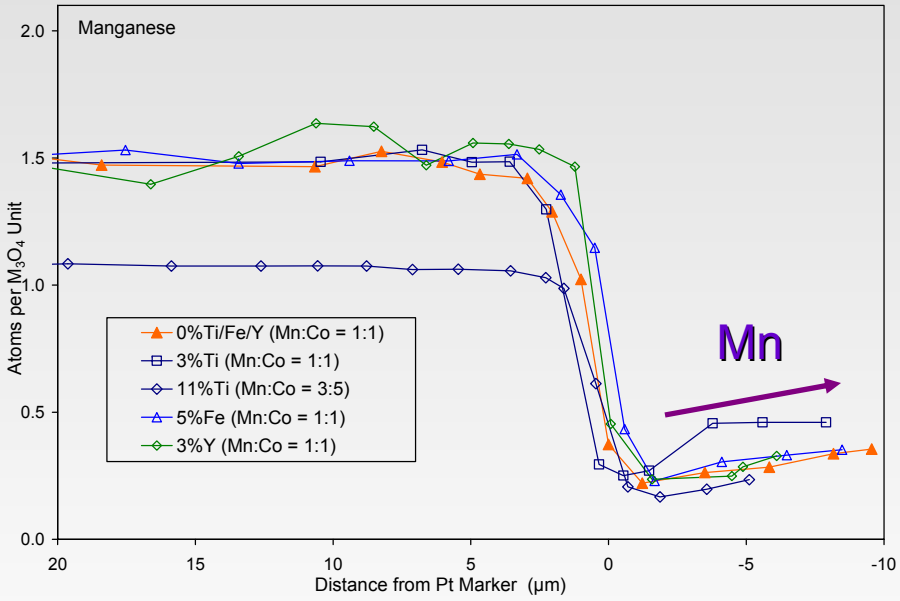
Distance from Pt marker

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

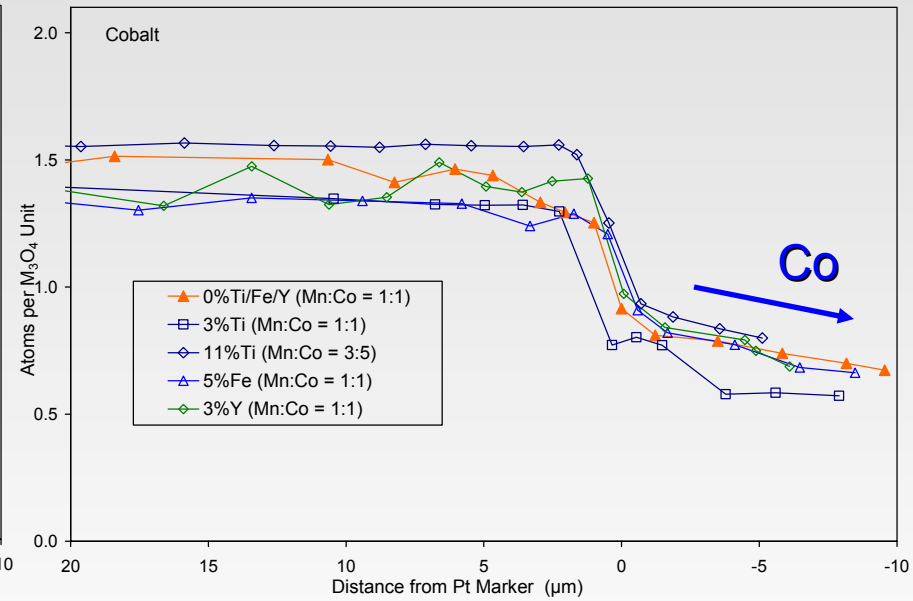
11% Ti: $MnCo_{1.66}Ti_{0.34}O_4$ **3% Y: $Mn_{1.455}Co_{1.455}Y_{0.09}O_4$**

Doped $(Mn,Co)_3O_4$ – 1000°C / 72 hr

Manganese



Cobalt

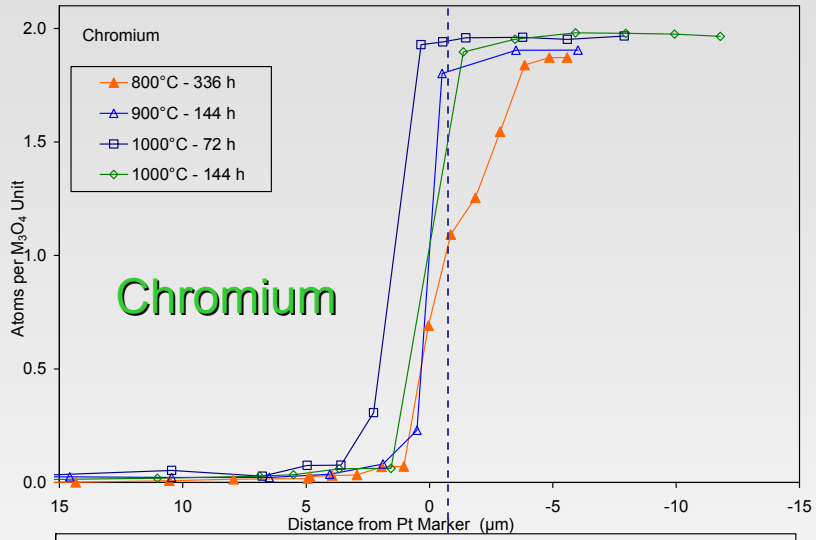


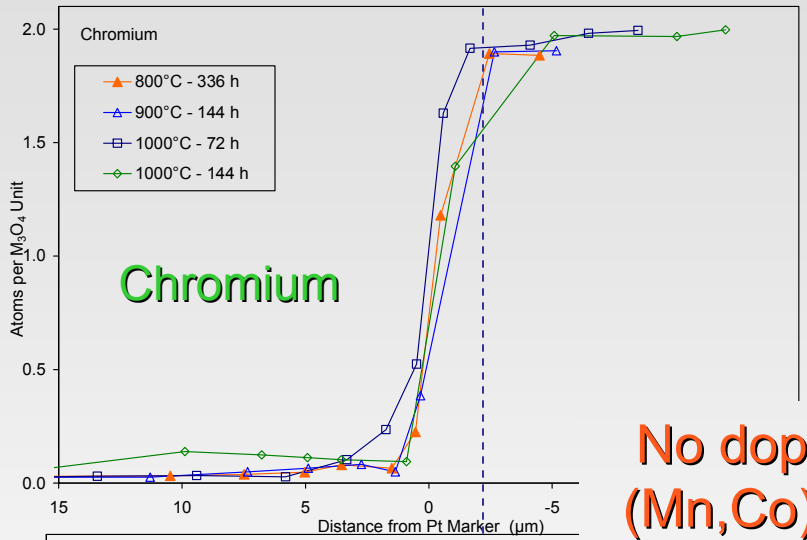
Distance from Pt marker

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

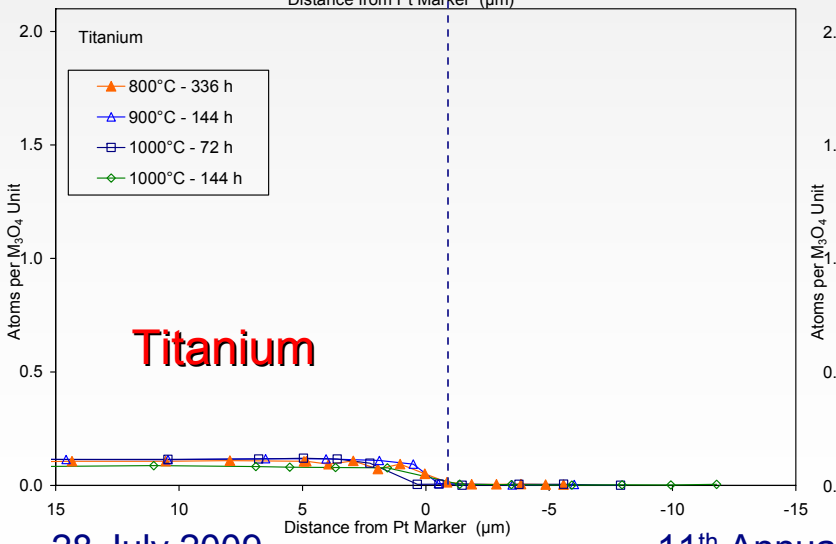
11% Ti: $MnCo_{1.66}Ti_{0.34}O_4$ **3% Y: $Mn_{1.455}Co_{1.455}Y_{0.09}O_4$**

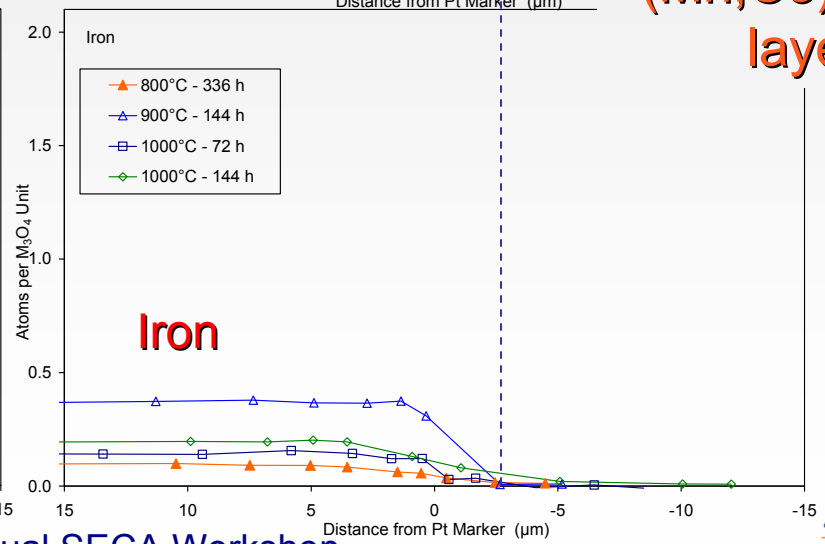
3%Ti Dopant Location 5%Fe



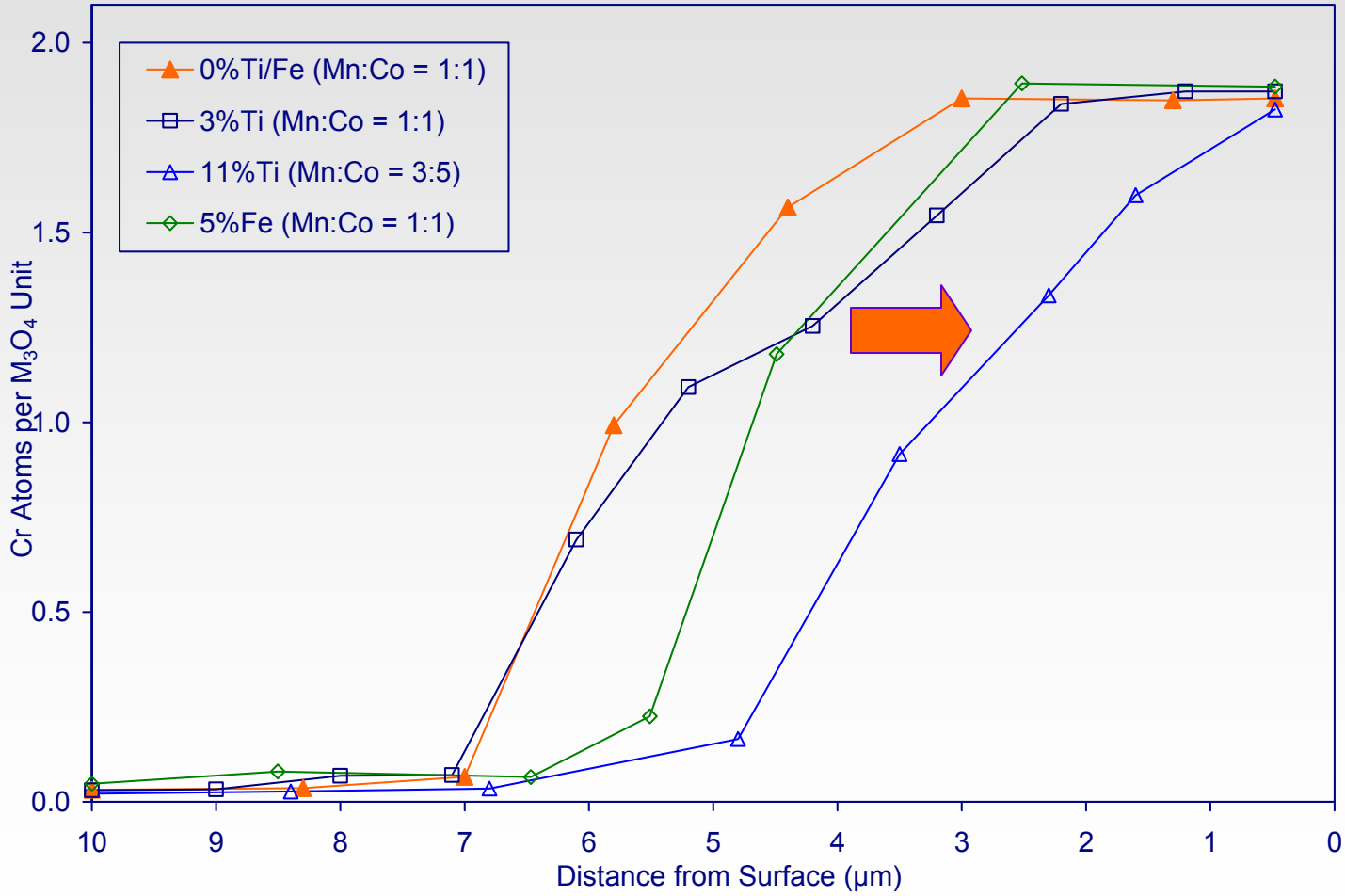


No dopant in $(Mn,Co)Cr_2O_4$ layer





Reaction Layer Thickness (800°C for 336 hrs)



Ti and Fe additions decrease the thickness of the reaction layer (reaction with Cr_2O_3) – Ti with high Co more effective

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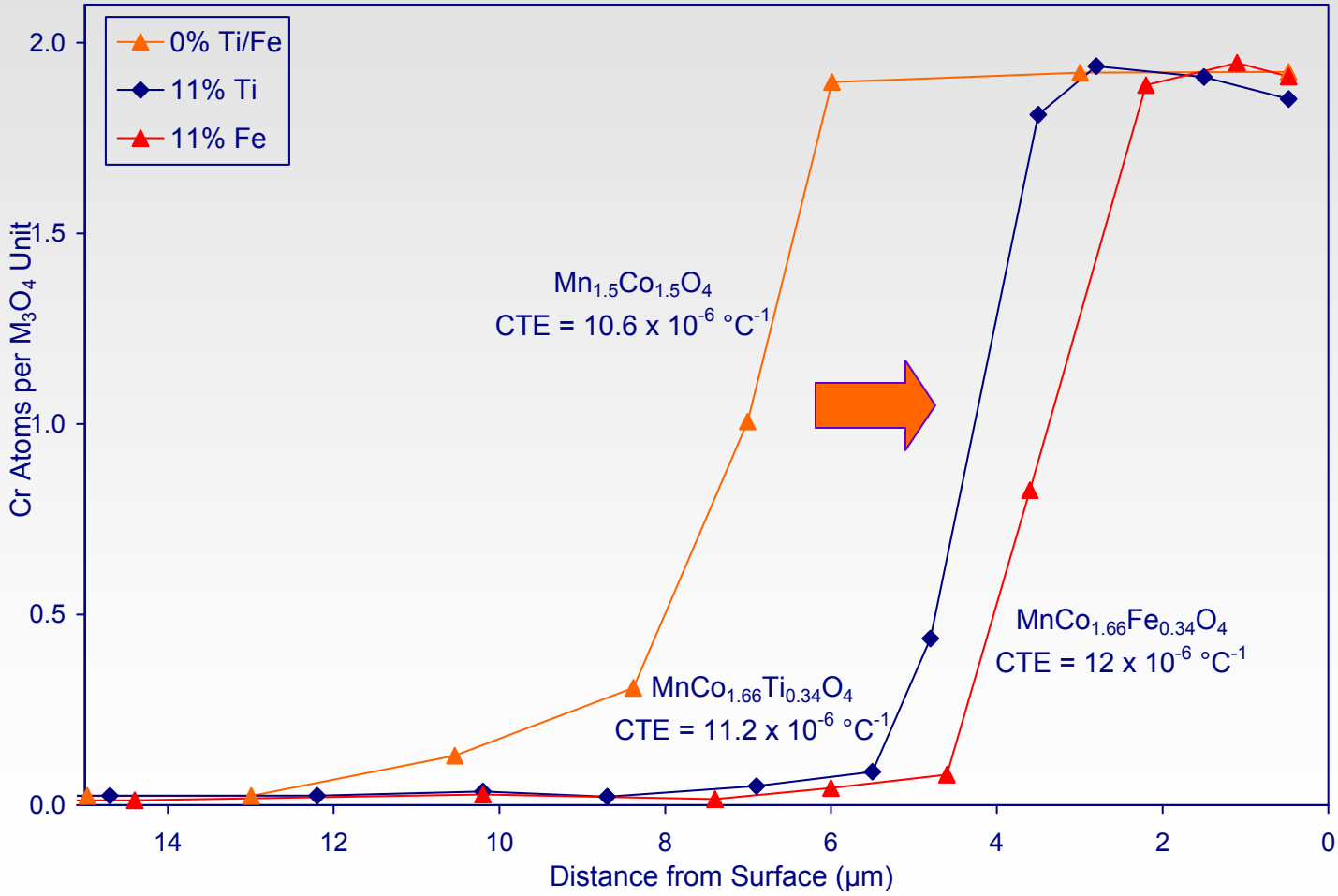
Reaction Layer Thickness (900°C for 144 hrs)



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

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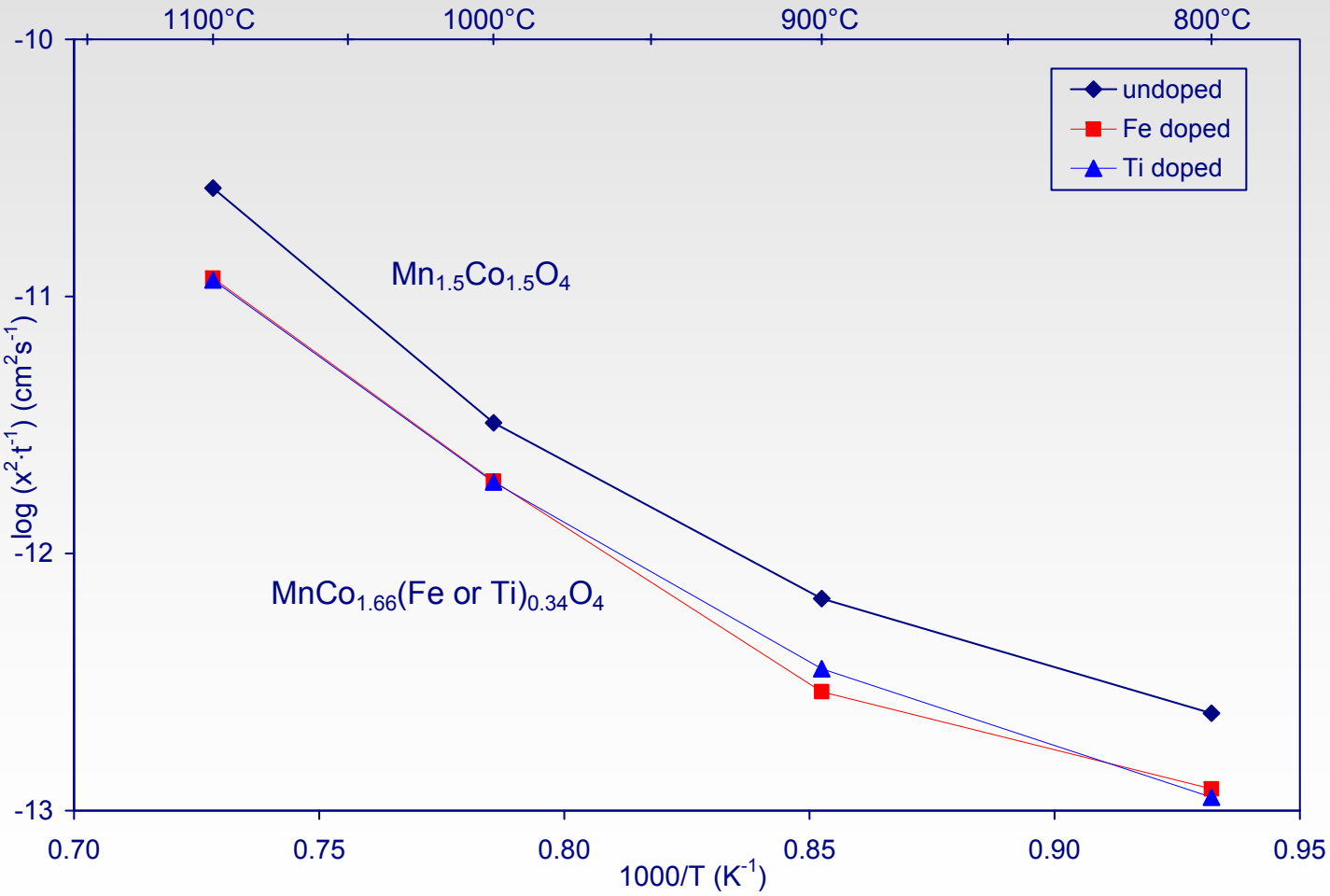
Reaction Layer Thickness – Temperature Dependence



Activations Energy:

- Decreases with decreasing temperature
- Similar for doped and undoped

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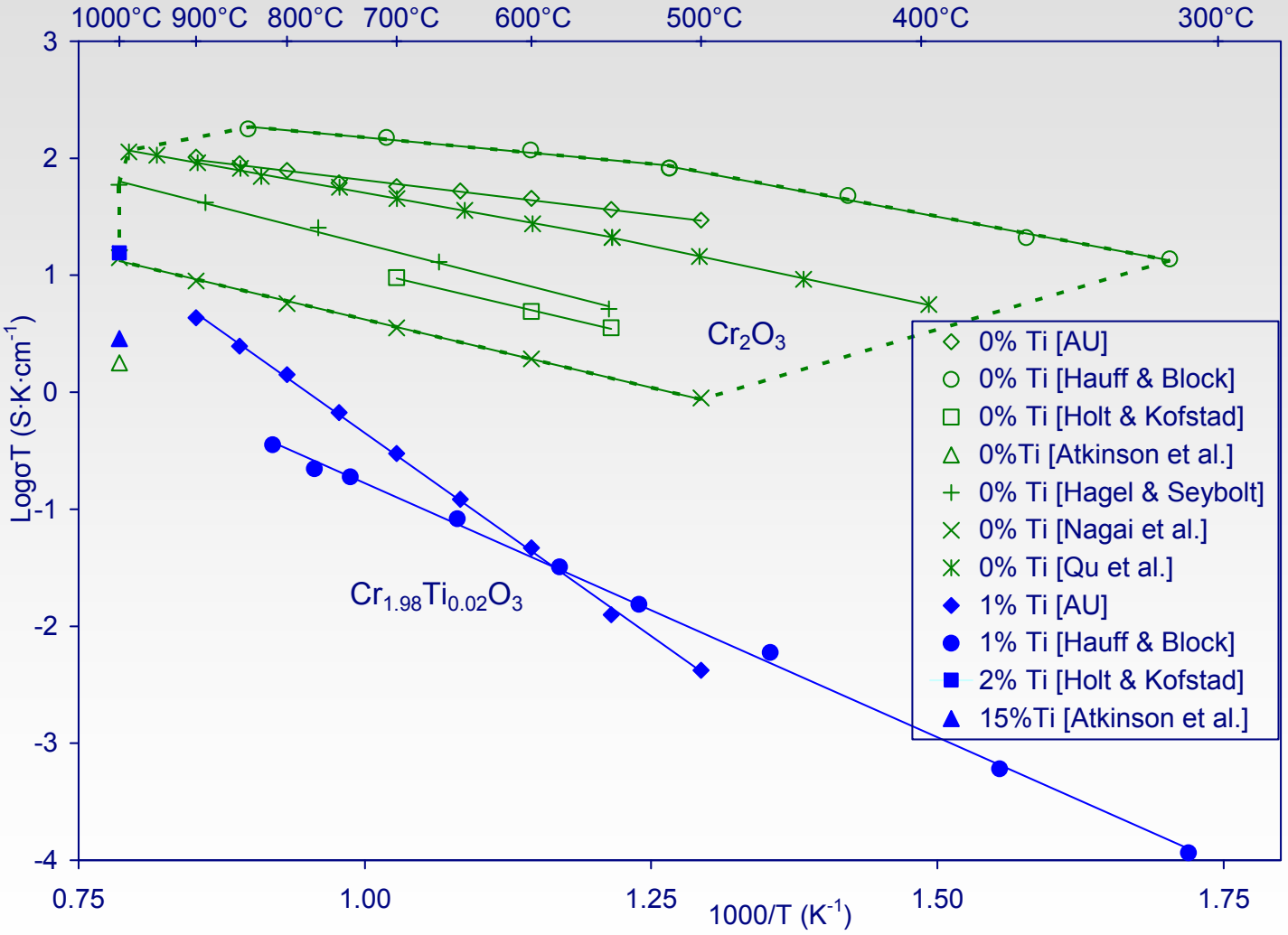
Conductivity

- Chromia scale
  - Effect of Ti doping
- Coating
  - Effect of Mn:Co
  - Effect of dopant
- Reaction layer
  - Effect of Cr content

Conductivity of Ti-doped Cr_2O_3



Ti-doping decreases conductivity in air

Increase observed at higher temperature / lower pO_2

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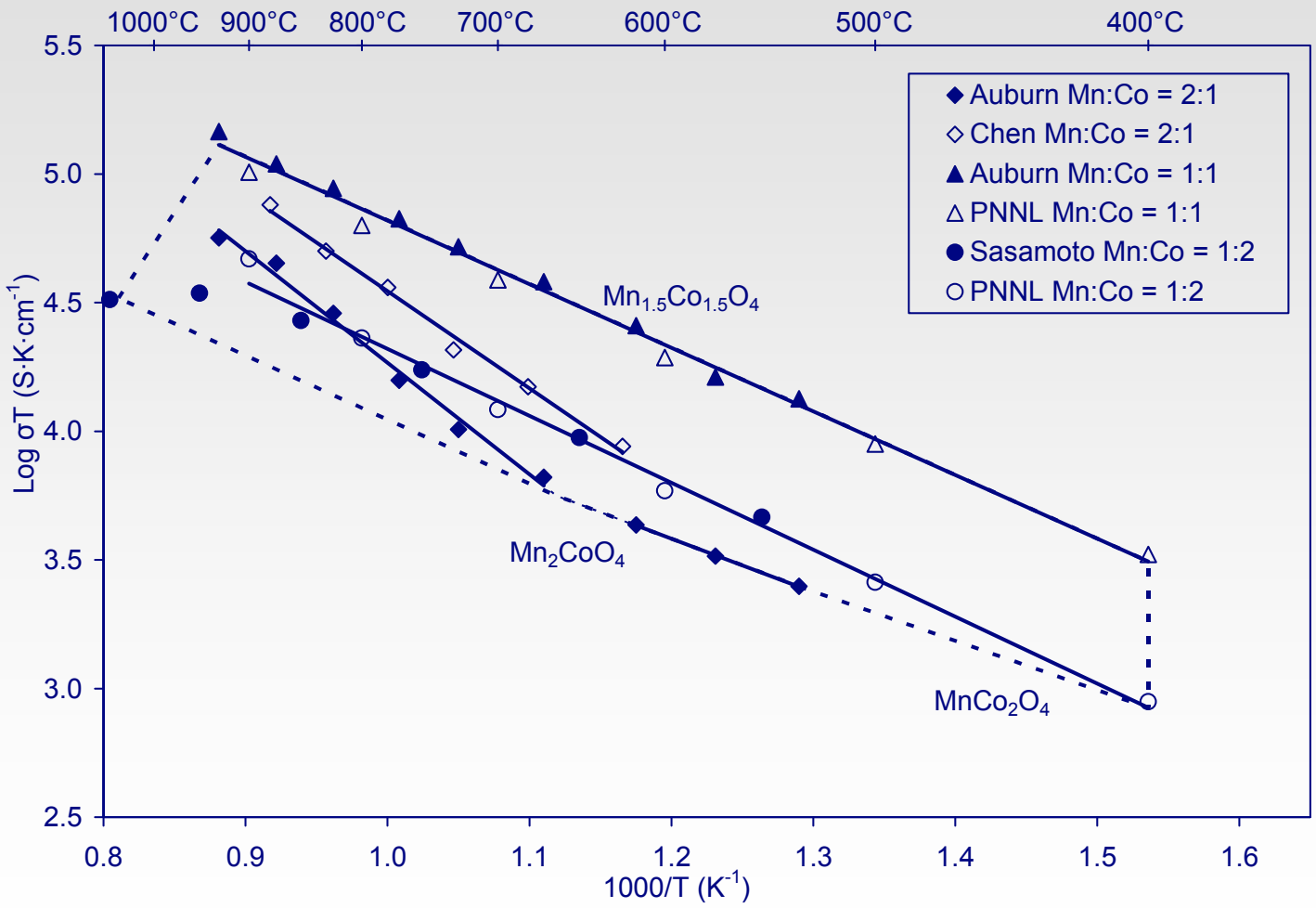
Conductivity of $(Mn,Co)_3O_4$



Mn:Co = 1:1 highest conductivity

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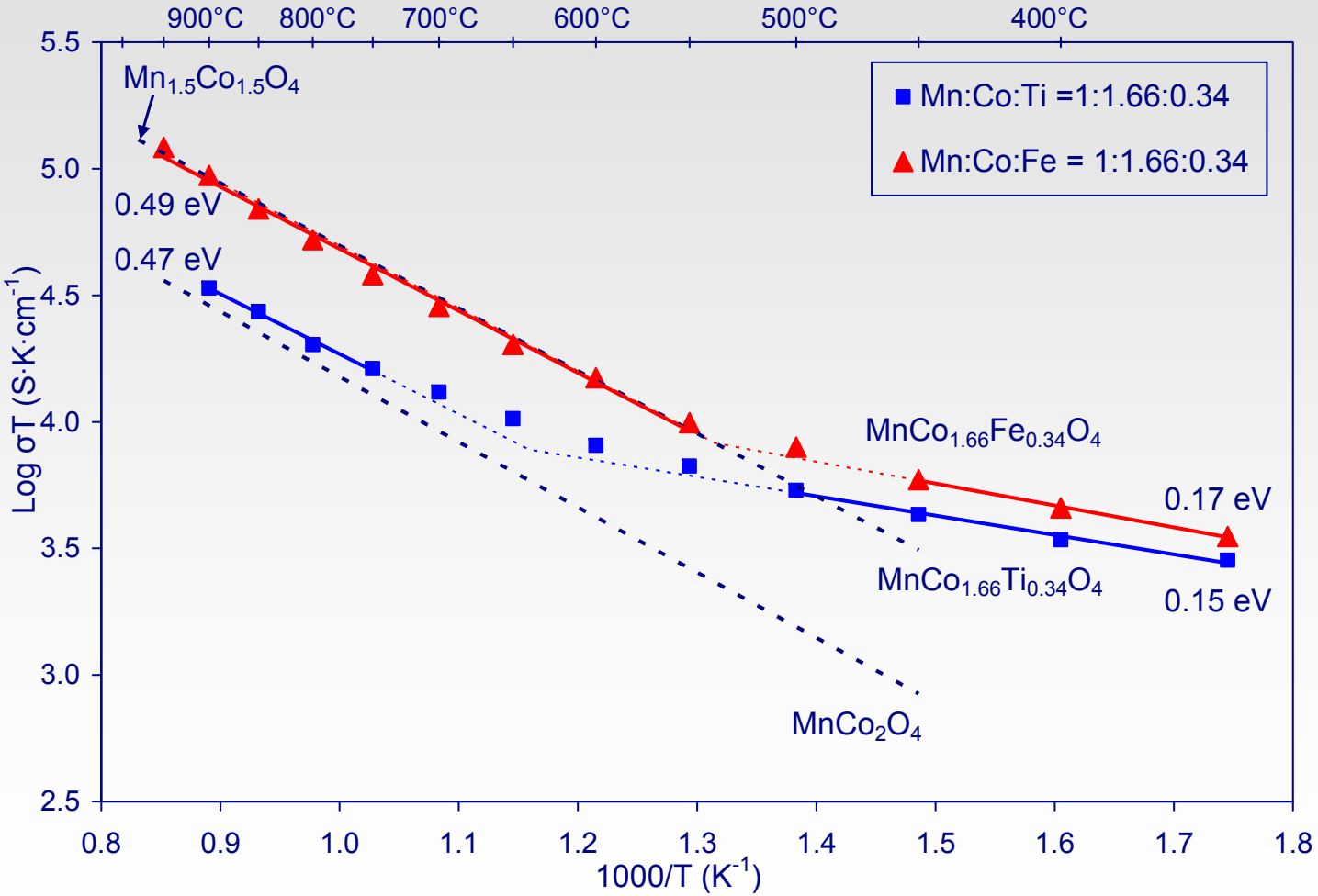
Conductivity of Fe- and Ti-doped $(Mn,Co)_3O_4$



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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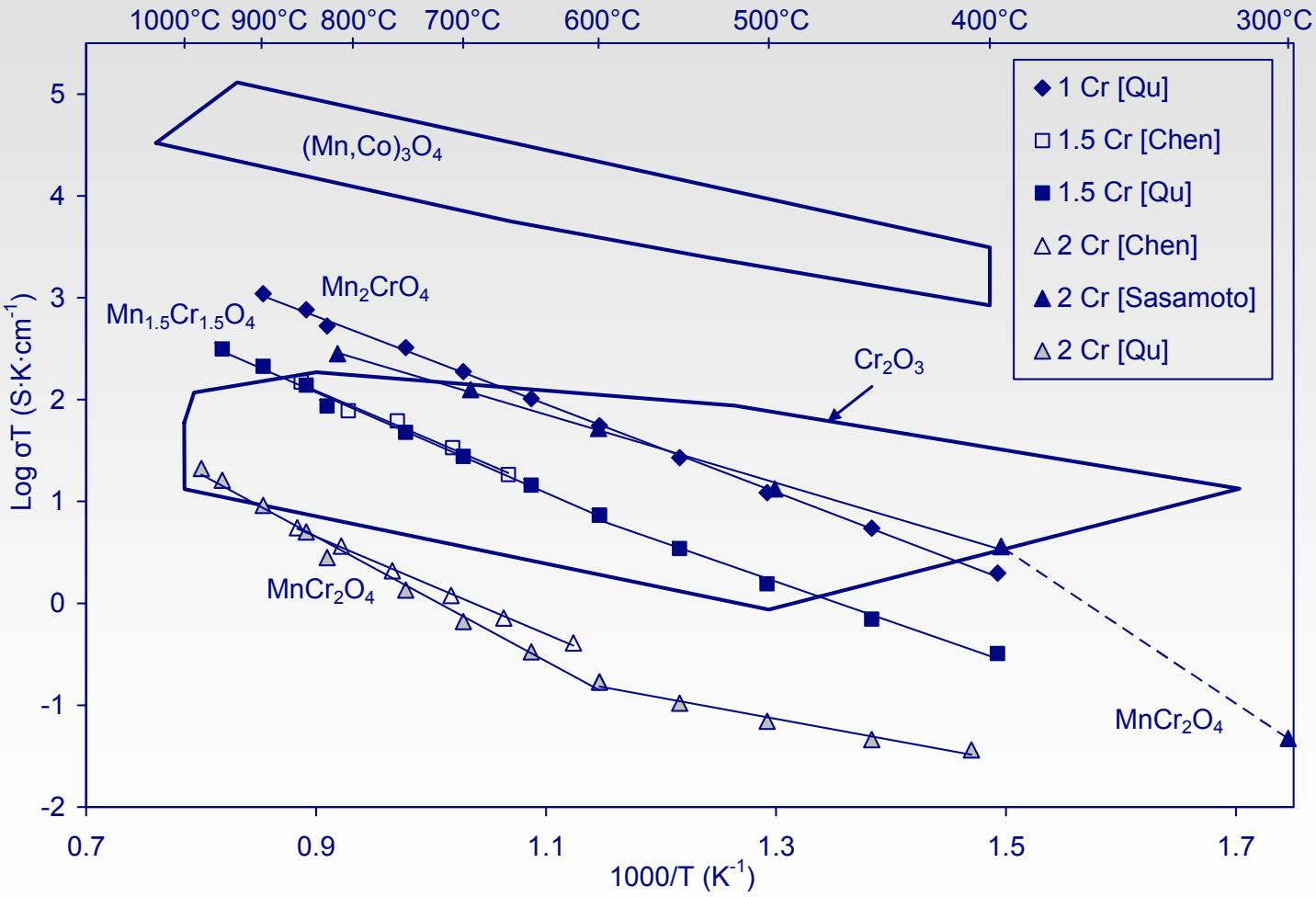
Conductivity of $(Mn,Cr)_3O_4$



Conductivity decreases with increasing Cr content

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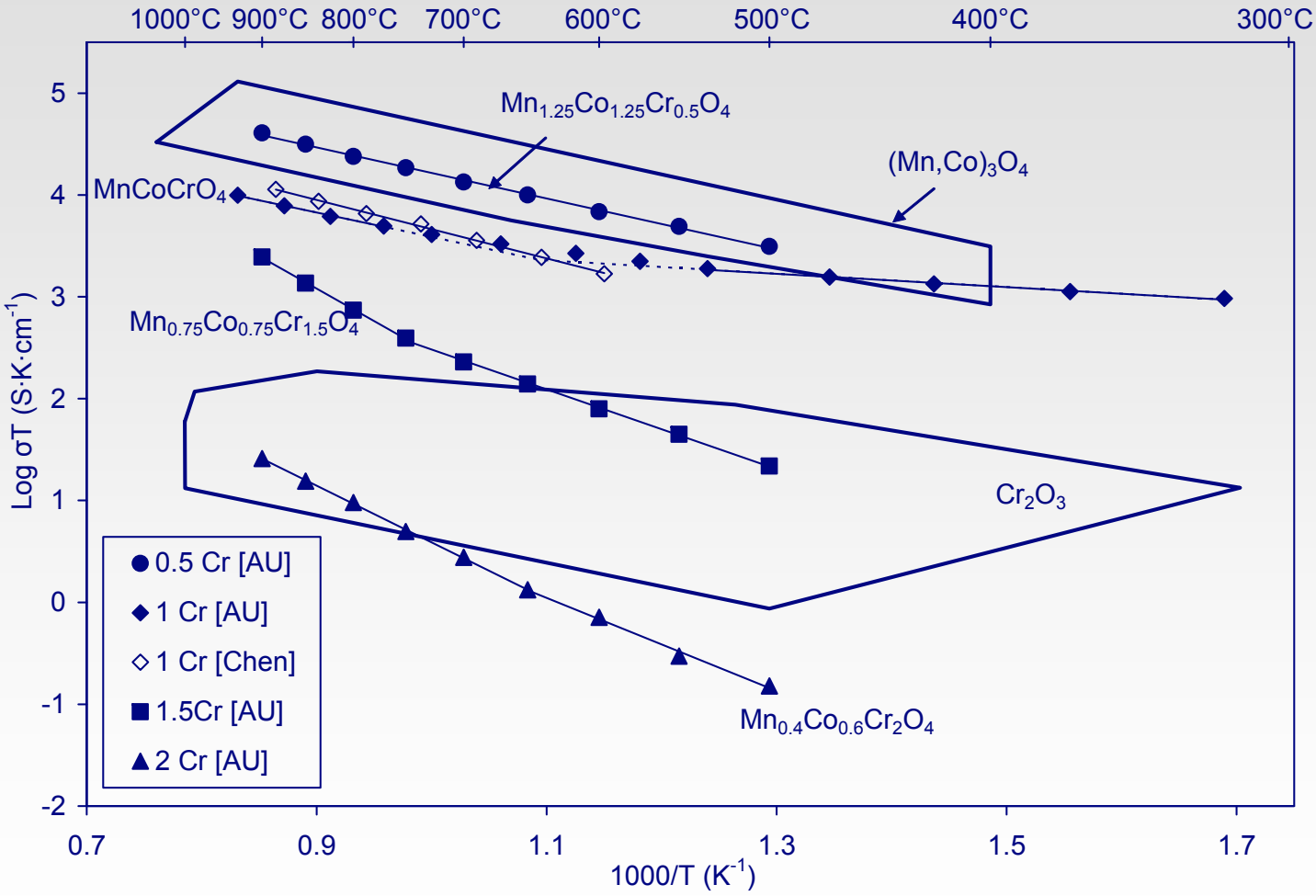
Conductivity of $(Mn,Co,Cr)_3O_4$



Conductivity decreases with increasing Cr content

Magnitude of decrease less than for $(Mn,Cr)_3O_4$

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Alloy Content

- Is minimum Cr content lower for coated alloy?
  - With coating, scale is modified by reaction with coating
  - Modified scale could be maintained with lower Cr content and/or have higher electrical resistance
  - ATI Allegheny Lundlum prepared alloys containing alloying additions in 441 with other Cr contents

Alloy	Concentration (wt%)					
	Fe	Cr	Mn	Si	Ti	Nb
H52	85.7	13.0	0.29	0.35	0.19	0.35
H53	83.7	15.1	0.30	0.35	0.20	0.35
H54	81.7	16.9	0.30	0.37	0.24	0.37
H55	80.7	17.8	0.30	0.35	0.22	0.36

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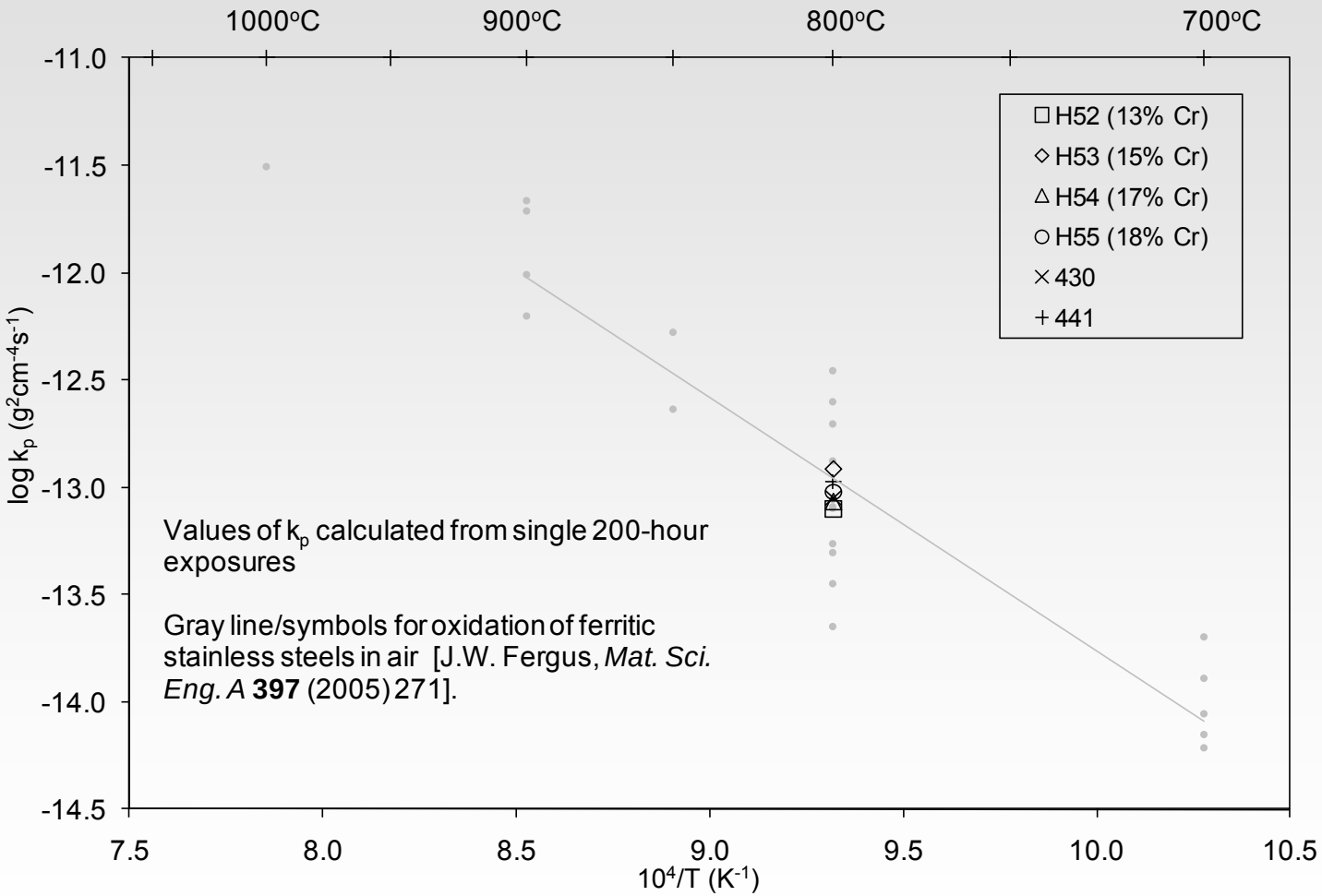
Oxidation Rates



Weight gains similar to each other and to other ferritic stainless steel alloys

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Future Plans

- Interconnect coating
  - Use coating-interconnect reaction and conductivity results to predict coating lifetime
- Interconnect alloy
  - Evaluate oxidation behavior of coated and uncoated 441 Cr variant alloys

Conclusions

- Low temperature mechanism similar with increasing dominance of Co/Mn diffusion
- Fe/Ti additions decrease reaction rates while maintaining similar electrical conductivities
- Ti decreases the electrical conductivity of chromia in air at SOFC operating temperatures
- Conductivity of spinel decreases with increasing Cr content

Interconnect Alloy-Coating Interaction