An Integrated Computational Approach to Predicting Protective Oxide Scale Formation on Alloys in FE-Relevant Environments

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2014 NETL Crosscutting Research Review Meeting
Pittsburgh, PA

May 21, 2014

Acknowledgement and Disclaimer

This work was funded by the Cross-Cutting Technologies Program at NETL and managed by Susan Maley (Technology Manager) and Charles Miller (Technical Monitor). Executed through NETL ORD's IPT FWP.

Computational Materials: Integrated Materials Initiative

Develop multi-scale computational simulations with targeted validation experiments to reliably predict the formation of protective scales in conditions of relevance to advanced FE systems.

Ni-Fe-Al; O_2, H_2, H_2O, CO_2

Computation

- *Z-K Liu (PSU), A. van Duin (PSU), J. Kitchin (CMU), G.F. Wang (Pitt), M. Gao (URS), D. Tafen (URS), D. Alfonso (DOE), Y. Wen (DOE)*

Experiment

- *B. Gleeson (Pitt), A. Gellman (CMU), D. Alman (DOE)*

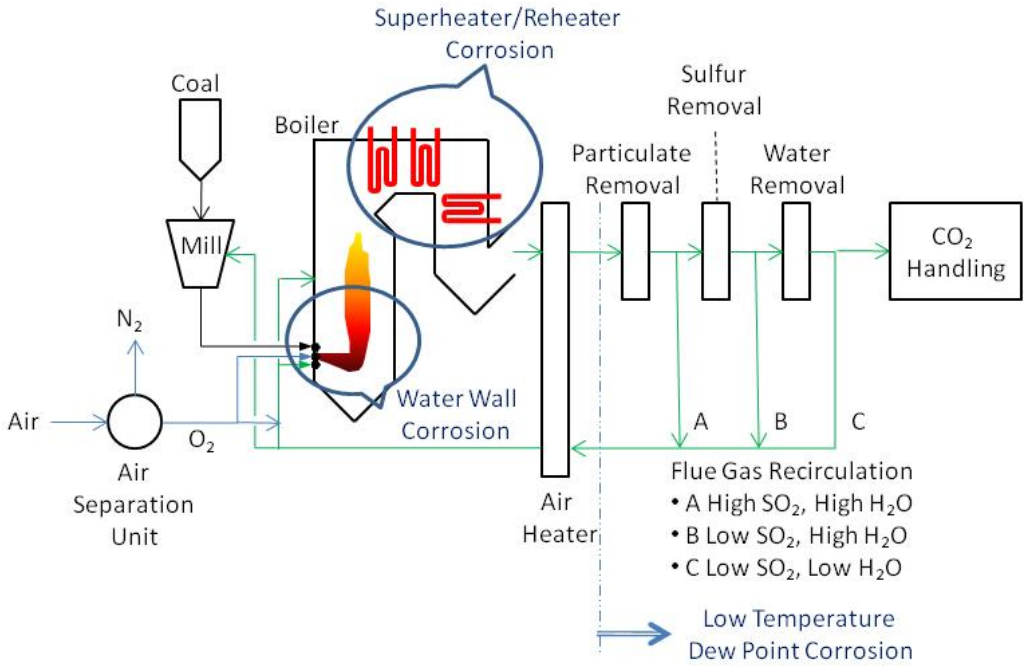
Atomic and System Level Simulations

- *Phase Diagrams; Lattice Parameters; Adsorption and Solubility Parameters; Diffusion Coefficients.*

Micro-kinetic Modeling

- *Critical Al content for Al_2O_3 formation in Ni-Fe-Al alloy in different environments – utilizing atomic simulations.*

NETL-RUA: Integrated Materials Initiative



URS

PENNSTATE.

Carnegie Mellon University

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Advanced FE Energy Systems: A-USC, Oxy-Comb, CLC, Comb Turbines

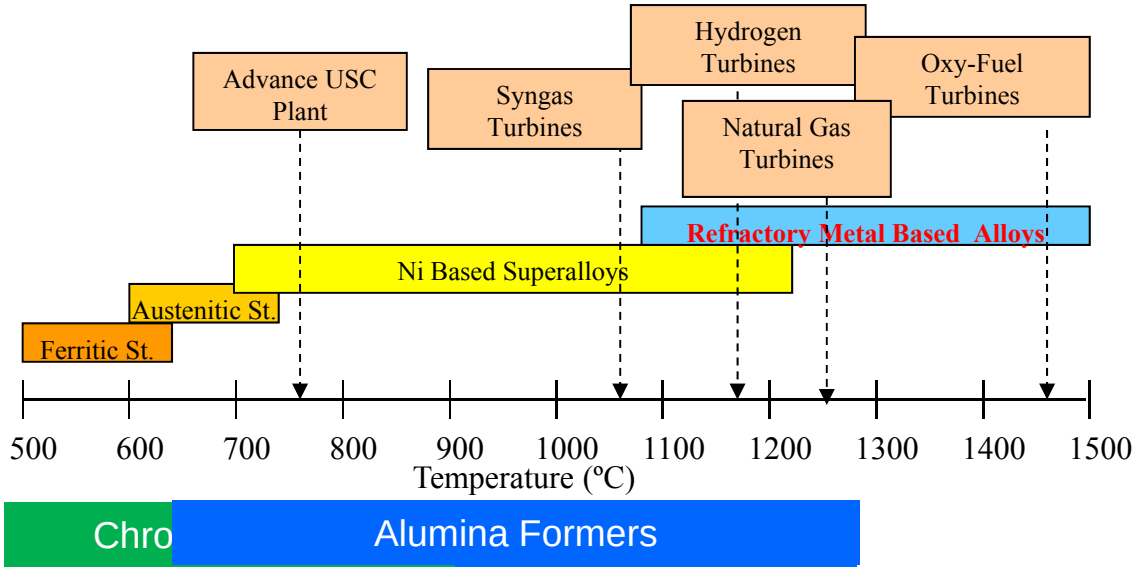
- Extreme environments (corrosive,T,P)
- Components need to last 10,000's to 100,000's hours

Need for reliable and fast methods for predicting materials performance to accelerate materials design and/or identification – accelerate deployment and enable advanced technologies.

Impact of Environment on Alloy Oxidation

Engineered alloys (nickel-base superalloys and stainless steels) rely on formation of Al_2O_3 or Cr_2O_3 oxide scales to protect the alloy from oxidation and corrosion.

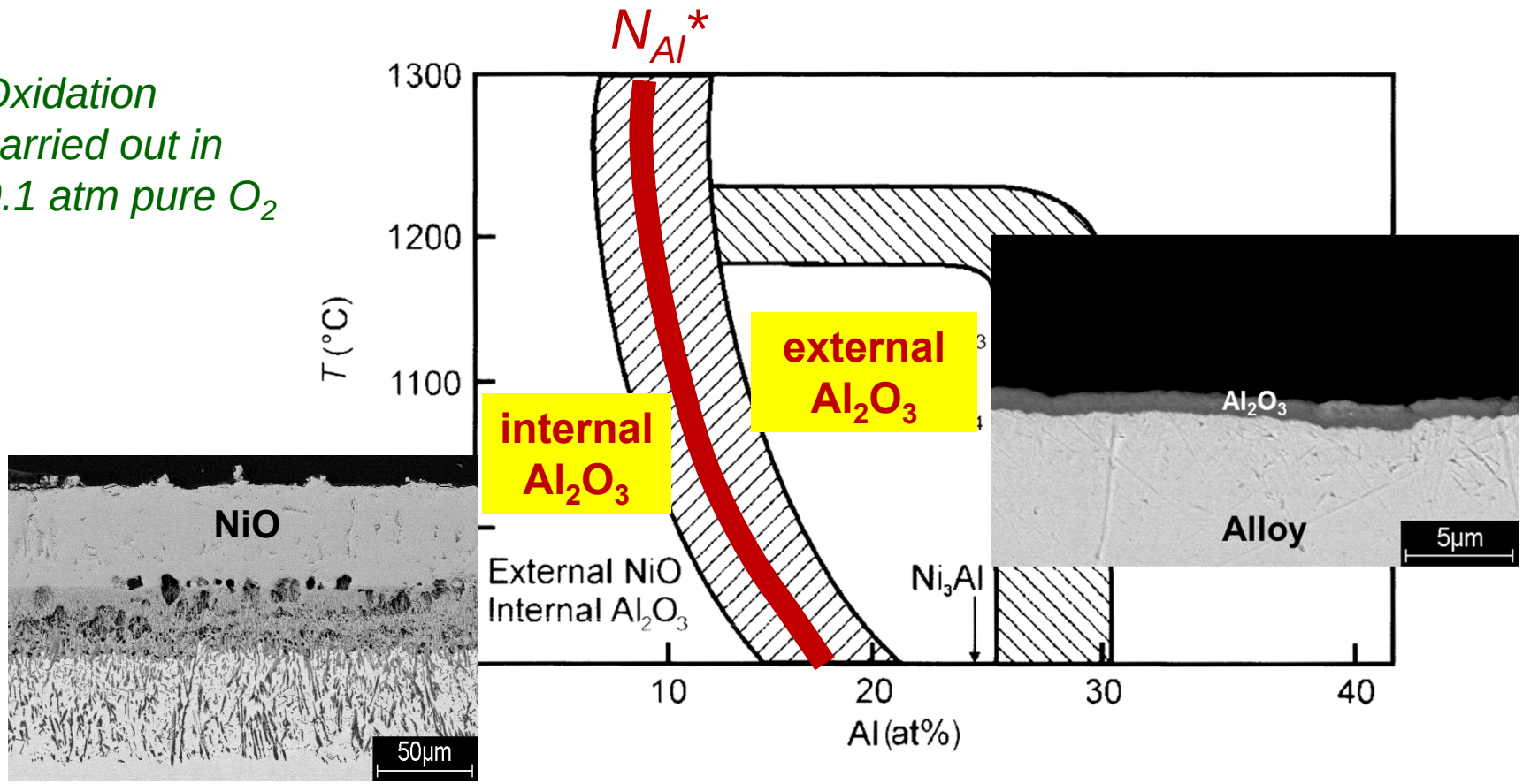
- Aggressive environments impact stable oxide scale formation
  (e.g., steam more aggressive than air/oxygen) .
- Need to predict alloy compositions to form stable oxide scales.



Accounting for steam

Alumina Scale Formation on Ni-Al Alloys

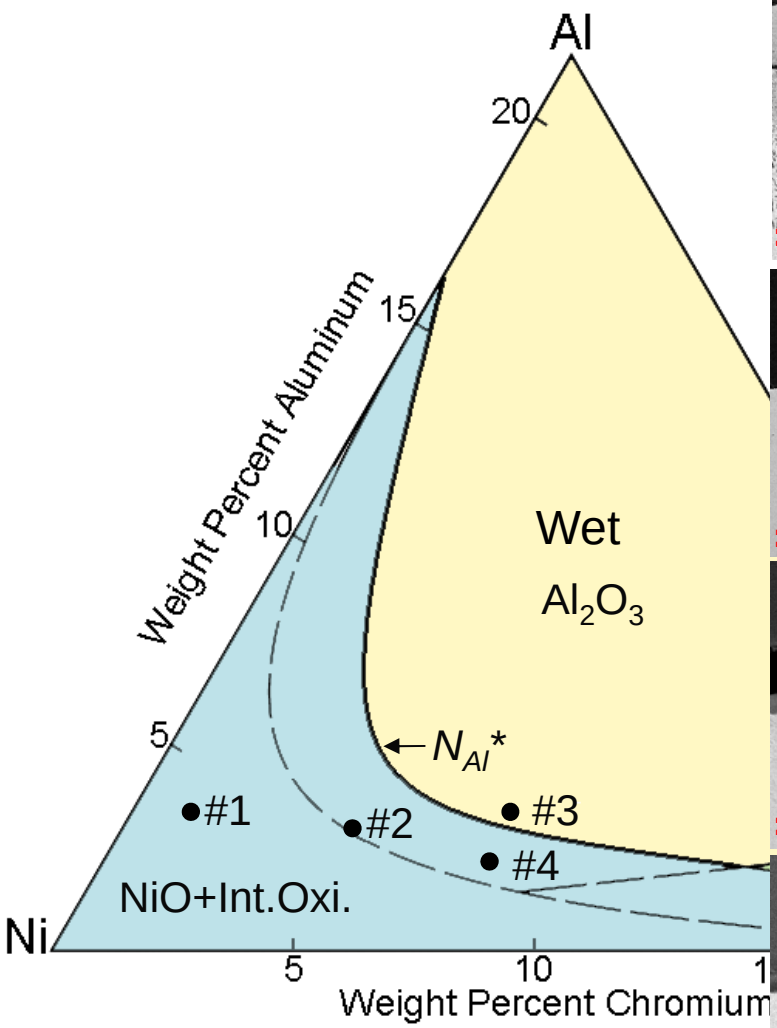
Oxidation carried out in 0.1 atm pure O_2



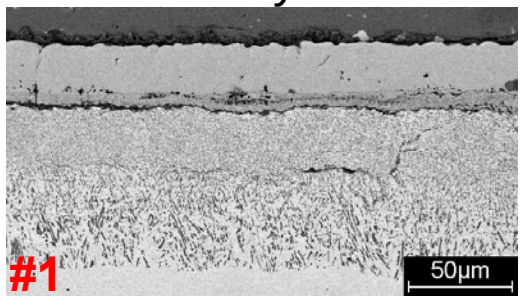
F.S. Pettit, “Oxidation mechanisms for Ni-Al Alloys at temperatures between 900 and 1300°C,” *AIME Met. Soc. Trans*., **239** (1967) 1296.

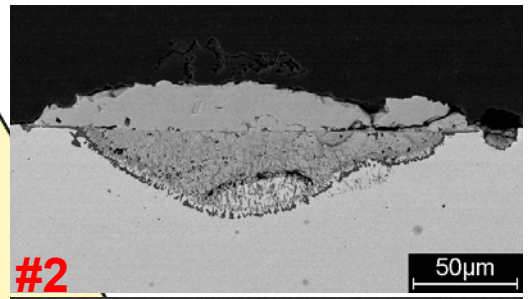
Promoting Al_2O_3-Scale Formation by Cr Addition

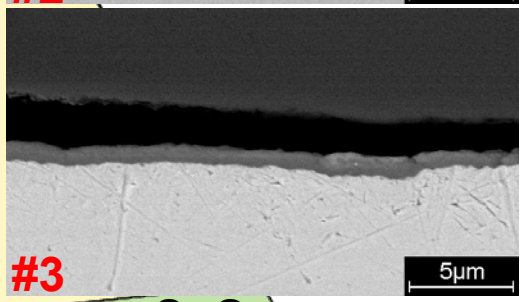
Giggins and Pettit established the following oxidation map for rolled Ni-Cr-Al alloys in 0.1atm O_2 at 1000°C.*

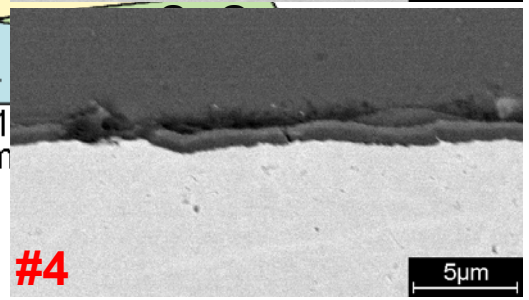


Dry

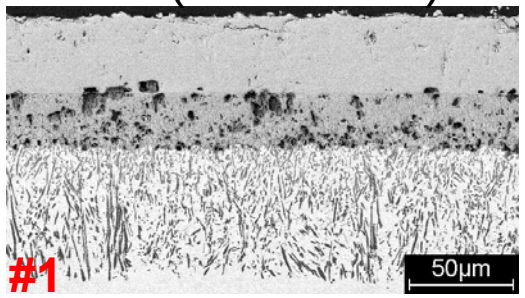


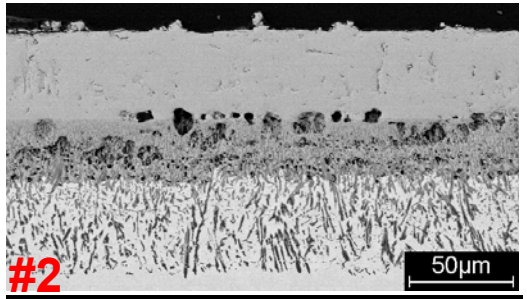


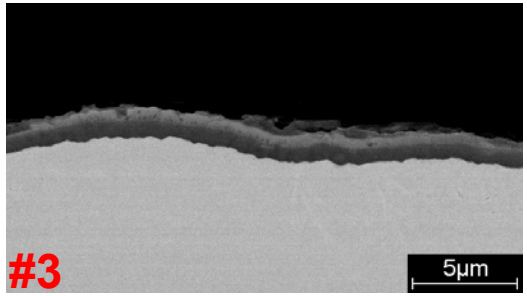


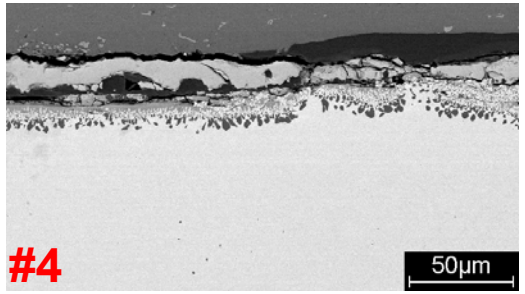


Wet (30% steam)









Limiting Theoretical Equation for Single-Phase Binary Alloys

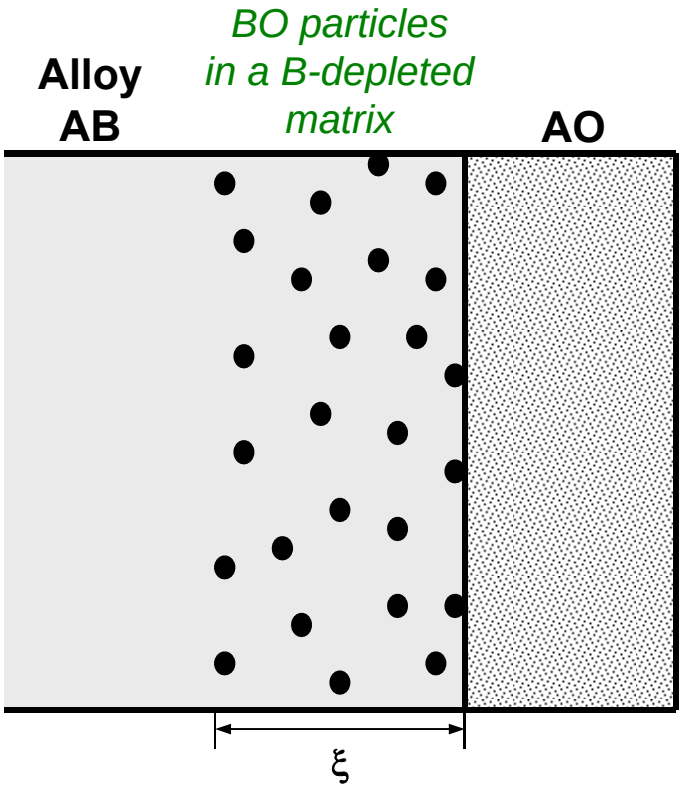
Critical Concentration of B for the Transition from Internal to External BO_v Formation

$$N_{B*}^{o} \geq \left[f^{*} \left(\frac{V_m}{V_{ox}} \right) \pi \frac{N_o^s D_o}{2\nu D_B} \right]^{1/2}$$

$N_o^s D_o$ = oxygen permeability into the alloy

D_B = diffusivity of B in the alloy

f^* = critical volume fraction of internal BO_v – *not rigorously defined!*



The validity of this model is intuitively correct, but it has not been adequately checked due to limited availability of accurate input data.

Current modeling can provide the input data

Prediction of N_{Al}^* for Ni-Al System at "High" P_{O_2}

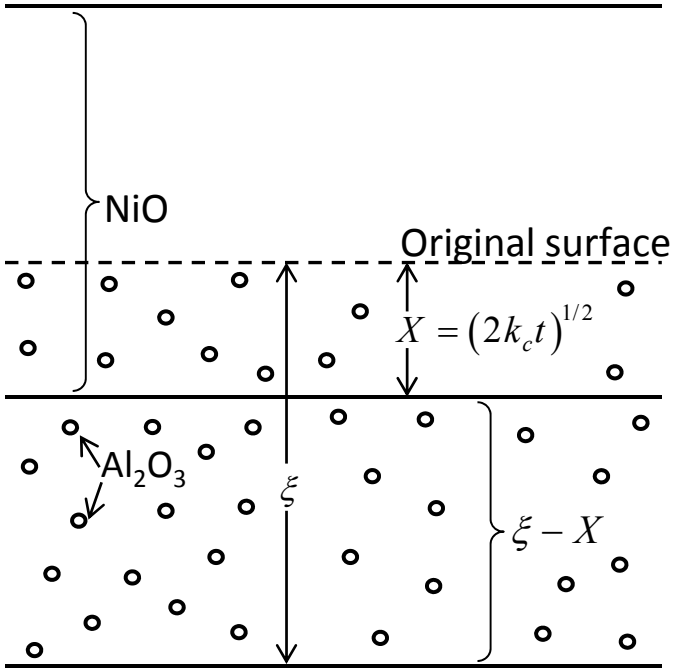
From theoretical analysis[1,2] N_{Al}^* for the transition from internal to external $AlO_{1.5}$ formation is:

$$N_{Al}^* = \frac{1}{\rho} F\left(\gamma\varphi^{1/2}\right) f_v^*$$

where $\rho = V_m^{AlO_{1.5}} / V_m^{NiAl}$, $\varphi = \mathrm{D_o} / \mathrm{D_{Al}}$, $F(r) = \pi^{1/2} r \exp(r^2) erfc(r)$, f_v^*: critical volume fraction of $AlO_{1.5}$ in the Ni-Al alloy.

To determine γ :

(1) Experimentally: $\xi = 2\gamma\left(D_O t\right)^{1/2}$



(2) Numerically

$$u = \left[k_c / \left(2D_O\right)\right]^{1/2}$$

$$\frac{N_O^s}{\nu N_{Al}^0} = \frac{erf\left(\gamma\right) - erf\left(u\right)}{erf\left(\gamma\right)} \frac{G\left(\gamma\right)}{F\left(\gamma\varphi^{1/2}\right)}$$

N_o^S = solubility of oxygen on the scale/alloy interface
N_{Al}^0 = mole fraction of Al in the bulk alloy
ν = 1.98 (effective stoichiometry factor[3])
$G(r) = \pi^{1/2} r \exp(r^2) erf\,(r)$

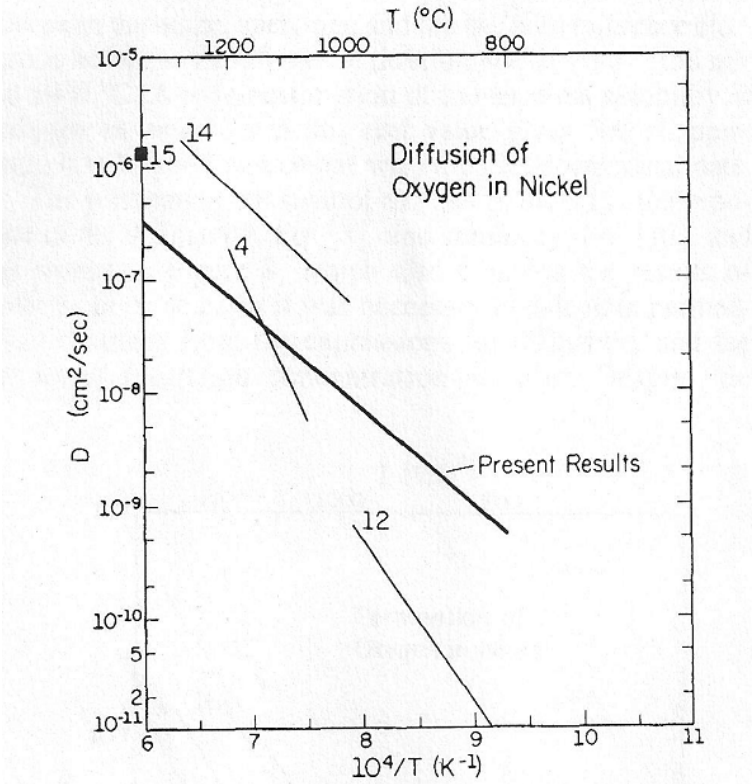
1 C. Wagner, Z.Elektrochem. 63, 772 (1959), F. Maak, Z. Metallkde. 52, 545 (1961)
2 F. Gesmundo and F. Viani, Oxid. Met. 25, 269 (1986), 3

Example of Uncertainties: D_o in Ni-Al system

Table I. Measured Diffusion Coefficients for Oxygen in Nickel*

Reference (Method)	D_0 (obs) (cm^2/sec)	Q (kJ/mole)	Temp. Range (°C)	D_0 (calc) (cm^2/sec)	$\frac{D_0 \text{ (calc)}}{D_0 \text{ (obs)}}$
Alcock and Brown[4] (gravimetric)	8.93×10^{7}	414	1050 to 1200	16.	1.2×10^{-7}
Zolobov and Malev[12] (desorption)	12.1	241	350 to 1000	0.72	6.0×10^{-2}
Kerr[14] (electrochem.)	2.06	182	1000 to 1300	0.24	0.12
Present results					
potentiometric	4.9×10^{-2}	164	850 to 1400	0.16	3.3
potentiostatic	1.7×10^{-5}	90	800 to 1000	4.7×10^{-2}	2.8×10^{3}

*Ramanarayanan and Rapp[15] reported a value of 1.32×10^{-6} cm^2/sec at 1393 °C.



Reports of D_o vary significantly … by up to orders of magnitude.

J. Park and C.J. Altstetter, *Metall. Trans. A*, Vol.18, p43, 1987

Important Factors to Predicting Reaction Behavior

Critical Concentration of B for the Transition from Internal to External BO_v Formation

$$N_{Al}^{*} = \frac{1}{\rho} F\left(\gamma\varphi^{1/2}\right) f_v^{*}$$

$$\frac{N_O^s}{vN_{Al}^0} = \frac{erf(\gamma) - erf(u)}{erf(\gamma)} \frac{G(\gamma)}{F\left(\gamma\varphi^{1/2}\right)}$$

N_O^S = oxygen solubility on the surface

D_O = diffusivity of oxygen

D_{Al} = diffusivity of B in the alloy

k_c = metal consumption rate

f_v^* = critical volume fraction of internal BO_v

Table of factors to determine the N_{Al}^*

Alloy	T (°C)	N_O^S	D_O (cm²/s)	D_{Al} (cm²/s)	k_c (cm²/s)	f_v^*	N_{Al}^* (Predict)	N_{Al}^* (Exp)
Ni-Al								

These are the input parameters we need from computation.

Oxygen Diffusivity in fcc Ni: *Journal Cover*

Featured article: JAP, 115, 043501 (2014)

JOURNAL OF APPLIED PHYSICS **115**, 043501 (2014)

First-principles studies on vacancy-modified interstitial diffusion mechanism of oxygen in nickel, associated with large-scale atomic simulation techniques

H. Z. Fang,[1,2] S. L. Shang,[1,2] Y. Wang,[1,2] Z. K. Liu,[1,2] D. Alfonso,[1,3] D. E. Alman,[1,3] Y. K. Shin,[1,4] C. Y. Zou,[1,4] A. C. T. van Duin,[1,4] Y. K. Lei,[1,5] and G. F. Wang[1,5]

[1]*National Energy Technology Laboratory Regional University Alliance, U.S. Department of Energy, Pittsburgh, Pennsylvania 15236, USA*
[2]*Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, USA*
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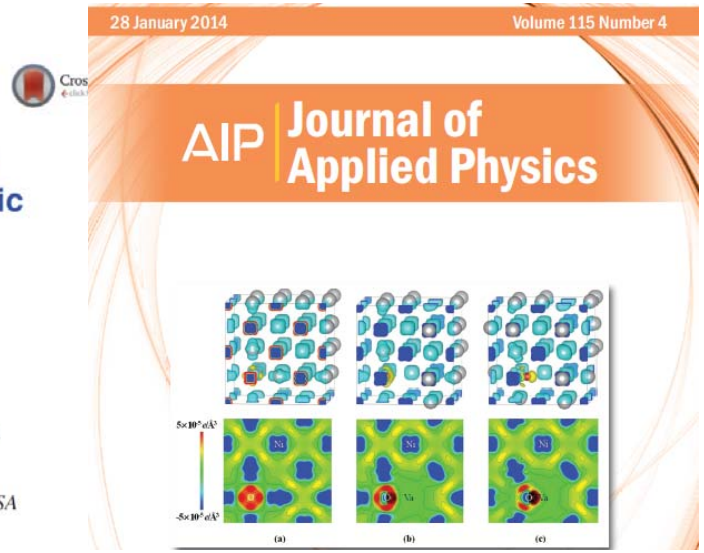
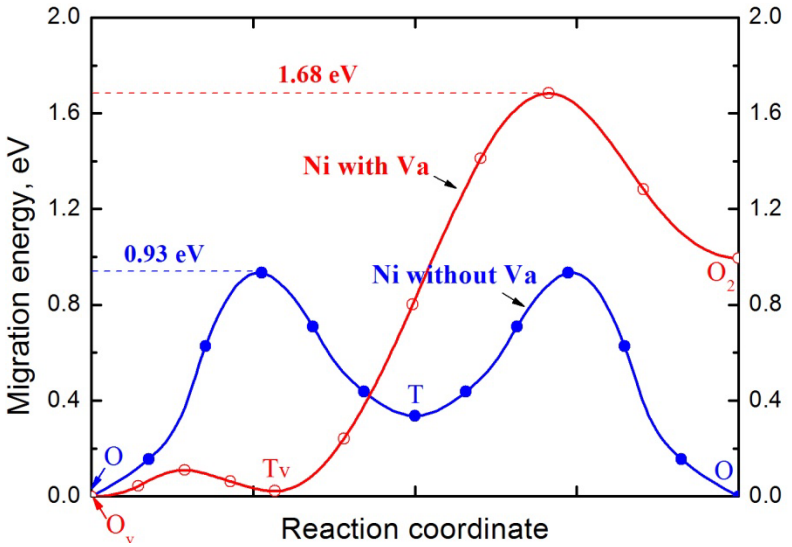
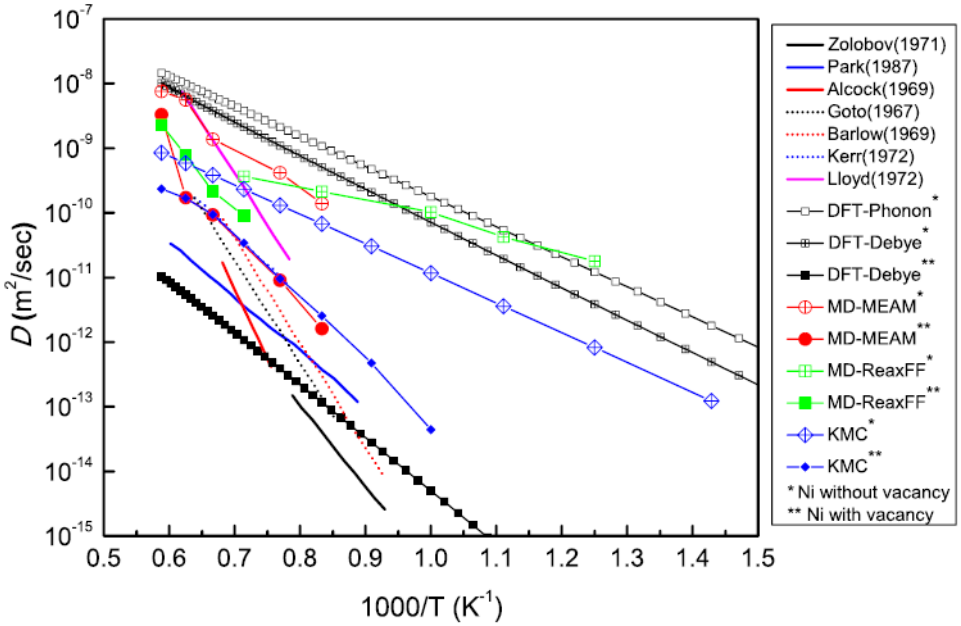
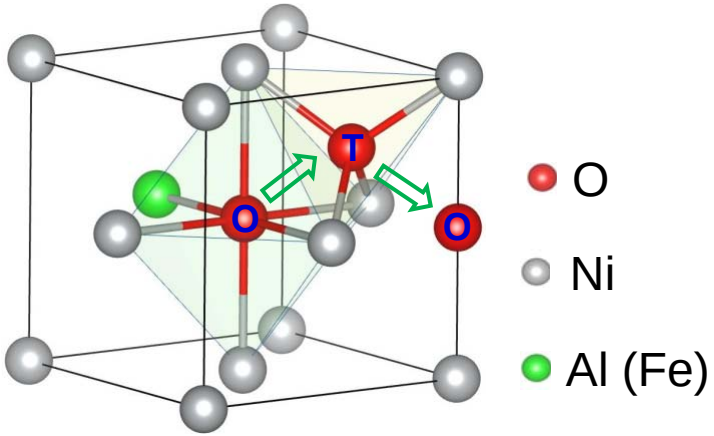
[5]*Department of Mechanical Engineering and Materials Science, University of Pittsburgh, Pennsylvania 15261, USA*

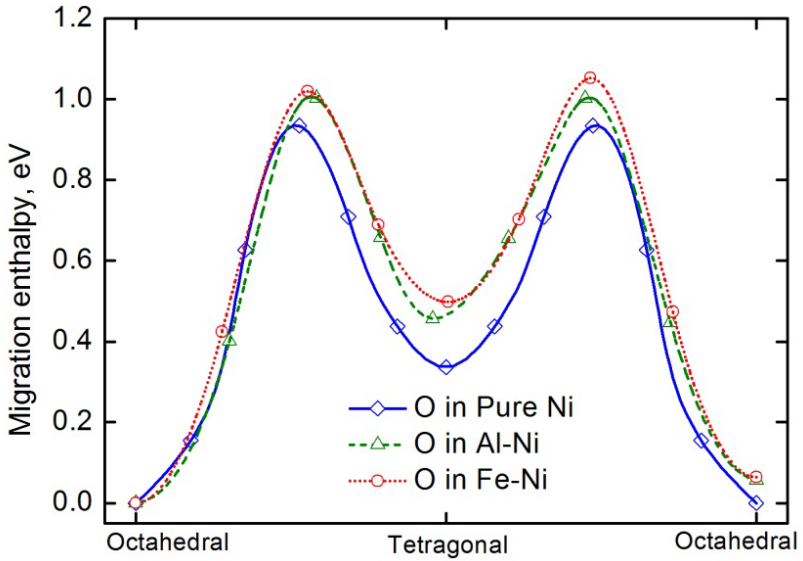


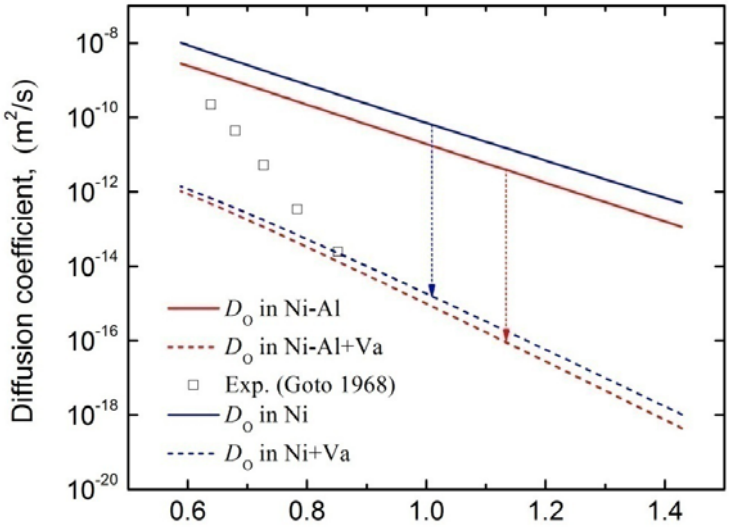


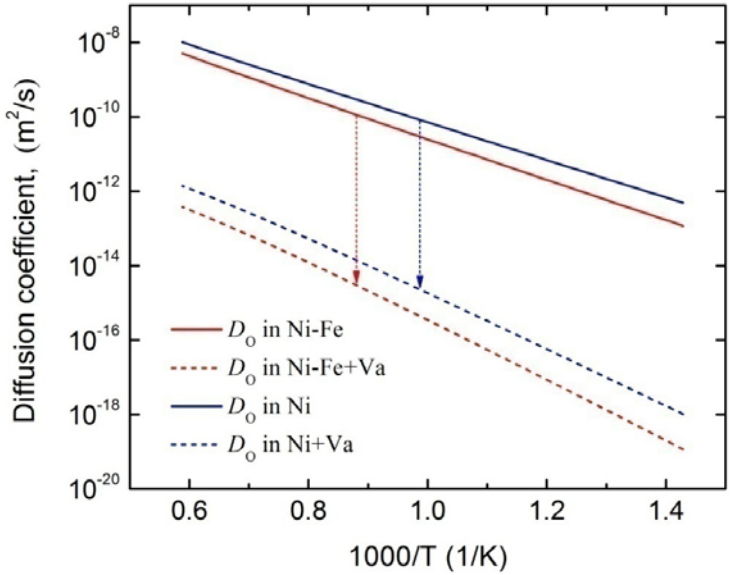


Oxygen in Ni-Al / Ni-Fe dilute solutions





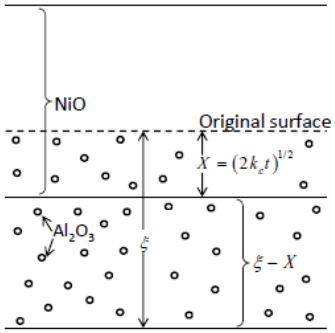


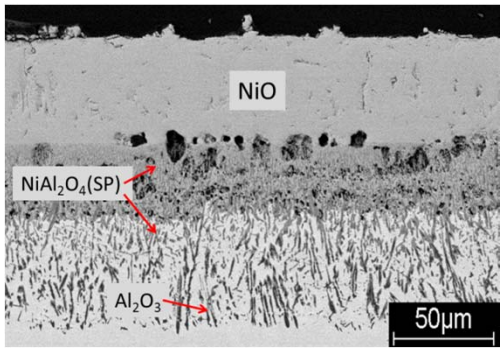


Addition of Al or Fe slightly decreases the D_O, but the effect of vacancy is still significant.

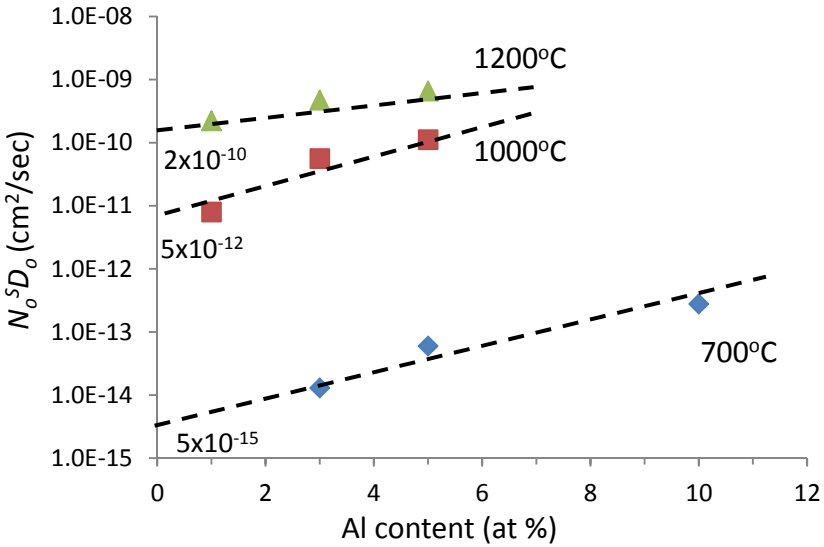
Oxygen Permeability in Nickel

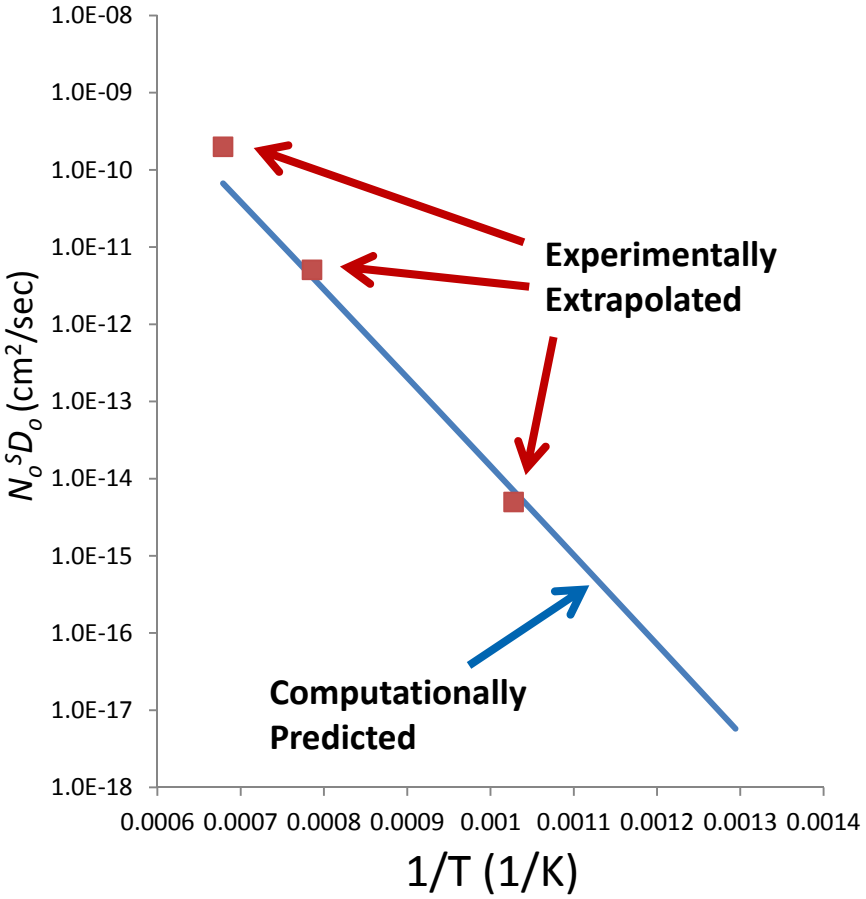
- Experiments were conducted to measure oxygen permeability based on the extent of internal oxidation.
- Computationally predicted permeabilities of O in Ni are in reasonable with experiments.





Ni-3at%Al 1000°C 98h





Molecular Dynamic Simulations to Determine Al Diffusivity in Ni

Concentration of Al:

$$0.025\ at.\%$$

for both MD and KMC simulations.

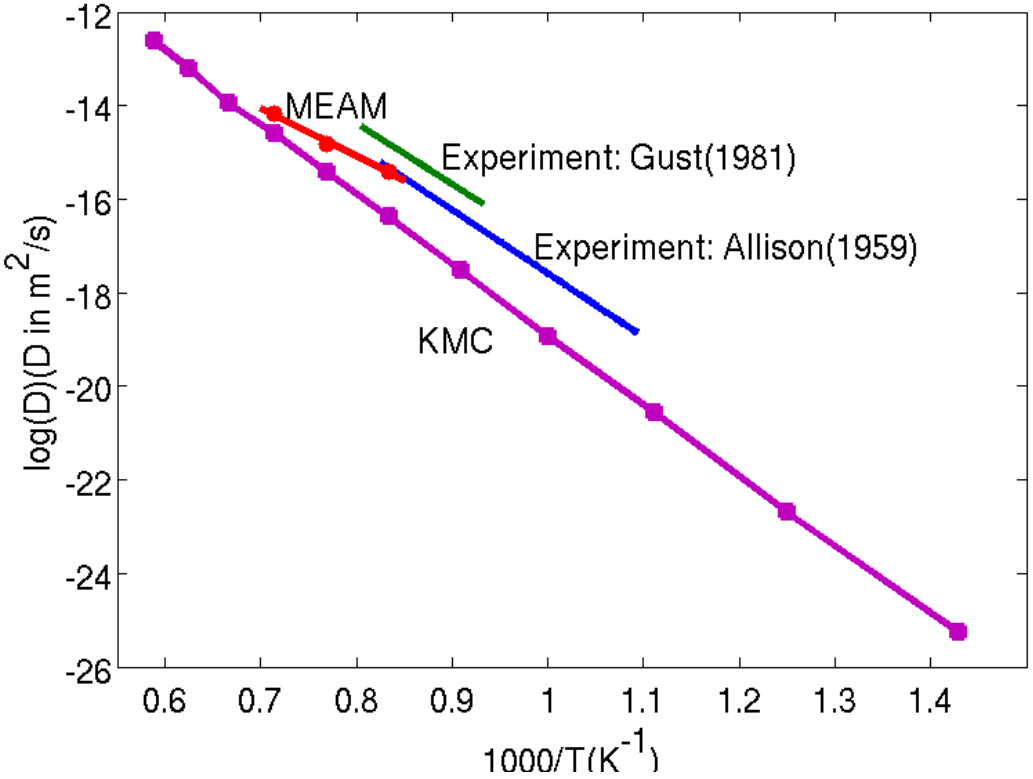
Activation energy from experiments[1,2]:

$$Q = 2.60\ eV$$

Fitted activation energy:

MEAM: $Q = 2.04\ eV$

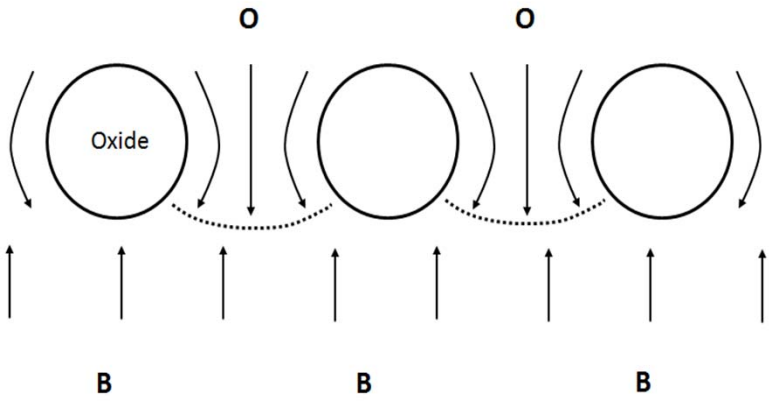
KMC: $Q = 2.98\ eV$

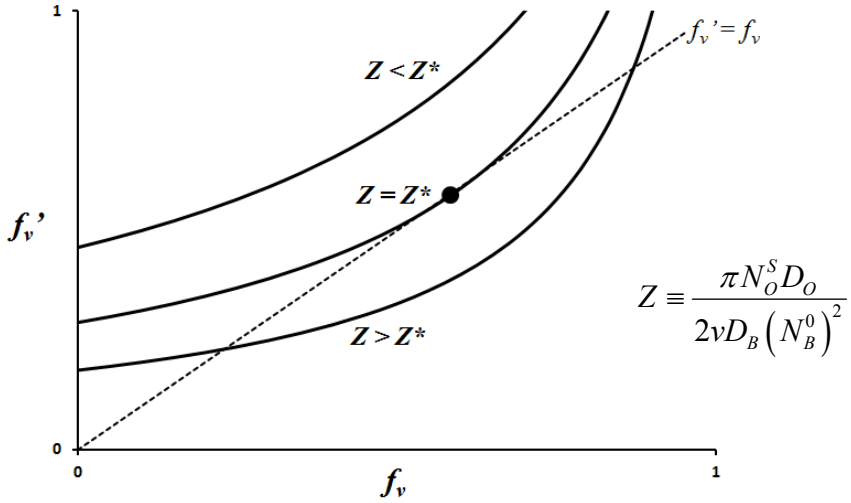


[1] W. Gust, *et al*, Phys. Stat. Sol. A, 64, 187-194 (1981).

[2] H. W. Allison, *et al*, J. Appl. Phys., 30, 1419 (1959).

Diffusion Analysis to Predict *f**





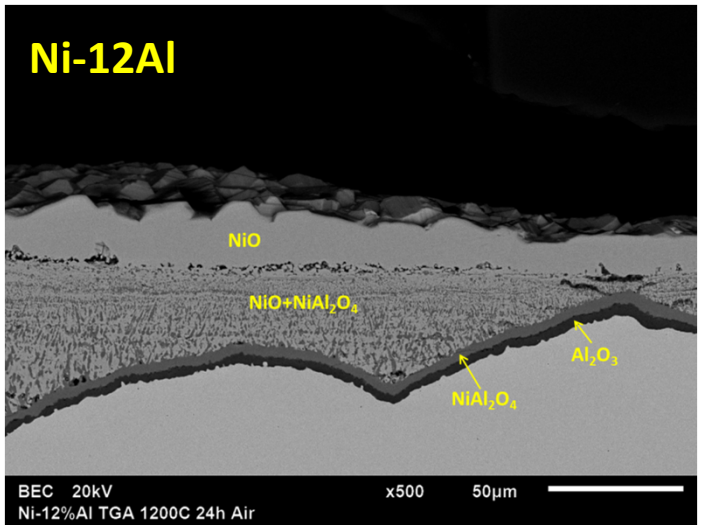
From the analysis, it is found

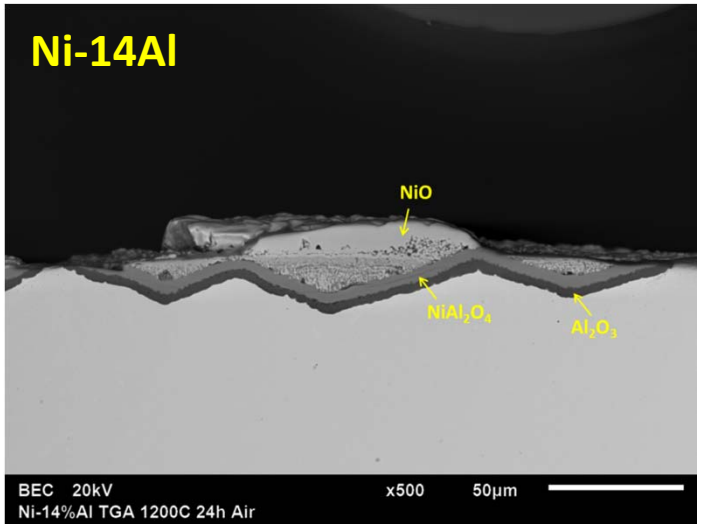
$$f_v^* = \frac{2\sqrt{V_m^{\,oxide} / V_m^{\,alloy}}}{\sqrt{6} + 2\sqrt{V_m^{\,oxide} / V_m^{\,alloy}}}$$

W. Zhang and B. Gleeson, *Oxidation of Metals*, to be published

Comparing N_{Al}^* in Ni-Al at 1200°C in Air

From experiment:





N_{Al}^* is slightly higher than 14%

From simulation and theory:

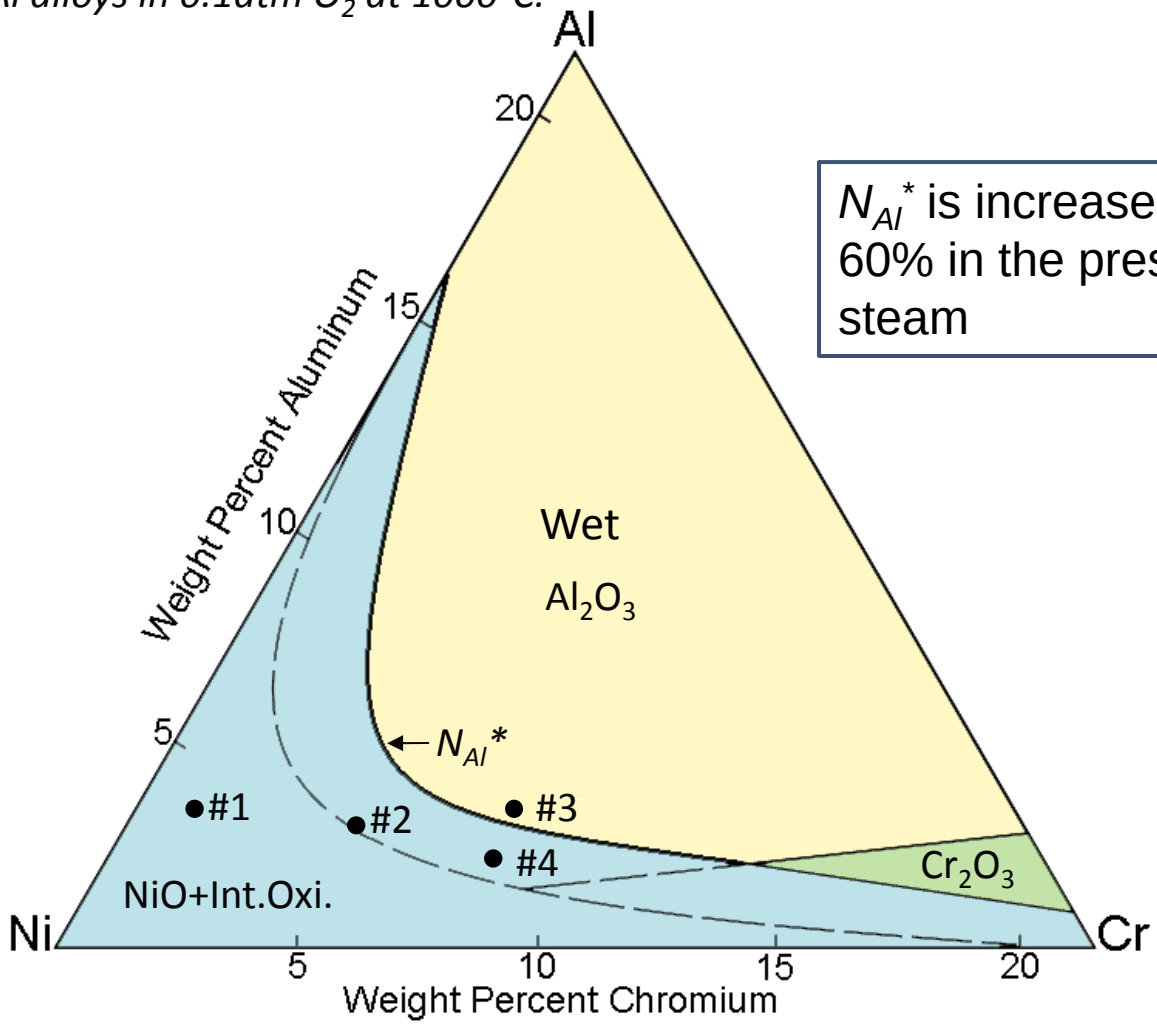
$$N_{Al}^* = \frac{V_m^{NiAl}}{V_m^{AlO_{1.5}}} F\left(\gamma\varphi^{1/2}\right) f_v^*$$

Alloy	T (°C)	N_O^S	D_O (cm²/s)	D_{Al} (cm²/s)	k_c (cm²/s)	f_v^*	N_{Al}^* (Predict)	N_{Al}^* (Exp)
Ni-Al	1200	9×10^{-4}	7×10^{-8}	$\sim1\times10^{-10}$	4×10^{-11}	0.30 [1]	0.10	>0.14
	1200	9×10^{-4}	7×10^{-8}	$\sim1\times10^{-10}$	4×10^{-11}	0.54 [2]	0.18	

[1] Rapp (1961) for Ag-In; [2] New prediction method developed by Zhao and Gleeson in this project

Steam Effect on Al_2O_3-Scale Formation

Giggins and Pettit established the following oxidation map for rolled Ni-Cr-Al alloys in 0.1atm O_2 at 1000°C.*



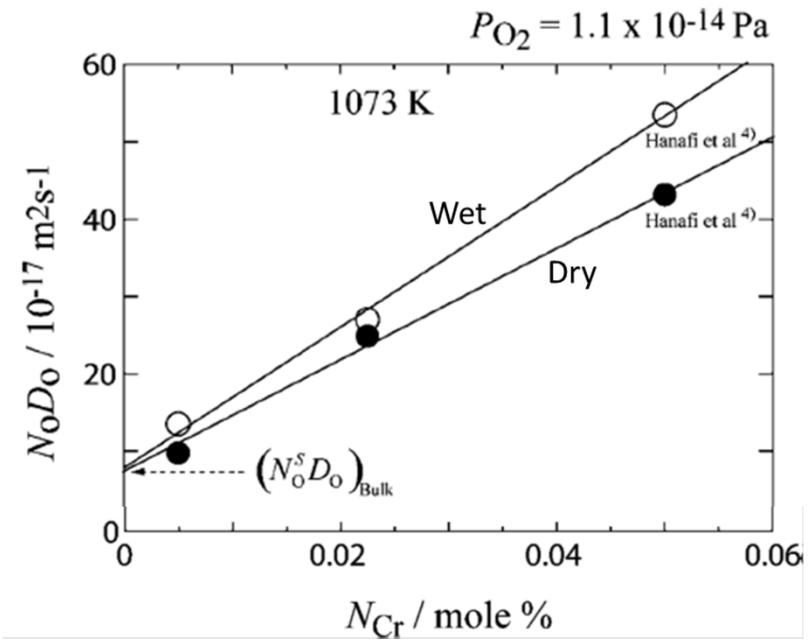
N_{Al}* is increased by around 60% in the presence of 30% steam

Previously Reported Interpretations of the Detrimental Steam Effect

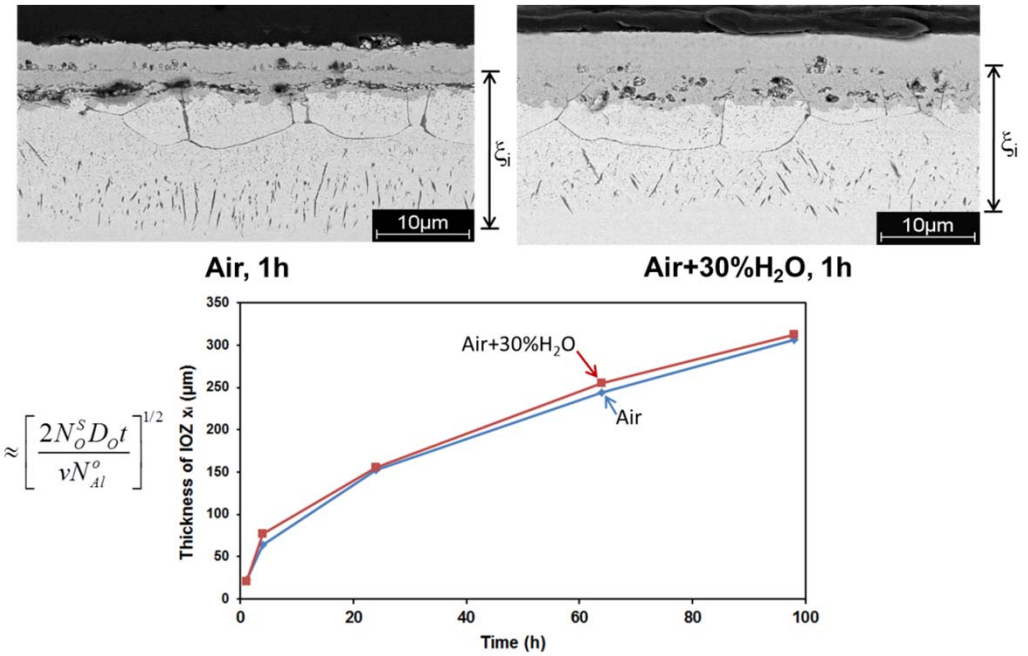
A number of recent studies on Fe-based alloys inferred that the presence of steam in the atmosphere causes increased oxygen permeability into the alloy

Example: Fe-Cr alloys

A.R. Setiawan et al., *ISIJ International*, **50** (2010) 259



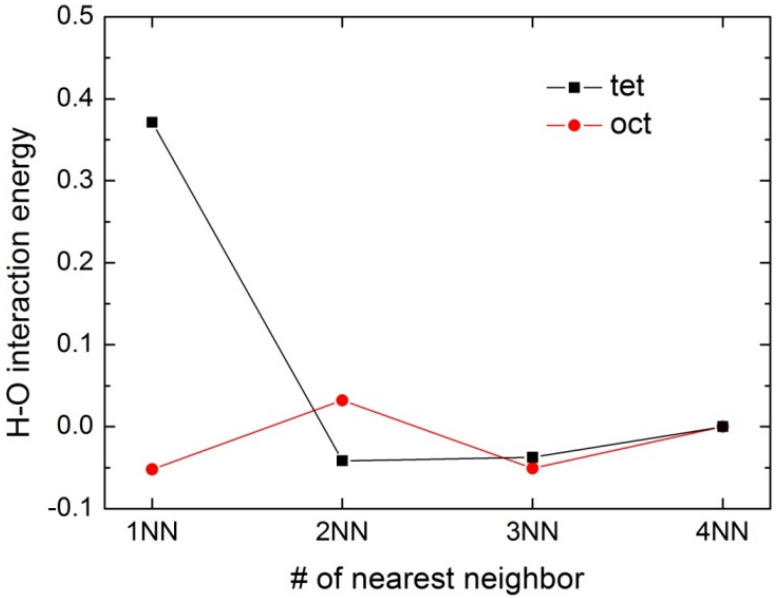
From our work: Ni-3at.%Al oxidized at 1000°C

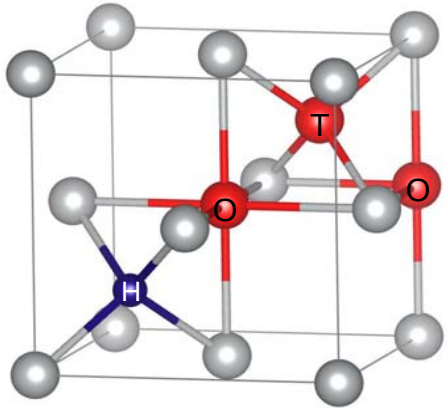


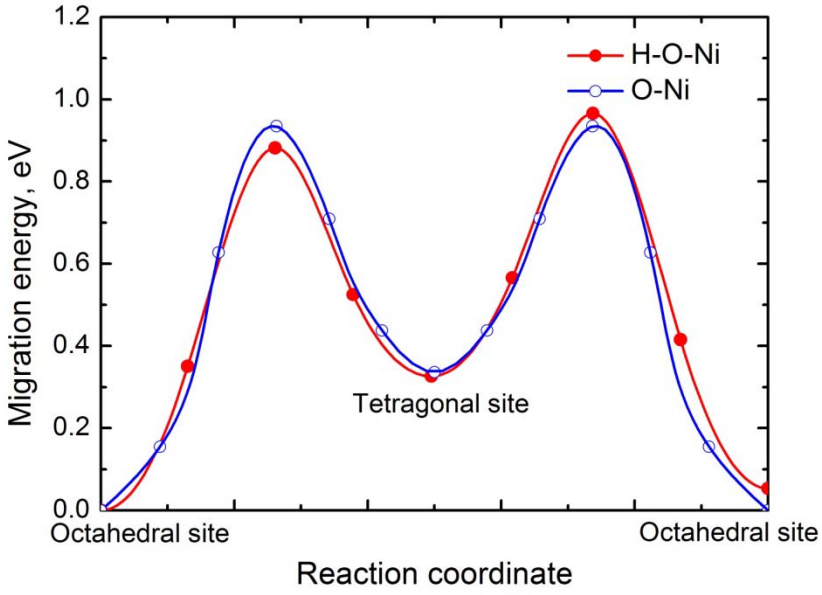
No significant enhanced oxygen permeability in the alloy when steam was present.

Effect of Hydrogen on Oxygen Diffusion in Ni

Binding energy of H and O *vs.* distance







Binding energy:

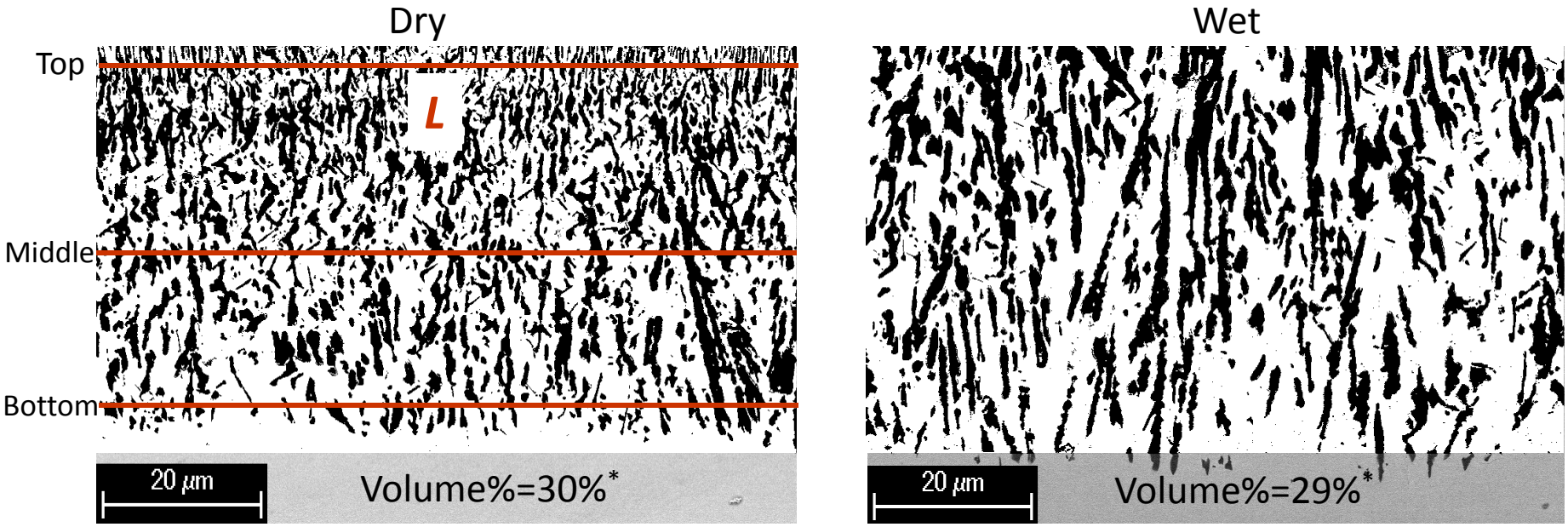
$$E_b = E(n\mathrm{Ni} + \mathrm{H} + \mathrm{O}) - E(n\mathrm{Ni} + \mathrm{H}) - E(n\mathrm{Ni} + \mathrm{O}) + E(n\mathrm{Ni})$$
$$= -0.043\,\mathrm{eV}$$

Hydrogen does not obviously affect the diffusion of oxygen in nickel since the binding energy between them is very small.

Accounting for the Increase in N_{Al}^*

$$N_{Al}^* = \frac{1}{R} F\left(\gamma\varphi^{1/2}\right) f_v^* \quad \text{and} \quad \gamma\varphi^{1/2} = f\left(D_{O,eff}, N_O^S, D_{Al}, k_c\right)$$

f_v^*: critical volume fraction of internal oxide.



* Average number from four images

Inter-particle distance *d* is found to be: $d = \left(1 - 2\sqrt{\frac{\overline{A_A}}{\pi}}\right)\frac{L}{N}$

d (μm)	Top	Middle	Bottom
Dry Air	0.3	0.5	0.9
Air + 30%H_2O	0.9	1.2	1.7

For Ni-based alloys forming whisker-like internal oxide precipitates, it is the inter-particle distance *d* that greatly influences the N_{Al}^*

Accounting for the Change in Internal Precipitate Size & Distribution

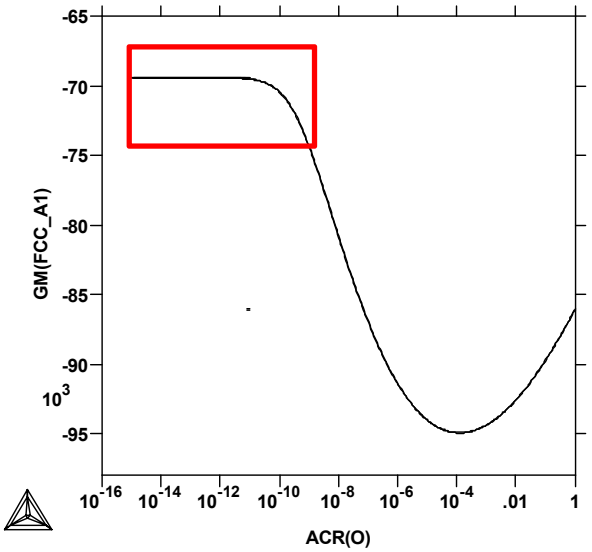
Energy Barrier to Nucleation: $\Delta G^{*}\uparrow = \dfrac{16\pi\gamma^{3}\uparrow}{3\left(\boxed{\Delta G_v}\right)^{2}\downarrow}$

where: γ is the Al_2O_3/alloy interfacial energy

ΔG_v is the volumetric free energy change before and after nucleation.

$\boldsymbol{\gamma}$ and $\boldsymbol{\Delta G_v}$ dictate magnitude of ΔG^{*}

Effect of H on the Gibbs energy for FCC γ



Ni-3%Al-O-H @ 1000°C

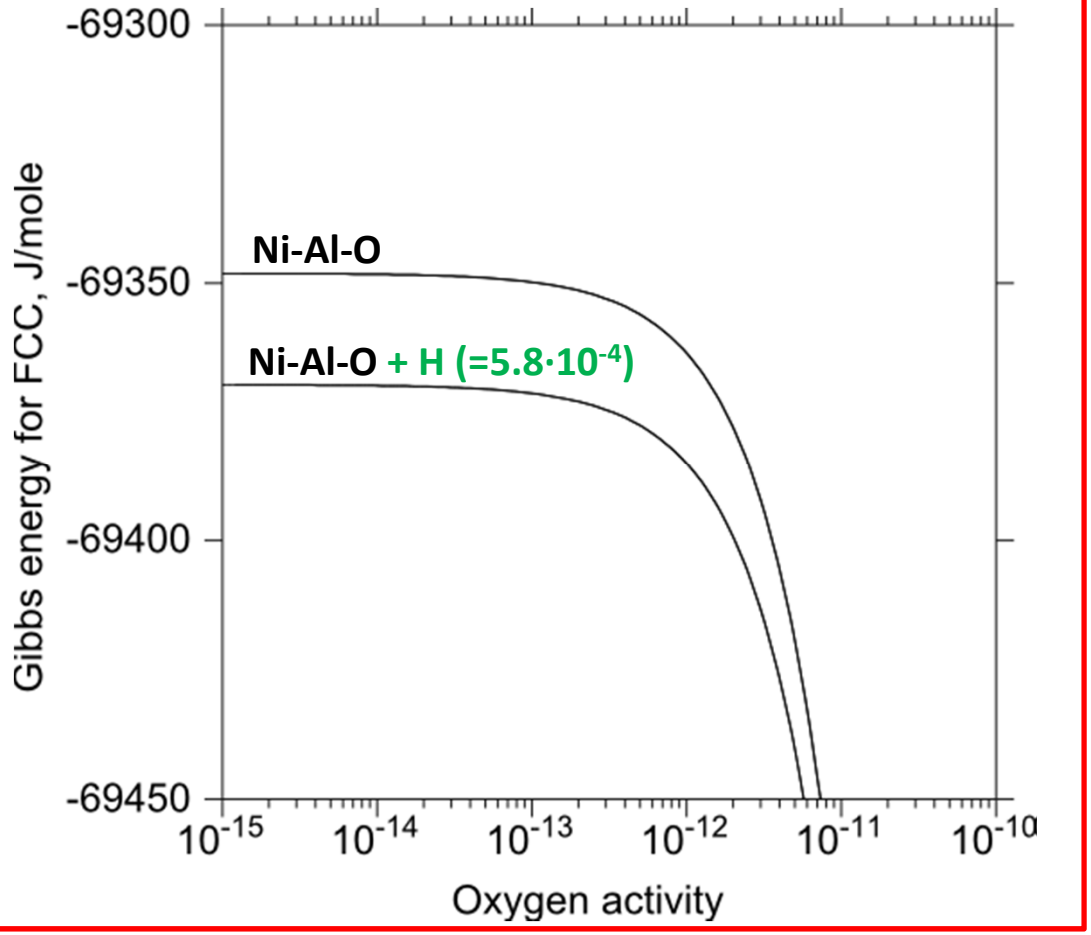
Calculated H fraction in FCC Ni-3%Al at 1000°C:

5.8×10^{-4}

Qualitatively:

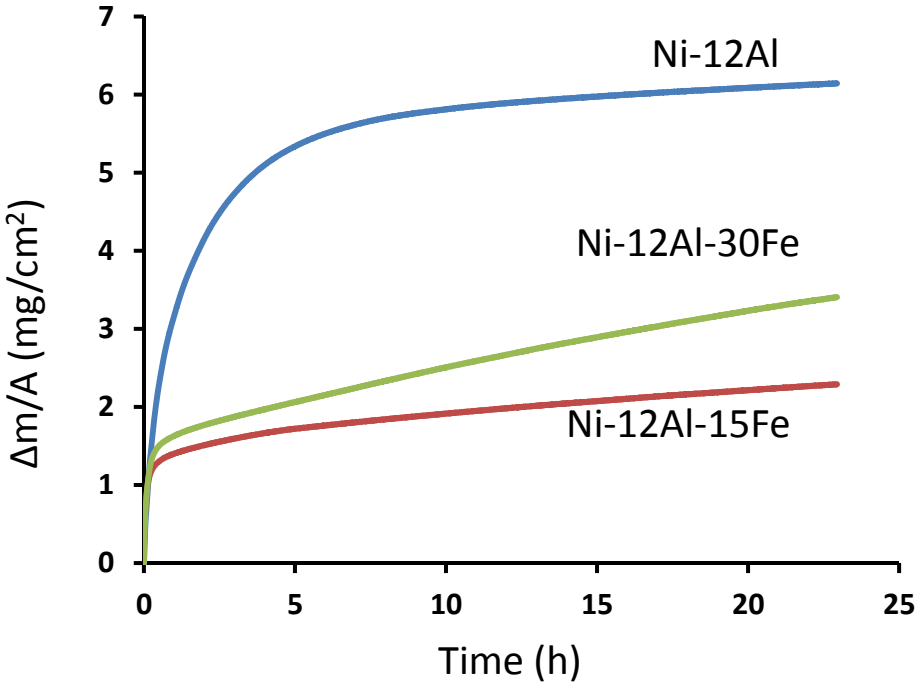
$G_{FCC} \downarrow \Rightarrow \Delta G_v \downarrow$

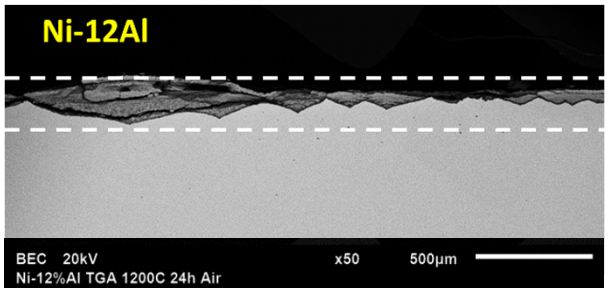
Nucleation occurs at the internal oxidation front, where N_O is extremely low.

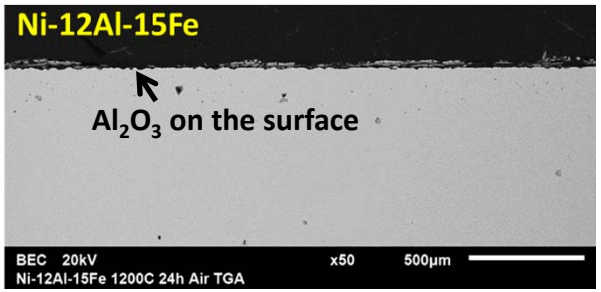


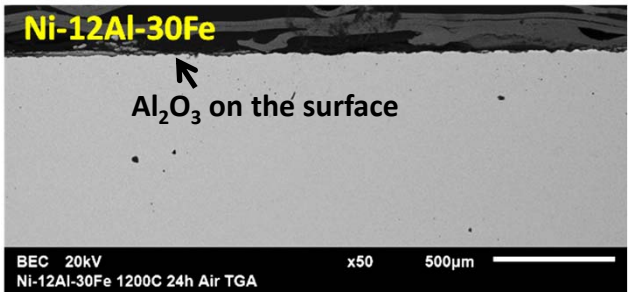
Shows that the presence of hydrogen decreases the driving force for nucleation and therefore increases ΔG*

Fe effect on oxidation behavior of Ni-*12*Al-(Fe) at 1200°C









For Ni-12Al, the protective layer was established in the alloy. With Fe addition, the protective layer was established very close or on the surface.

Fe reduces the time required for the establishment of the protective layer ➡ N_{Al}^{*} ↓

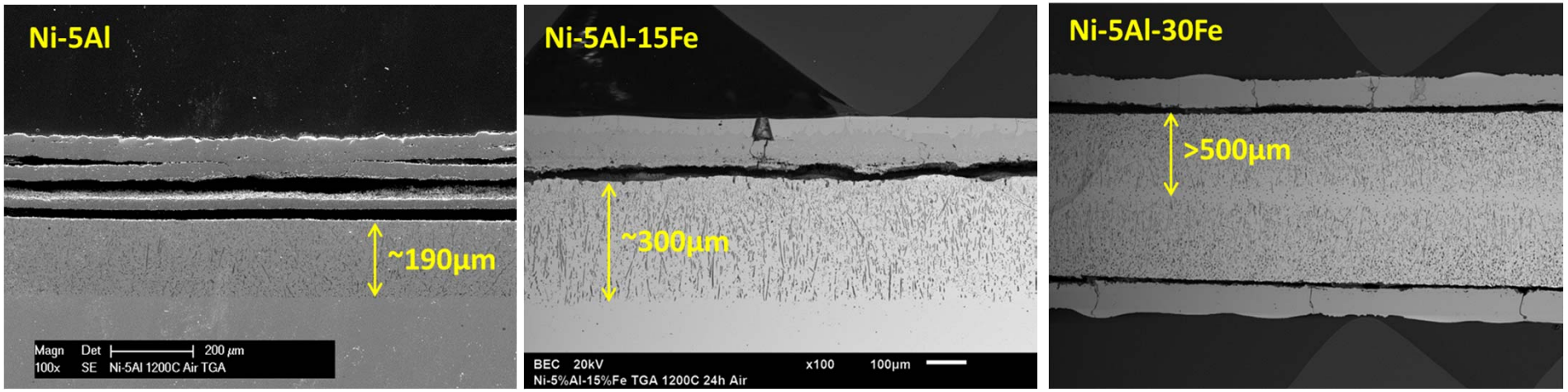
Predictions Using Simulated Data for Ni-Al-Fe Systems

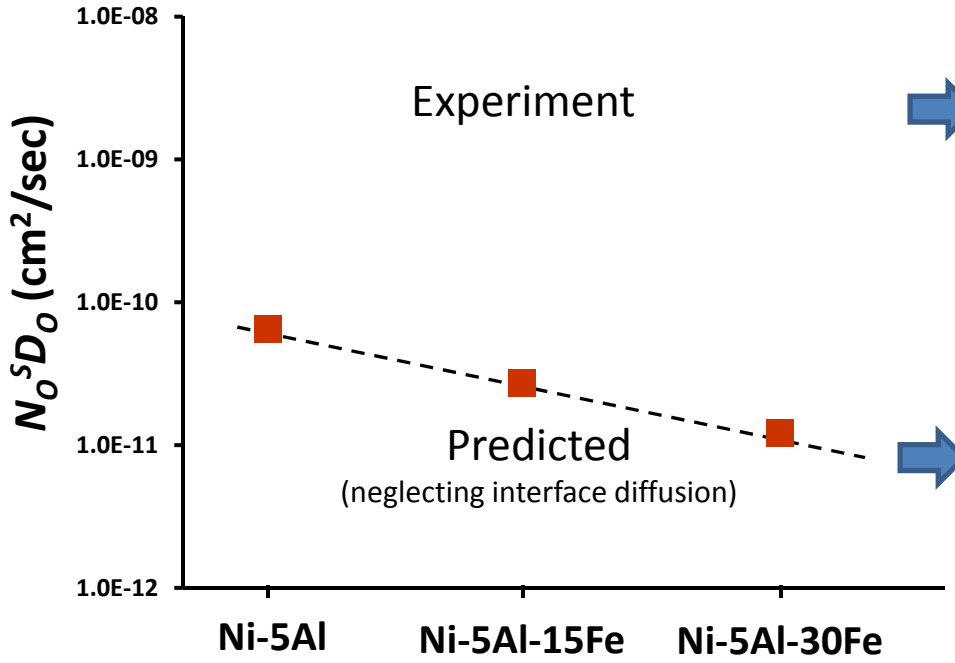
Alloy (at%)	T (°C)	N_O^S	D_O (cm²/s)	D_{Al} (cm²/s)	k_c (cm²/s)	f_v^*	N_{Al}^* (Predict)	N_{Al}^* (Exp)
Ni-Al	1200	9×10^{-4}	7×10^{-8}	1×10^{-10}	0	0.54	0.18	0.14
Ni-15Fe-Al	1200	7×10^{-5}	4×10^{-7}	9×10^{-11}	0	0.54	0.15	0.12
Ni-30Fe-Al	1200	4×10^{-5}	3×10^{-7}	1×10^{-10}	0	0.54	0.11	0.12

Note: k_c is assumed to be zero in the calculation. From previous calculation, it has been found that k_c has very limited effect on N_{Al} when alloys form NiO initially.*

- Using the simulated input parameters, the trend in the change of N_{Al}^* is correct. The predicted values are reasonable close to experiment.
- However, a closer look reveals that more aspects need to be considered.

Fe Effect on Oxygen Permeability at 1200°C





Experiment → $N_{Al}{}^*$ ↑

Predicted
(neglecting interface diffusion)

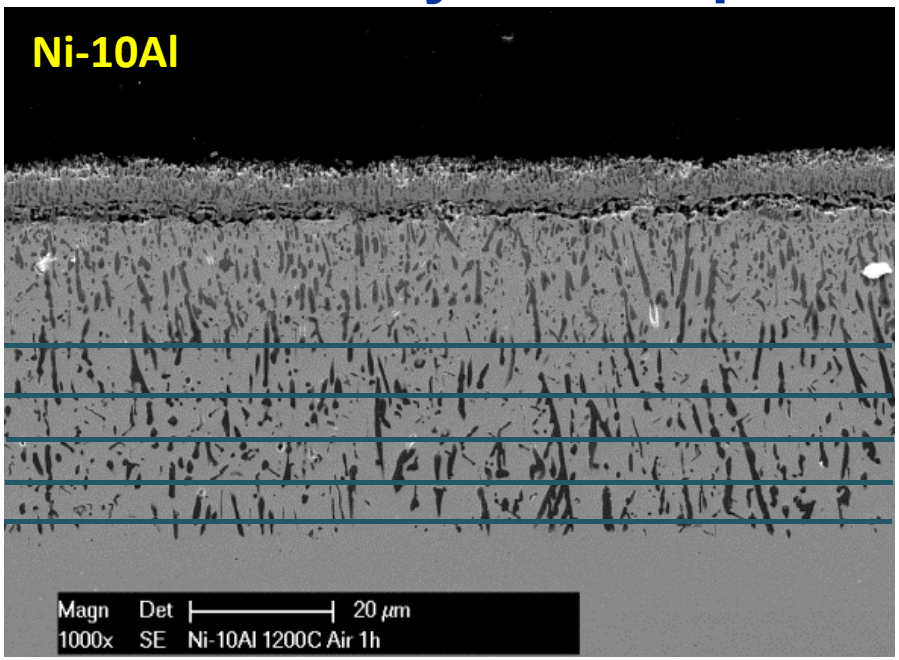
$N_{Al}{}^*$ ↓

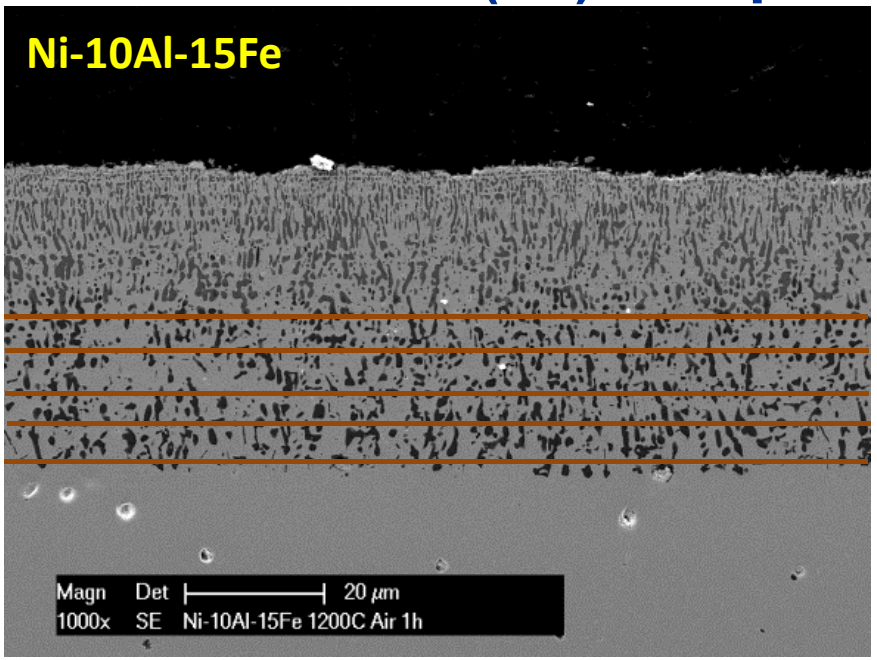
Fe addition must have a more significant effect on other aspect(s) to overcome the increased $N_O{}^S D_O$.

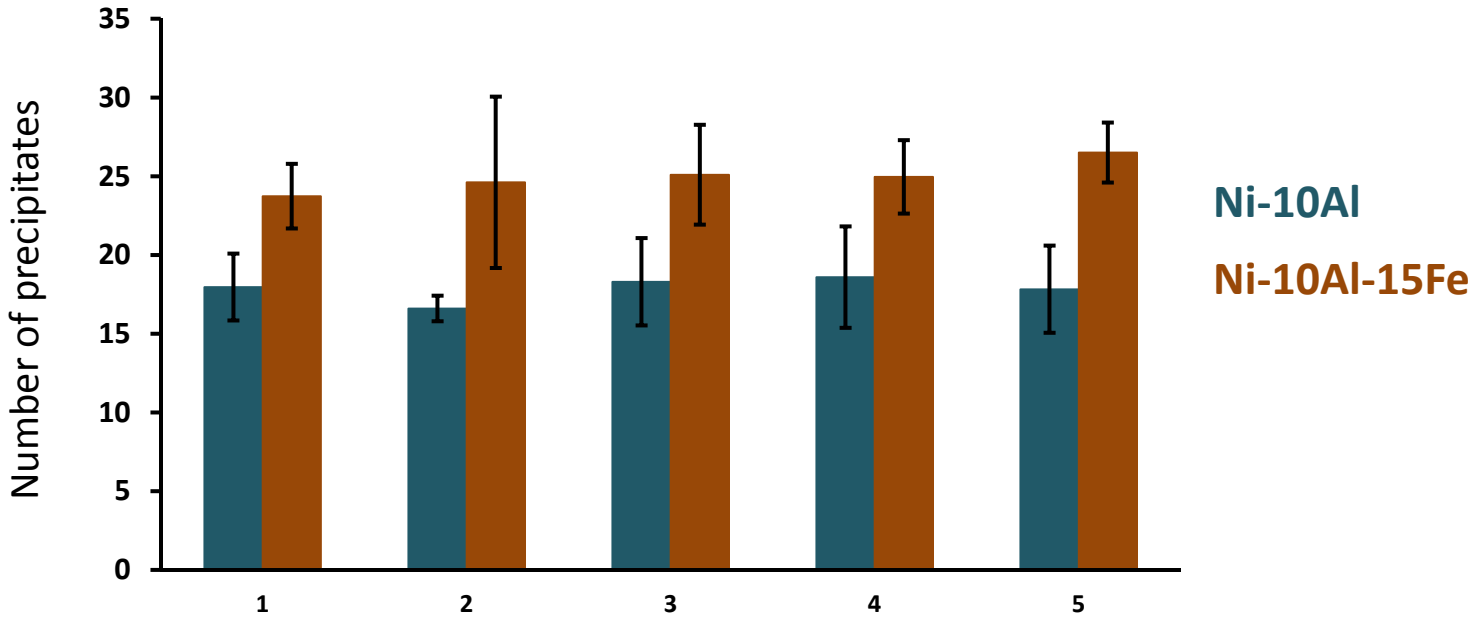
however...

This missing effect has to be studied for reliable estimation on $N_{Al}{}^*$ for complex alloy systems

Number Density of Precipitates Formed in Ni-Al-(Fe) Samples

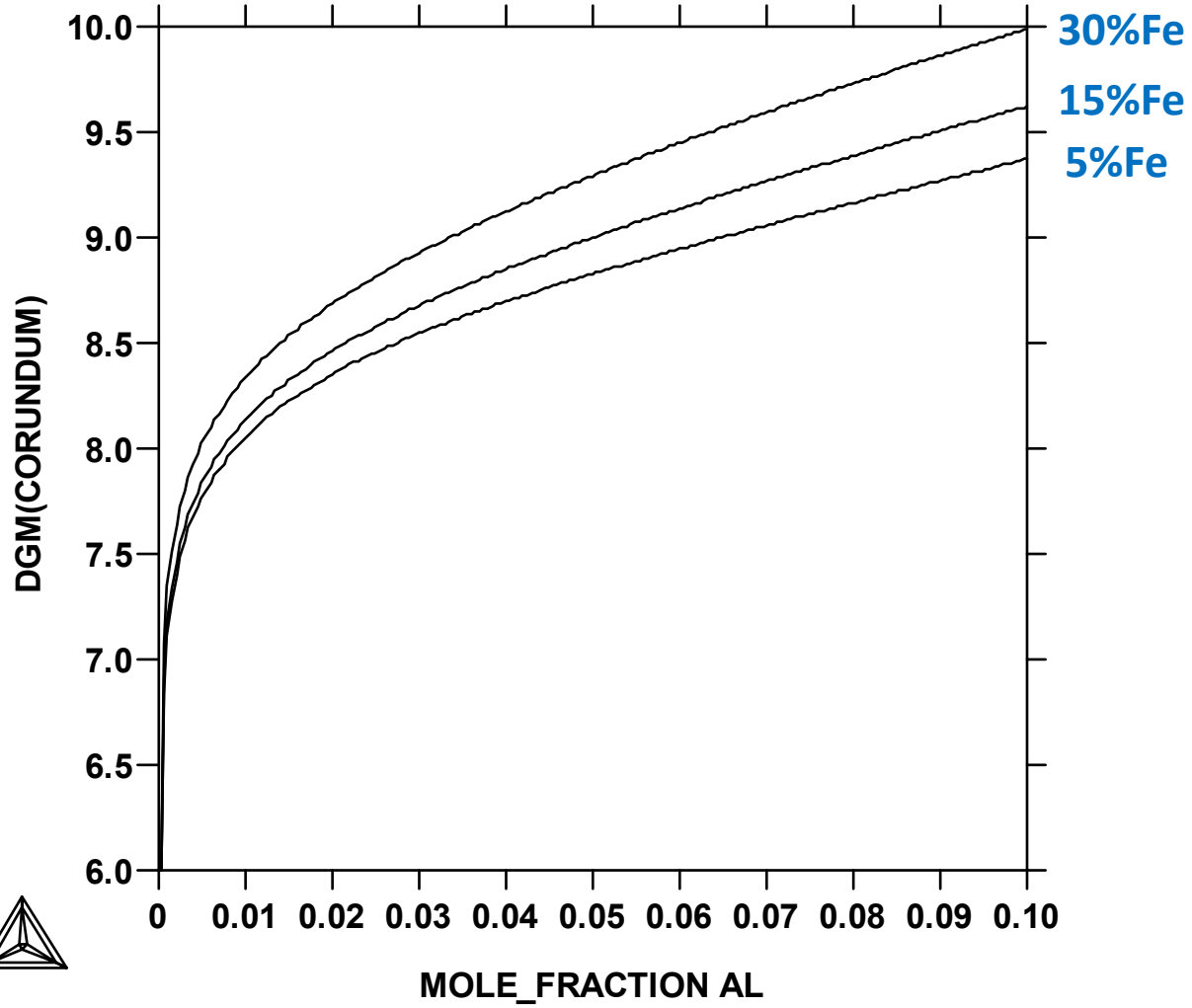






Nucleation rate is increased by Fe addition.

Effect of Fe on the Gibbs Free Energy for FCC-Ni



Oxygen partial pressure: 5e-11

The same trend is observed also for higher O partial pressures.

Qualitatively:

$G_{FCC}\uparrow \Rightarrow \Delta G_v\uparrow \Rightarrow N_{Al}^{*}\downarrow$

Similar to the effect by steam (or Hydrogen), nucleation behavior may be an important factor to determine the alloy performance.

Summary: *Impacts and achievements*

- A strong foundation for computationally determining key input parameters for using Wagner's theory of alloy oxidation has been established, *i.e.*,

  D_O, N_O^S, D_{Al} ➡ N_{Al} as a function of alloy composition and temperature*

- Predictions are particularly good for Ni-Al alloys exposed to dry oxidizing conditions when a revised f* is used.

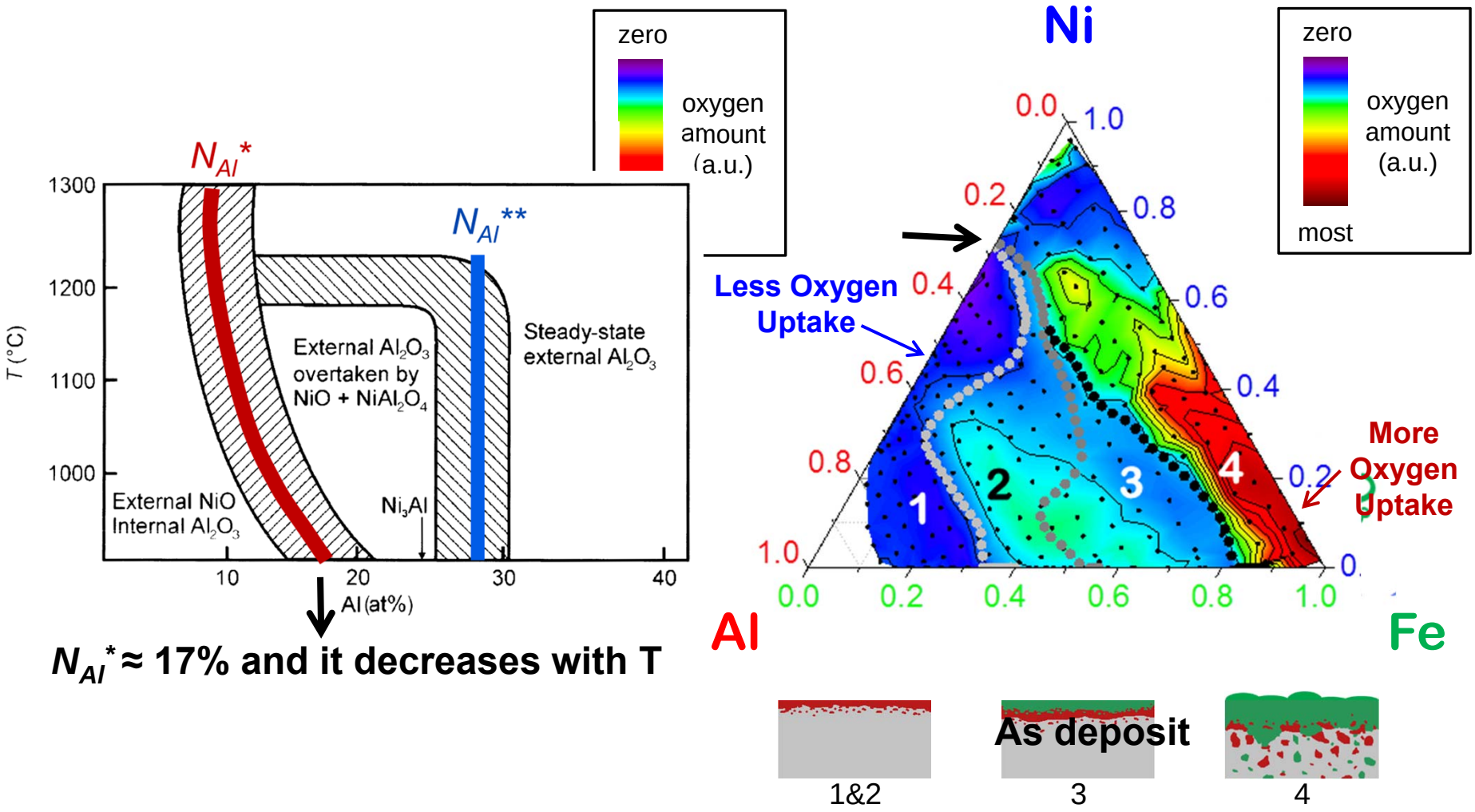
- The importance of nucleation behavior/energetics – which relates to f* – is identified to be of significant importance ➡ *must be accounted for to accurately predict N_{Al}* in steam-containing environments and/or high-order systems.*

- Directions in trends stemming from steam and alloying additions may be understood by considering effects on the energetics of oxide nucleation ➡ *computation on energetics provides guidance and new insights for alloy design.*

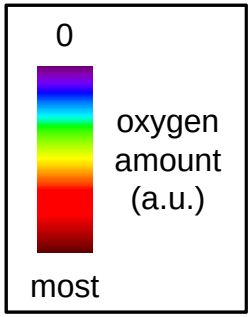
Way forward: Modify Wagner's theory to account for oxide nucleation behavior/energetics

Thank you for your attention.

Application of $Al_xFe_yNi_{1-x-y}$ CSAF to study of alloy oxidation



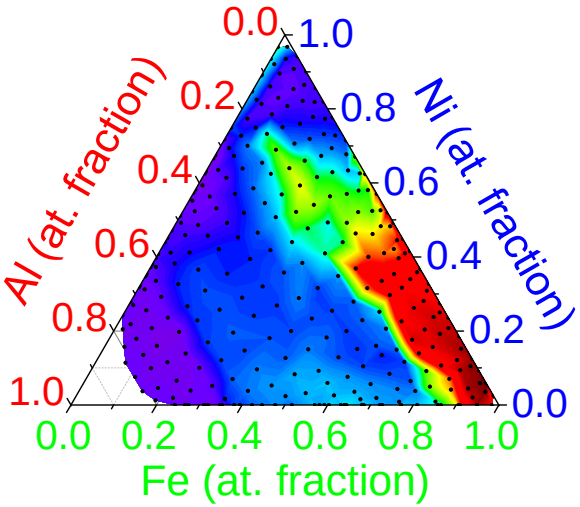
F.S. Pettit, "Oxidation mechanisms for Ni-Al Alloys at temperatures between 900 and 1300°C," *AIME Met. Soc. Trans.*, **239** (1967) 1296.

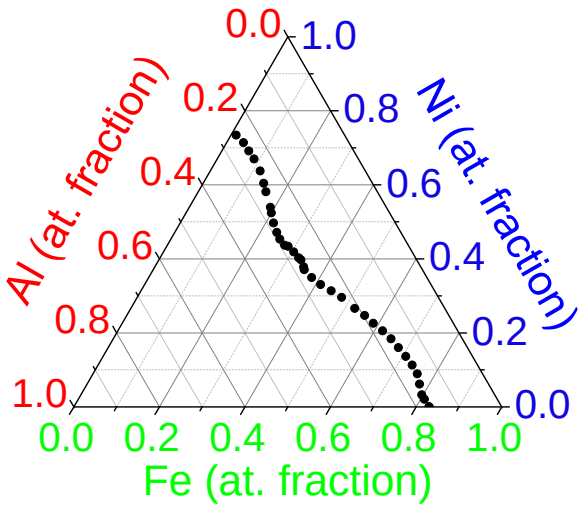


Total oxygen content in $Al_xFe_yNi_{1-x-y}$ thin film:

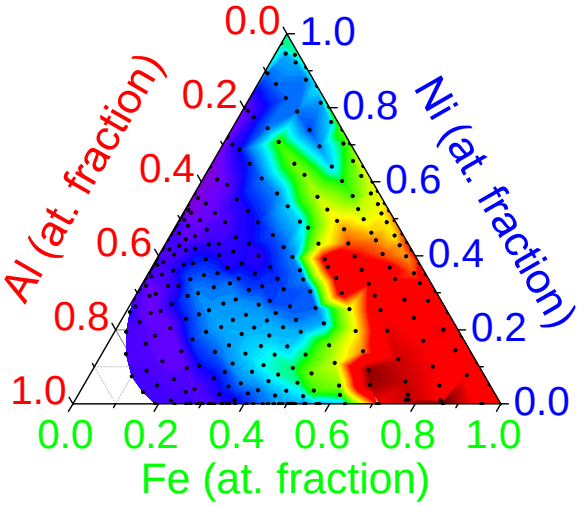
$N^*_{Al}(x, y)$:

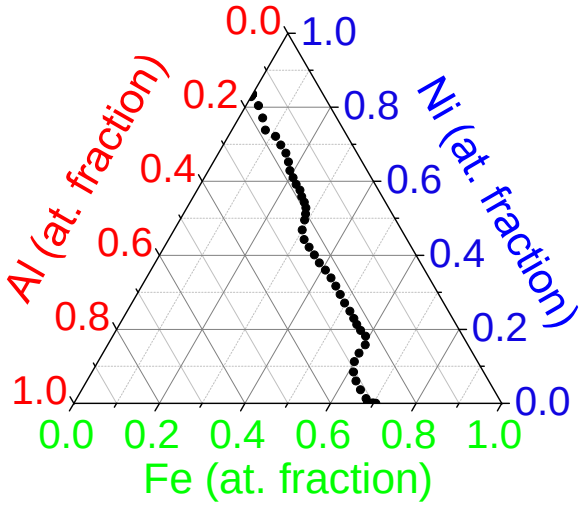
dry air, 700 K →

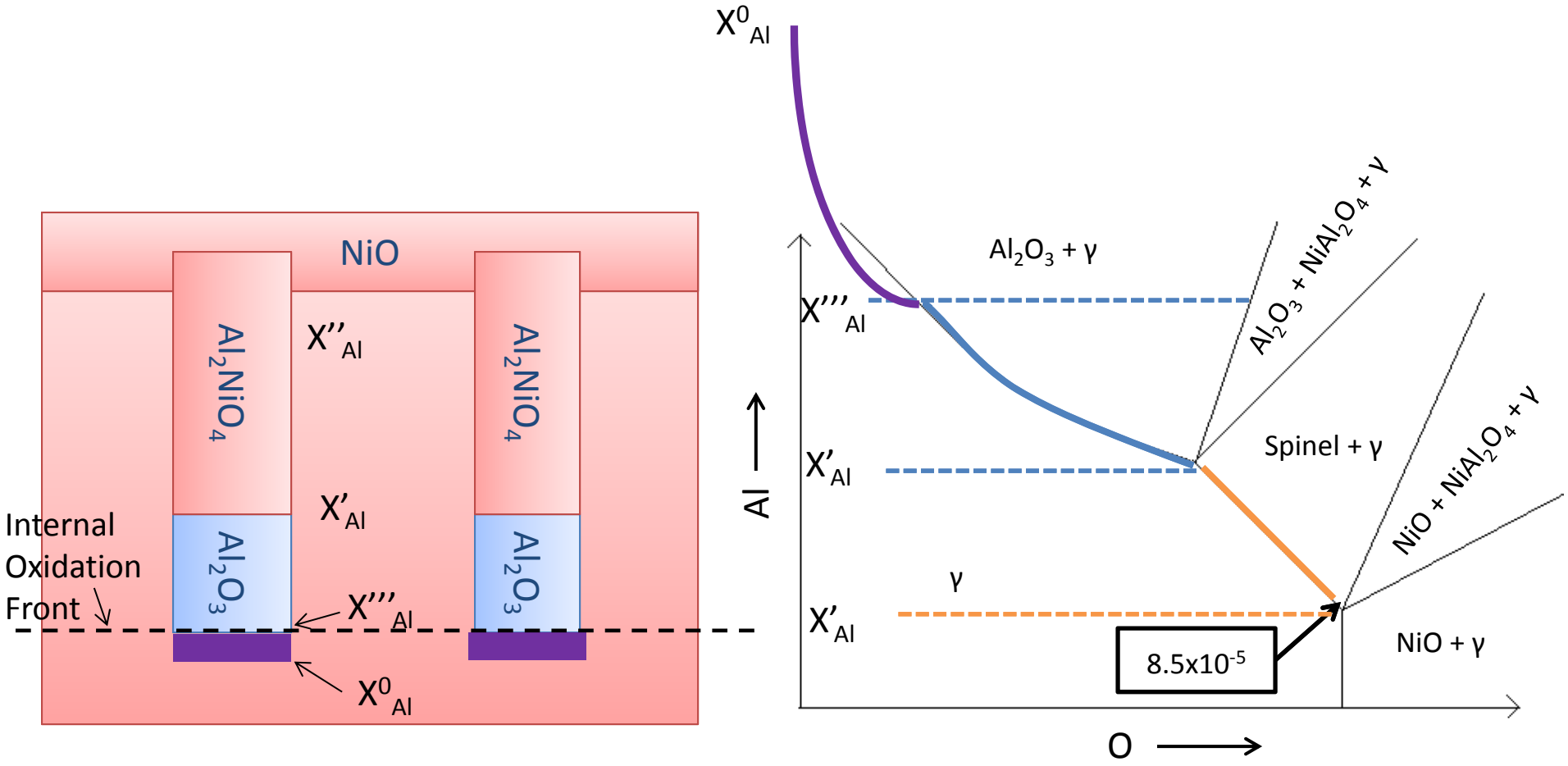




10% humid air, 700 K →



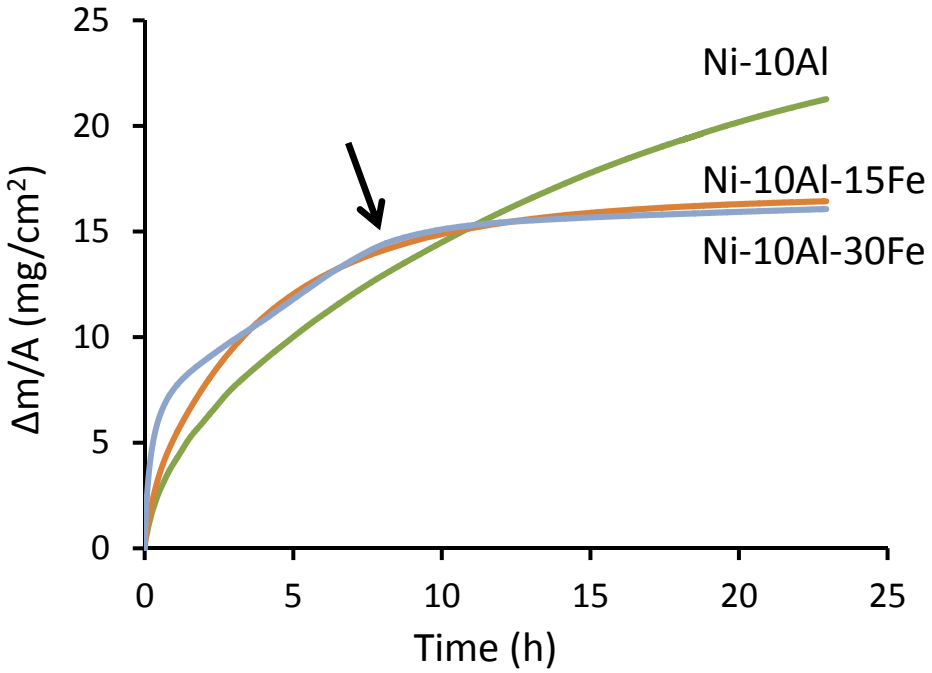


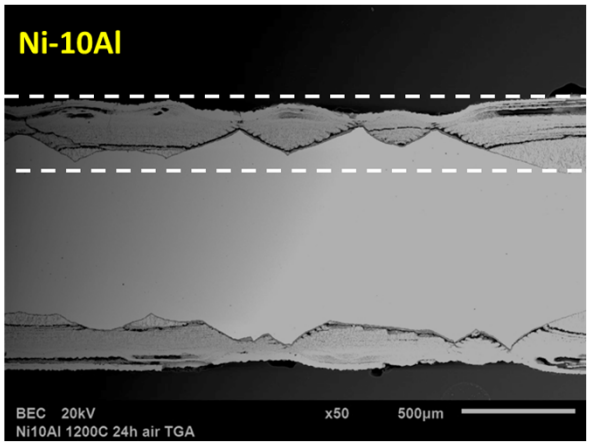


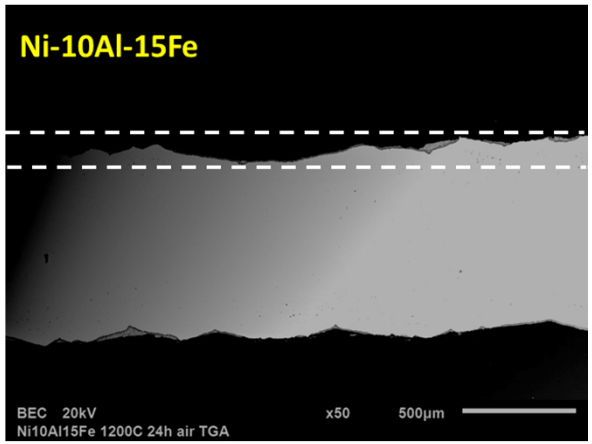
The N_O and N_{Al} values used to calculate the driving force should be around X'''_{Al} and X'''_{O}.

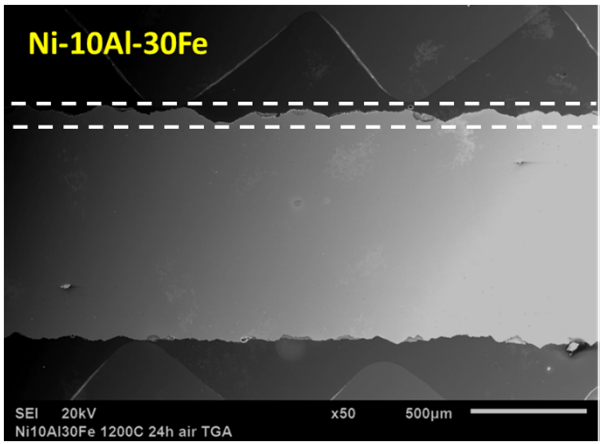
It is quite reasonable that X'''_{O} is orders of magnitude smaller than 8.5e-5, and therefore P_{O2} is smaller than 1e-8

Fe effect on oxidation behavior of Ni-*10*Al-(Fe) at 1200°C



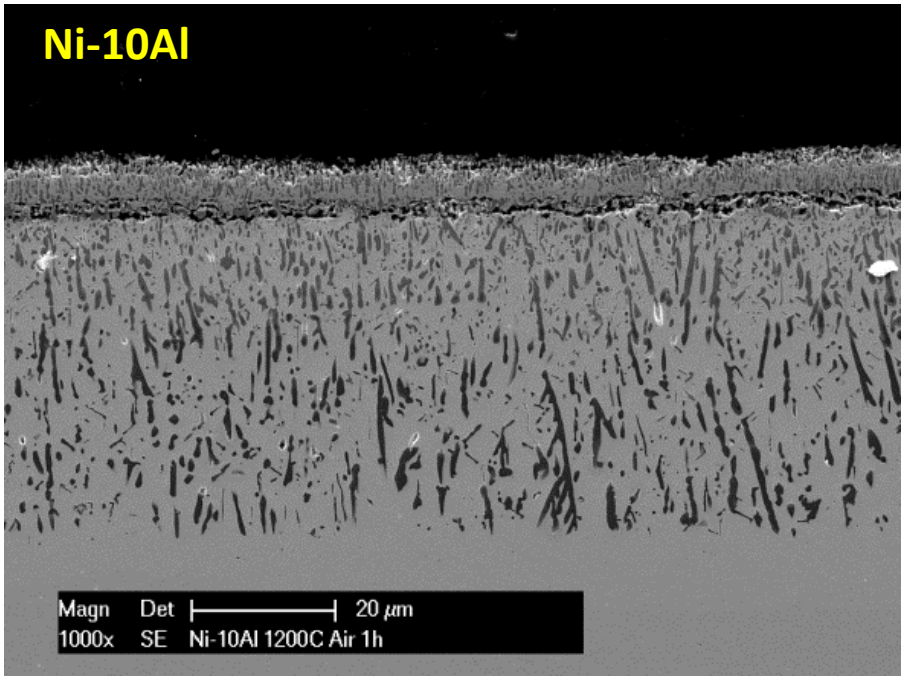


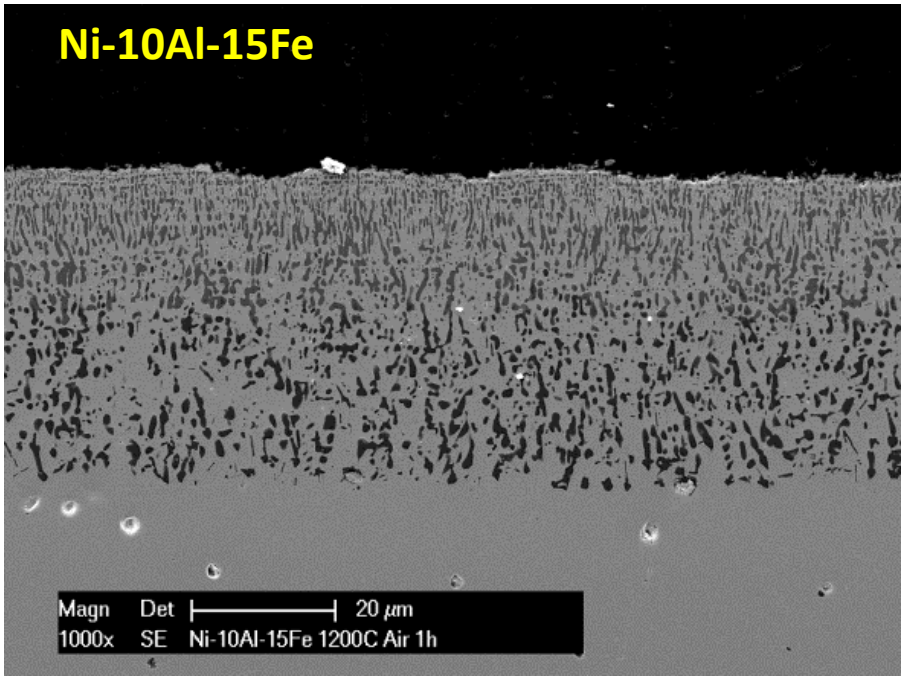




A continuous and protective layer was established in the alloys with Fe addition

General Observations on Cross-sectional Morphology





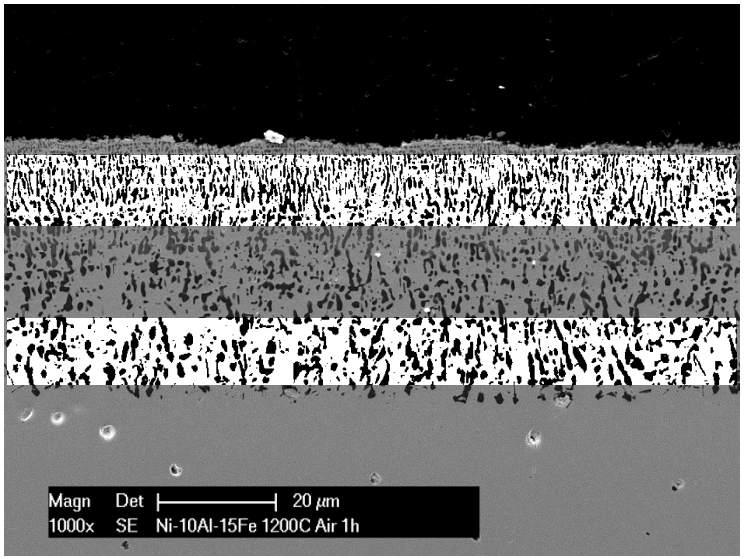
Note: Spinel (gray) is formed closer to the surface and Al_2O_3 (black) is formed deeper in the IOZ.

Observations for both phases (spinel and Al_2O_3).
With Fe addition:

- Volume fraction is increased.
- Number densities of precipitates is increased.

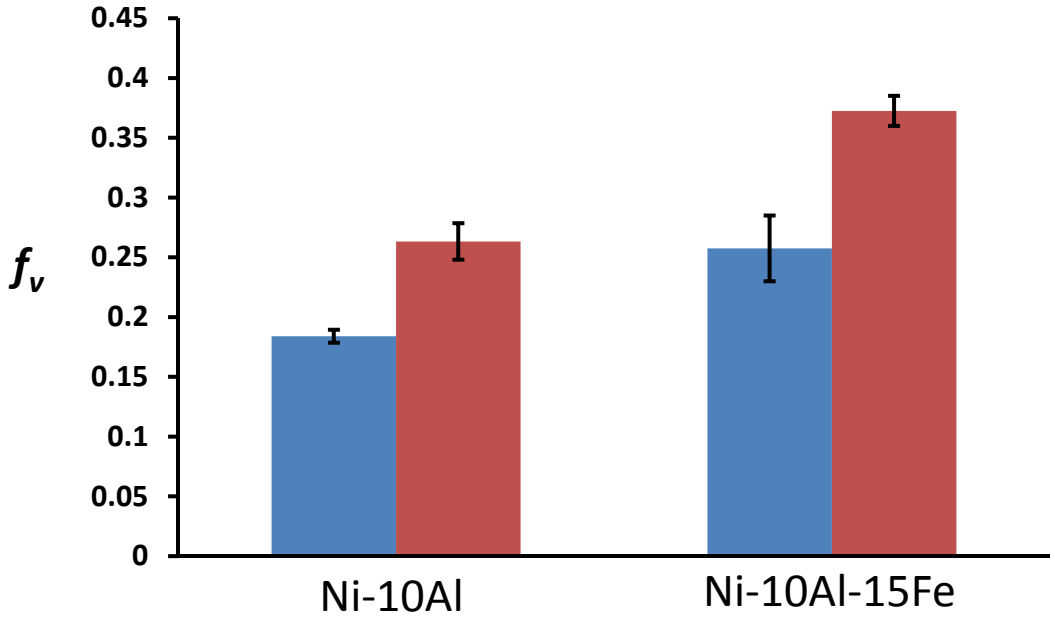
Volume Fraction of Precipitates formed in Ni-Al-(Fe) Samples

The data and the standard deviation bars are from 4 to 5 images from different places on each sample.



f_v(spinel)=0.26

$f_v(Al_2O_3)$=0.17



f_v(spinel), red

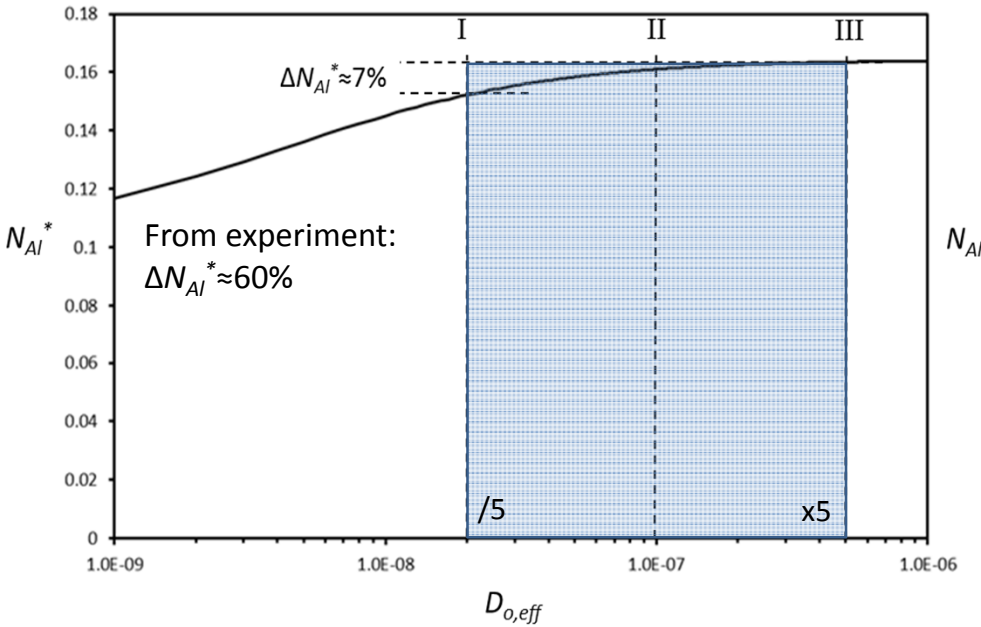
$f_v(Al_2O_3)$, blue

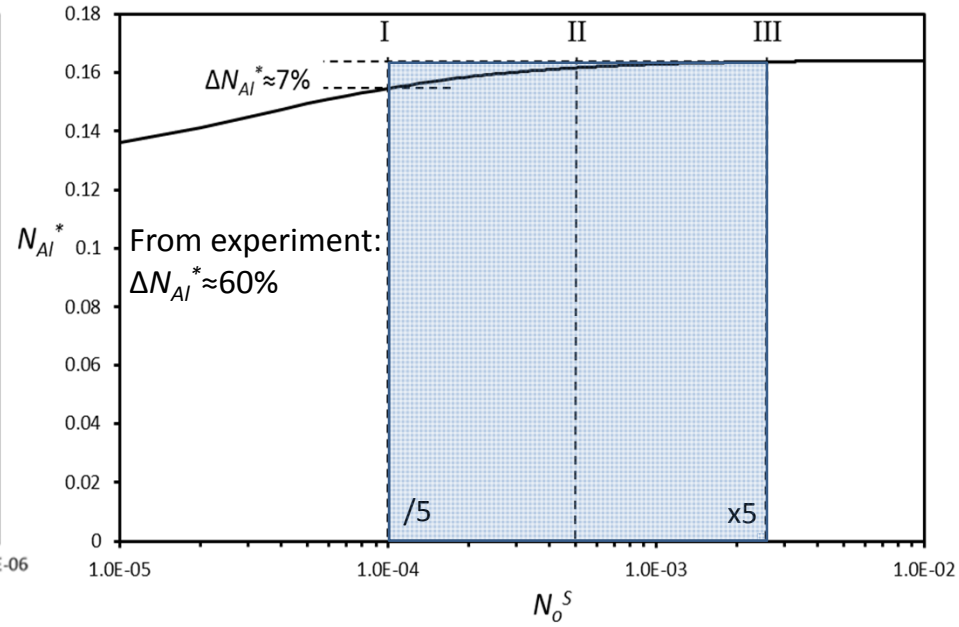
Fe addition increases the volume fraction of spinel and Al_2O_3 that formed in the IOZ.

Accounting for the Increased Critical Concentration of N_{Al}^*

$$N_{Al}^* = \frac{1}{\cancel{R}} F\left(\gamma\varphi^{1/2}\right) f_v^* \quad \text{and} \quad \gamma\varphi^{1/2} = f\left(D_{O,eff}, N_o^S, \cancel{D_{Al}}, \cancel{k_c}\right)$$

The increase in k_c found by experiment can only give 0.1% increase in N_{Al}^*





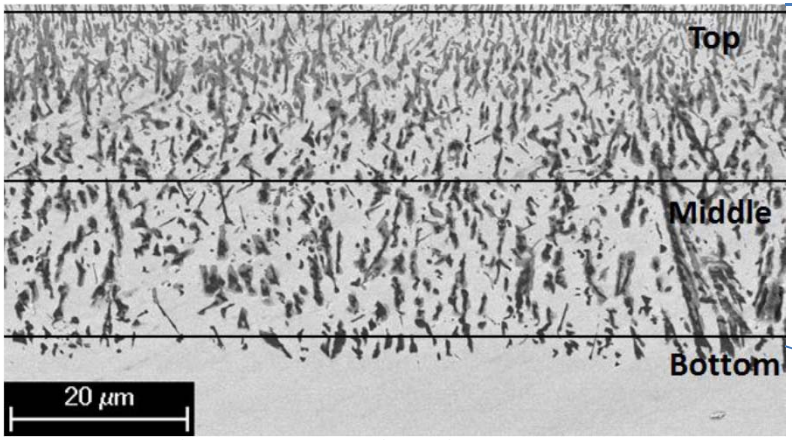
Differences in $D_{o,eff}$ *and* N_o^S between wet and dry conditions cannot explain the ~60% difference in N_{Al}^* determined experimentally.

Predicting Critical Al Concentration (N_{Al}^*) in Ni-Al at 1200°C

For oxidation in air:

Alloy	T (°C)	N_O^s	D_O (cm²/s)	D_{Al} (cm²/s)	k_c (cm²/s)	f_v^*	N_{Al}^* (Predict)	N_{Al}^* (Exp)
Ni-Al	1200	$9x10^{-4}$	$7x10^{-8}$	$\sim 1x10^{-10}$	$4x10^{-11}$	0.2 [1]	0.08	>0.14
Ni-Al	1200	$9x10^{-4}$	$7x10^{-8}$	$\sim 1x10^{-10}$	$4x10^{-11}$	0.54 [2]	0.18	

- The prediction of N_{Al}^* with using simulated data is reasonable close.
- The value of f_v^* has a significant effect on the accuracy of N_{Al}^*.



Ni-5Al-5Cr exposed in dry air at 1000°C

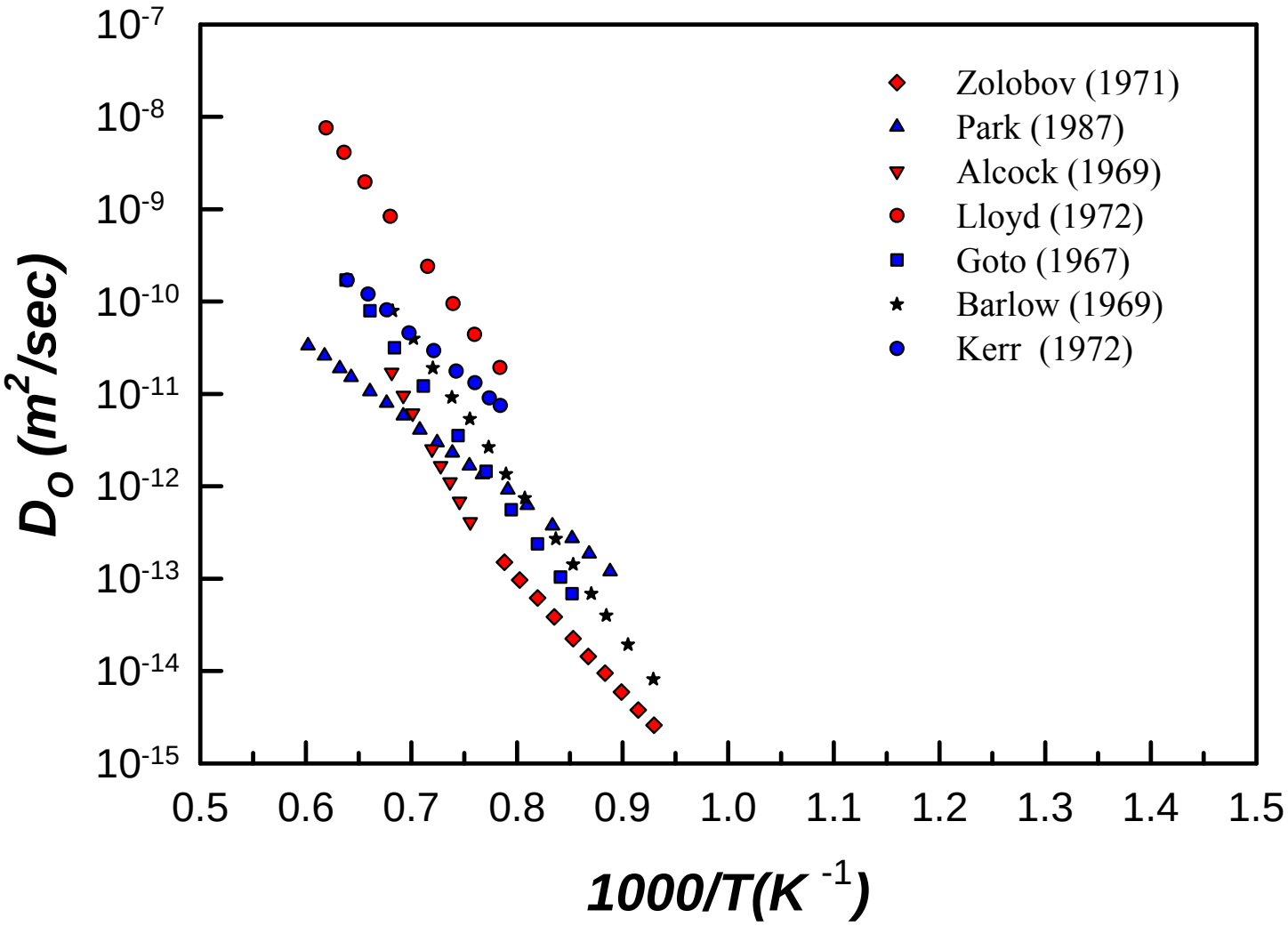
$f_v \approx 0.3$ ($> f_v^*$ from literature)

The understanding of f_v^* is important.

[1] J. A. Nesbitt (1989); [2] New prediction method developed by Zhao and Gleeson in this project

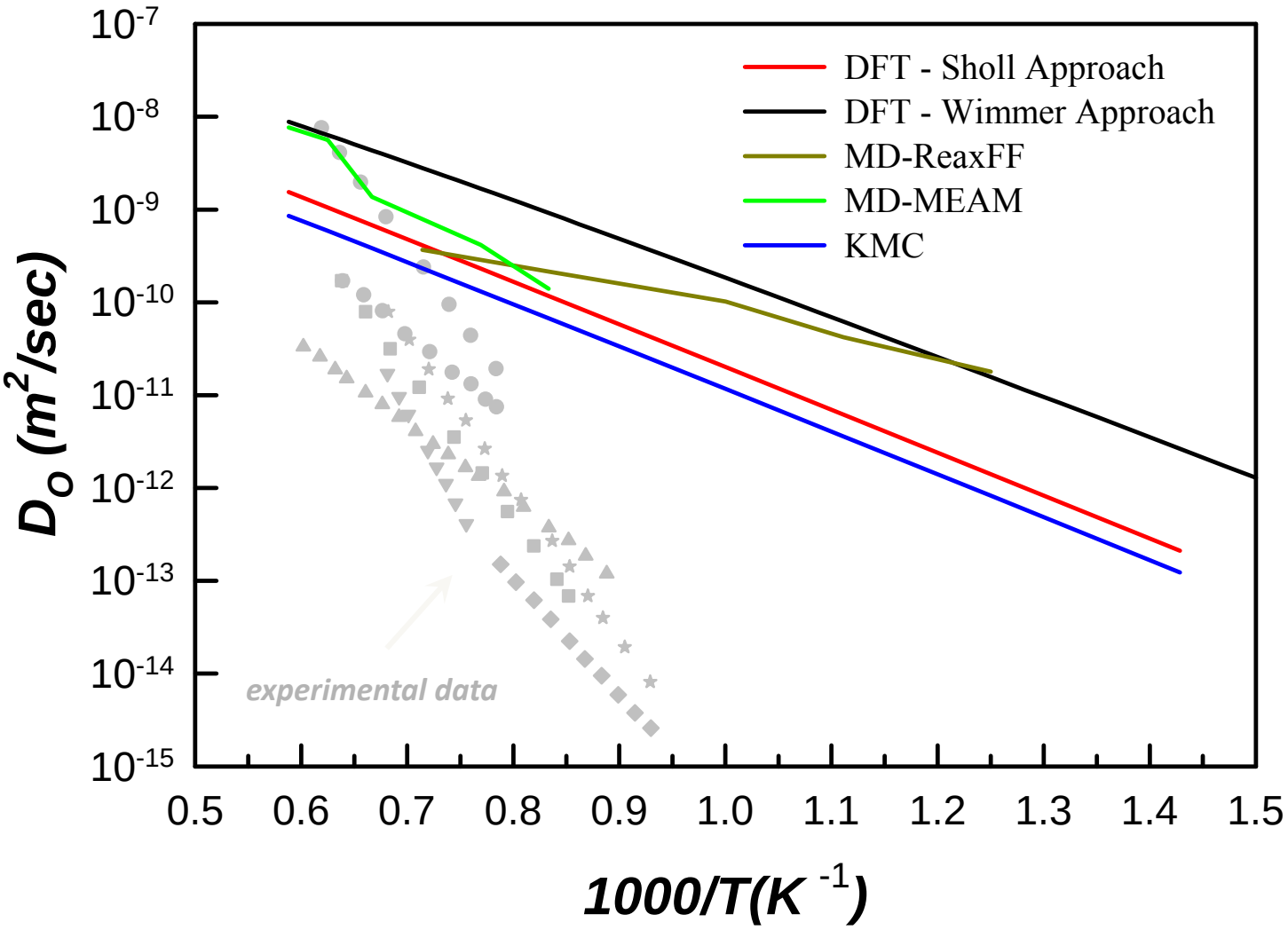
Simulations to Predict Oxygen Diffusivity in Nickel

D_o from experiments in the literature

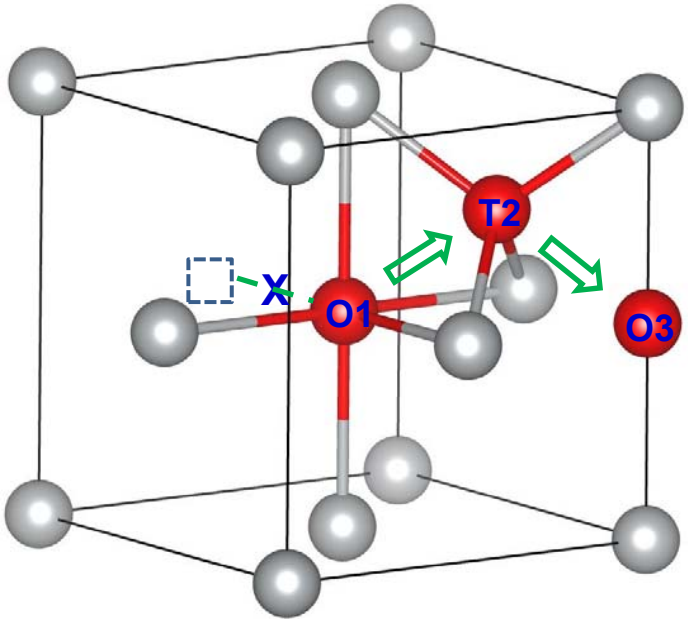


Simulations to Predict Oxygen Diffusivity in Nickel

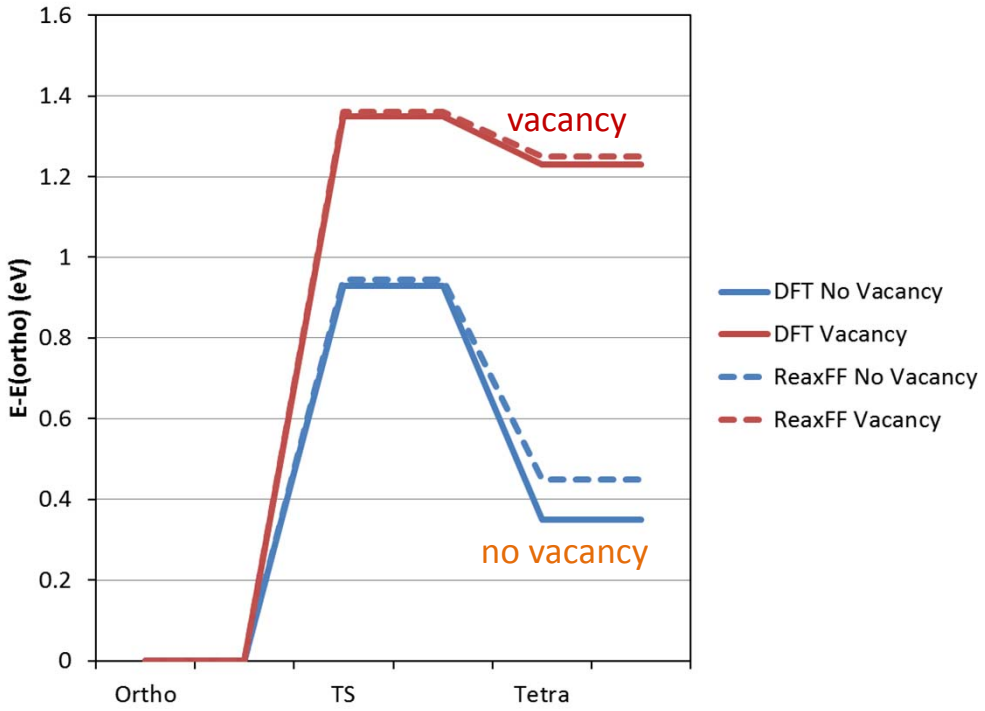
Predictions for D_O in a perfect Ni lattice (i.e., no vacancies)



DFT and ReaxFF Approaches to Determine Oxygen Diffusivity in Nickel - *Effect of Vacancy*

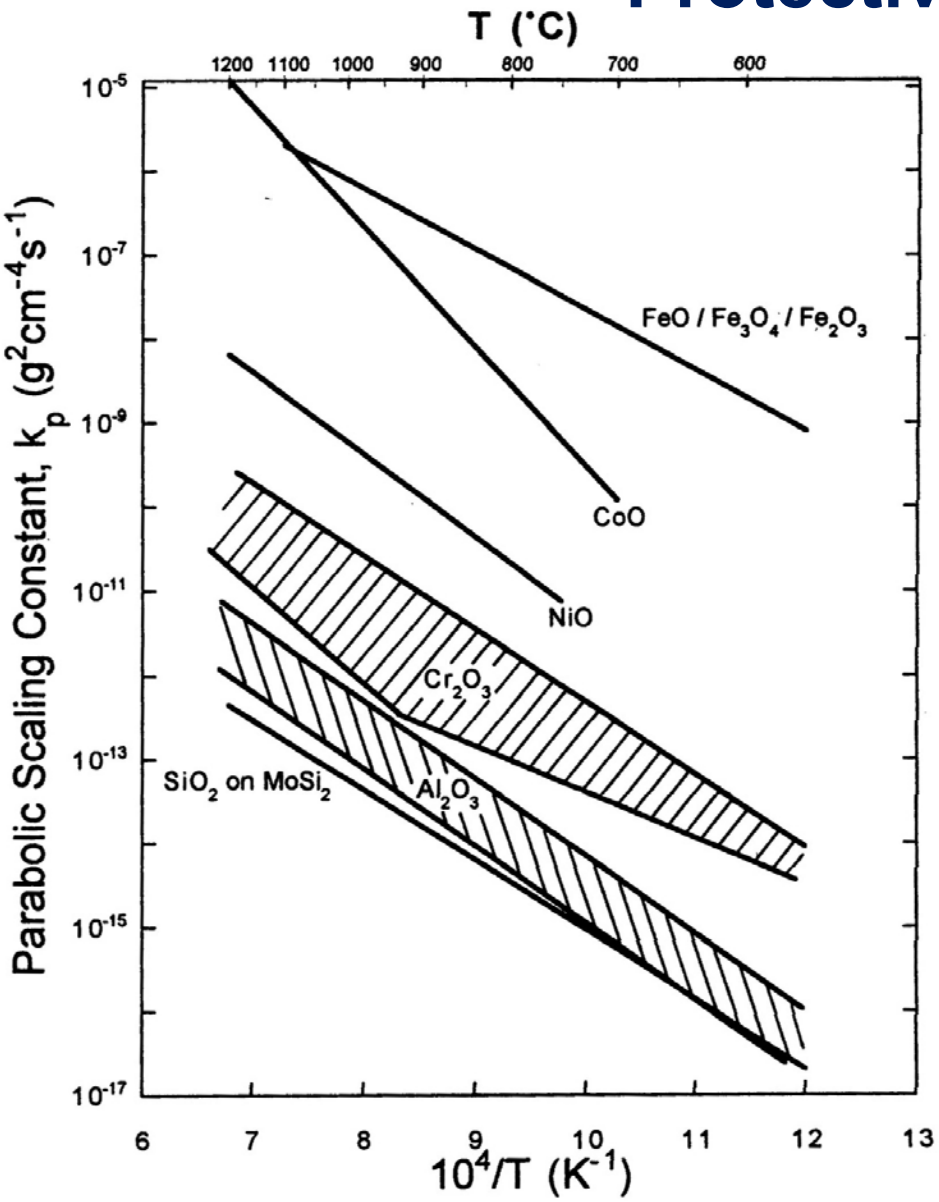


vacancy site



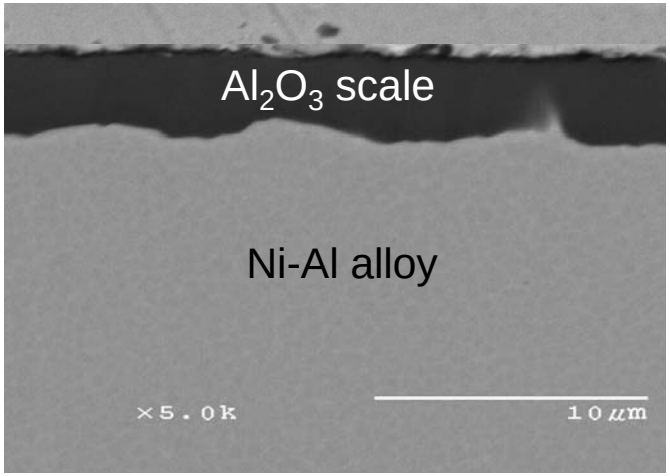
There is a very strong binding energy of ~1.25 eV between oxygen and vacancy. To diffuse away from the vacancy, the oxygen has to overcome a barrier which is 2.1~2.3 times higher than the one without vacancy!

Protective Scales



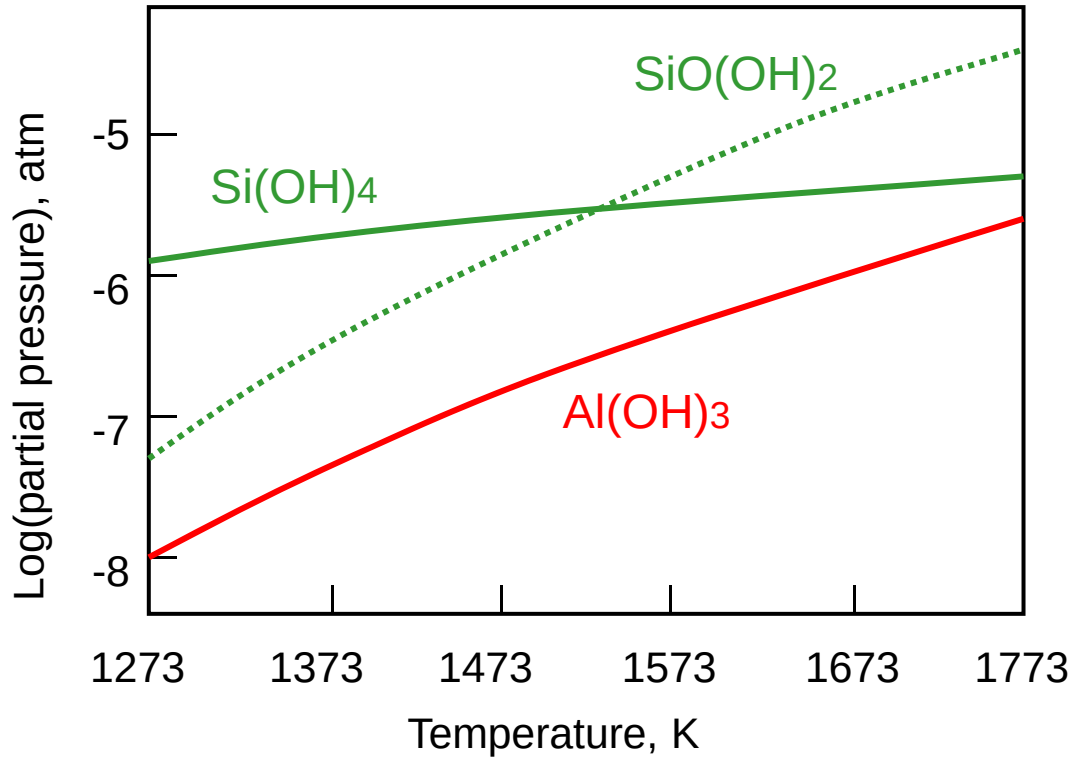
See that the slow-growing oxides in air are:

- Cr_2O_3 (chromia)
- Al_2O_3 (alumina)
- SiO_2 (silica)



B. Gleeson, Corrosion and Environmental Degradation, *Materials Science and Technology Series*, Vol. II, p. 179

Water vapor is present in the combustion environments, so that the coating of choice must be stable in water vapor at these elevated temperatures.

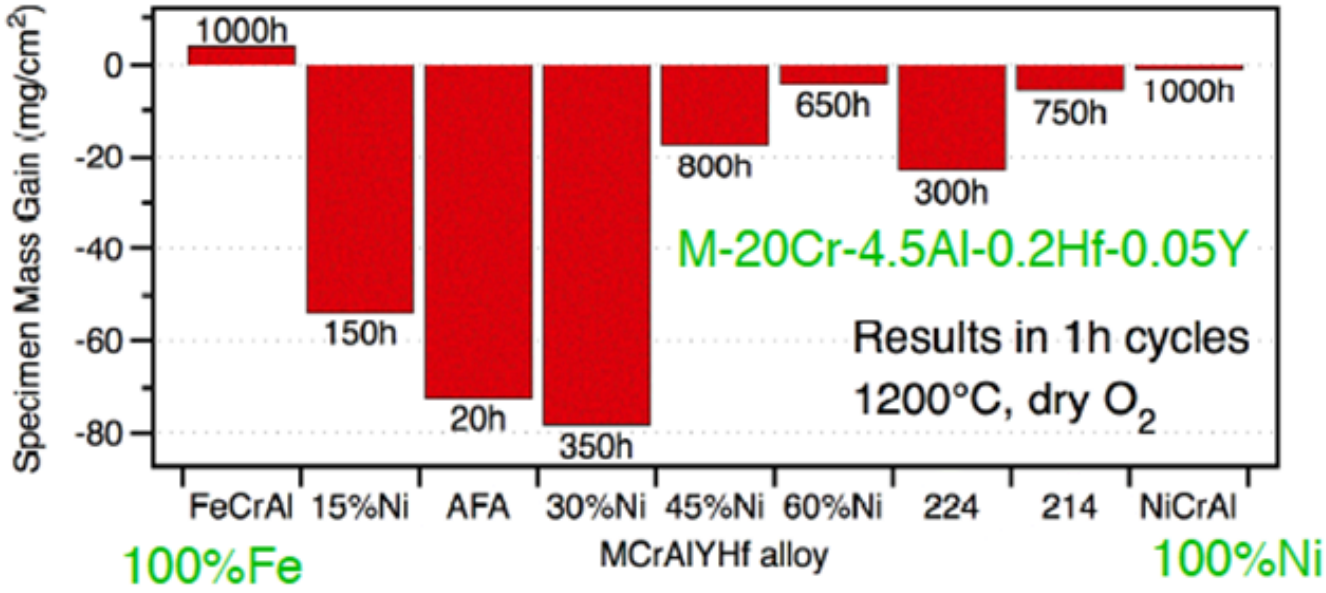


$Cr_2O_2(OH)_2$ *is way off the scale*

Comparison of silica and alumina volatility in 1 atm water vapor.
[*after E.J.Opila and D.L. Mayers (2003)*]

See that an alumina-scale forming system is preferred in steam-containing environments

An important practical aspect of this project



Possible Mechanisms:

- N_{Al}^{*} may change markedly with Ni:Fe ratio.
- D_{Al} may be different, which can affect the healing ability of a given alloy.
- k_c may be different.
- Coefficient of thermal expansion (CTE) may vary significantly with change in Ni:Al ratio.

Figure from: B. Pint, *Materials Science Forum*, **696** (2011) pp. 57-62.