NETL-RUA
Regional University Alliance

U.S. DEPARTMENT OF ENERGY

# An Integrated Computational Approach to Predicting Protective Oxide Scale Formation in FE Relevant Environments

David E. Alman

NETL · Carnegie Mellon · PENNSTATE · University of Pittsburgh · VirginiaTech · WestVirginiaUniversity · URS

# Acknowledgement and Disclaimer

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# Project Scope and Team

**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 ➡ $O_2$, $H_2O$, $CO_2$**

## *Computational*

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

## *Experimental*

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

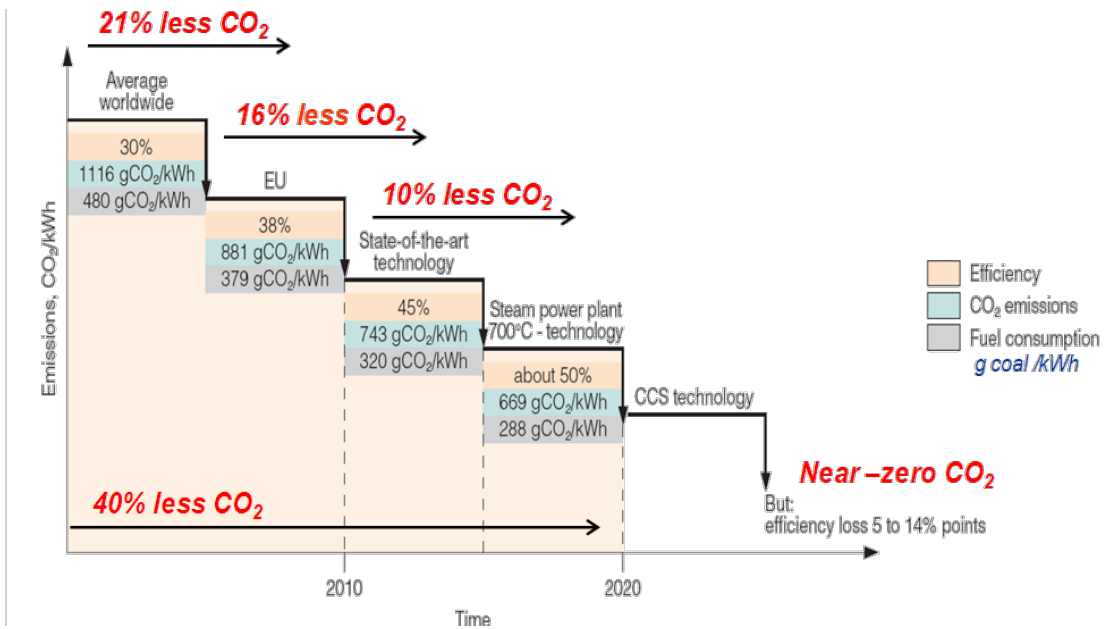
## *Task 1 Atomic Level Simulations*

- *Phase Equilibria; Structural Parameters (EOS); Solubility Parameters; Diffusion Coefficients, CTE.*

## *Task 2 Micro-kinetic Model Development*

- *Critical Al content for $Al_2O_3$ formation in Ni-Fe-Al alloy in different environments – utilizing atomic simulations; Extension to $Cr_2O_3$; Extension to kinetic rate determination*

# NETL-RUA: Integrated Materials Initiative



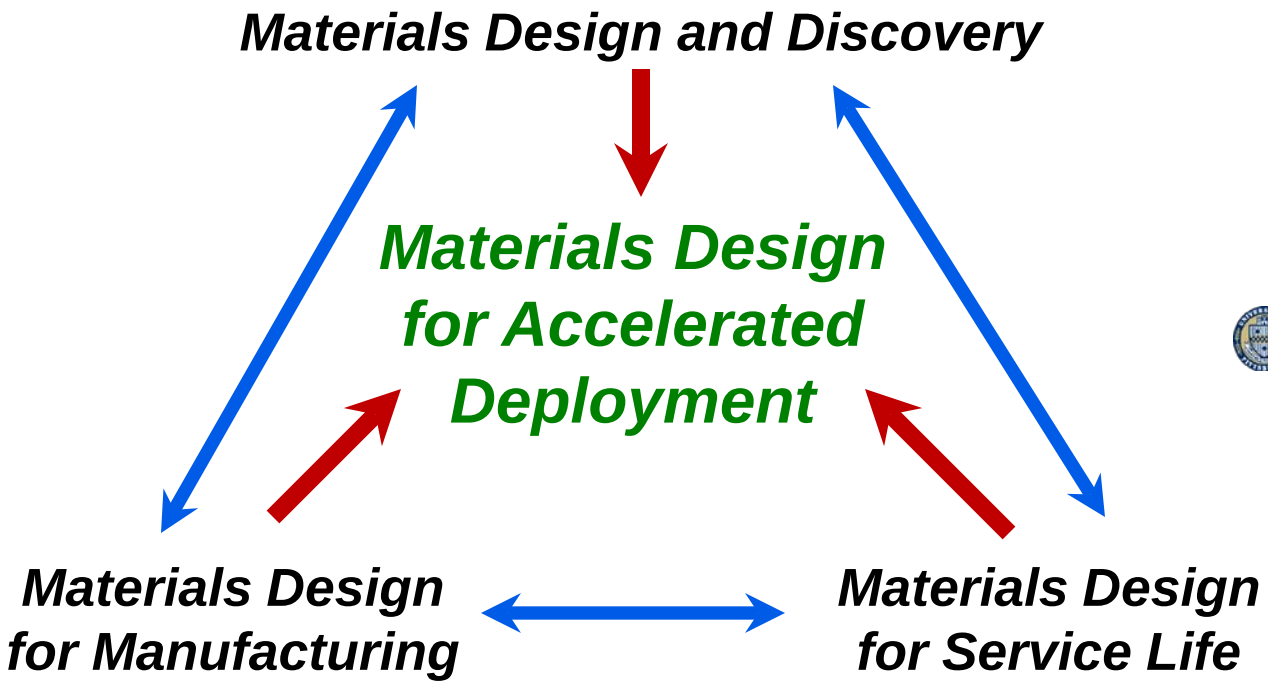

## Advanced Energy Systems: A-USC, Oxy-Comb, CLC, Comb Turbines

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

***Need for reliable and fast methods for predicting materials performance to accelerate materials design or identification – accelerate deployment and enable advanced technology***

***Develop a set of inter-related computational tools to predict performance of alloys in environments and time scales relevant to FE systems.***

# NETL-RUA: Integrated Materials Initiative

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URS

PENNSTATE

Carnegie Mellon University

VirginiaTech Invent the Future

University of Pittsburgh

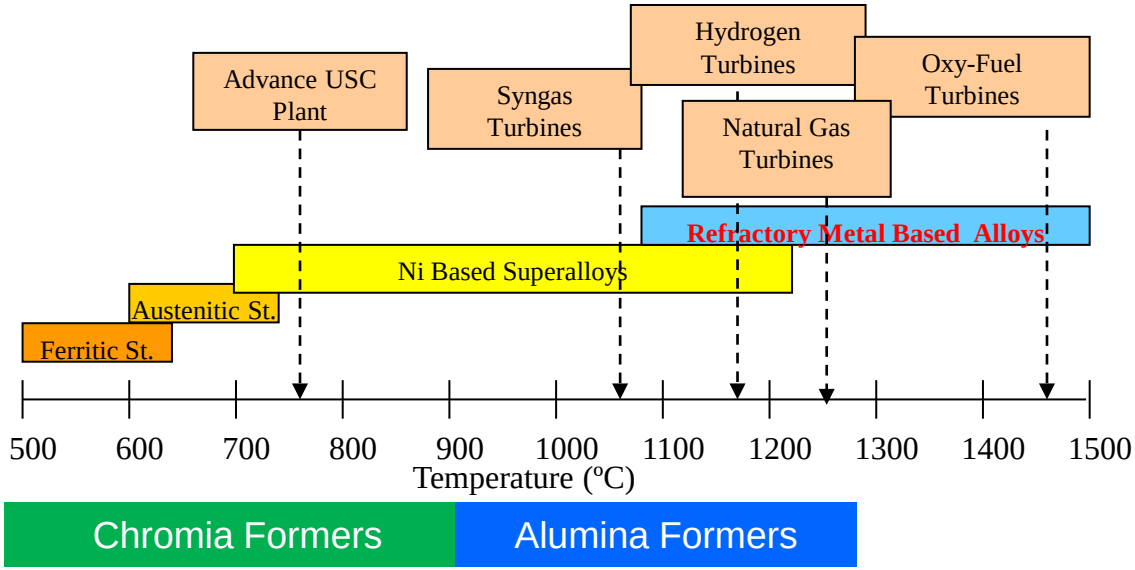
WestVirginiaUniversity

NETL

# Principal Project Goal

**Develop computational tools to reliably predict the formation of protective scales in conditions of relevance to advanced FE systems.**

- Compositions necessary for protective-scale formation
- Initial focus will be on $Al_2O_3$ formers.



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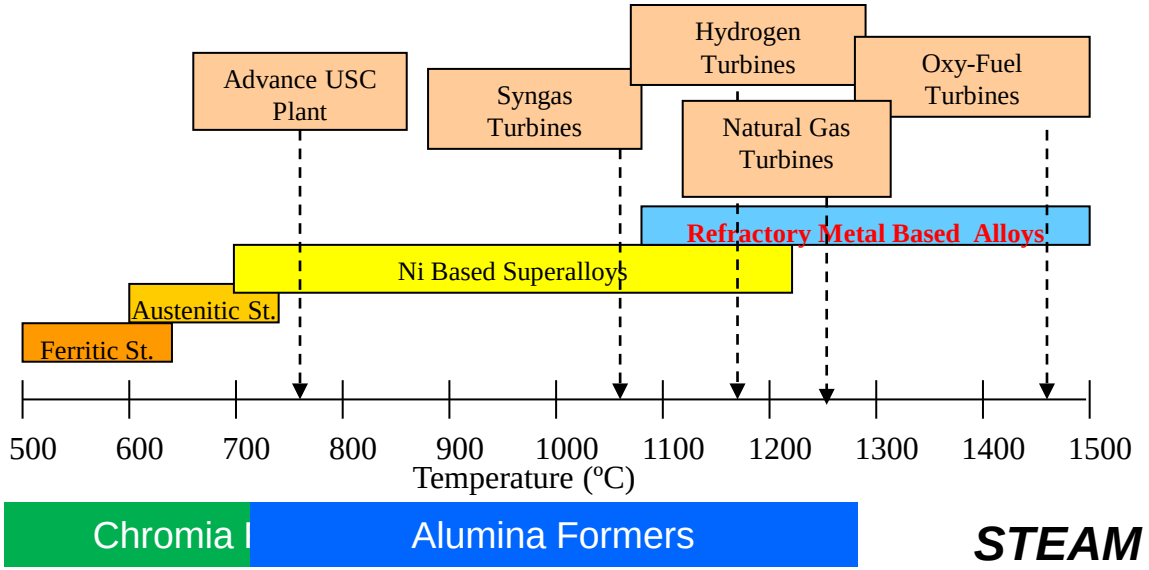
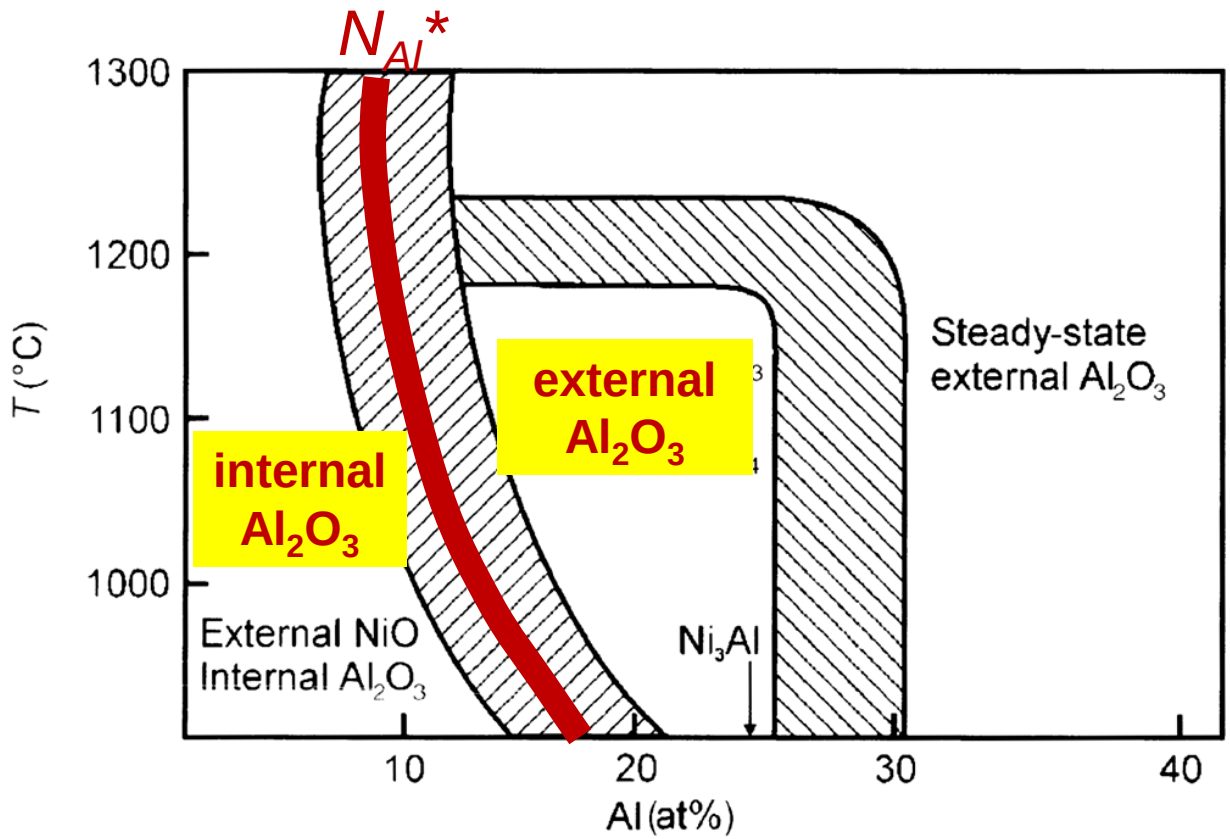


# Alumina Scale Formation on Ni-Al Alloys

*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.

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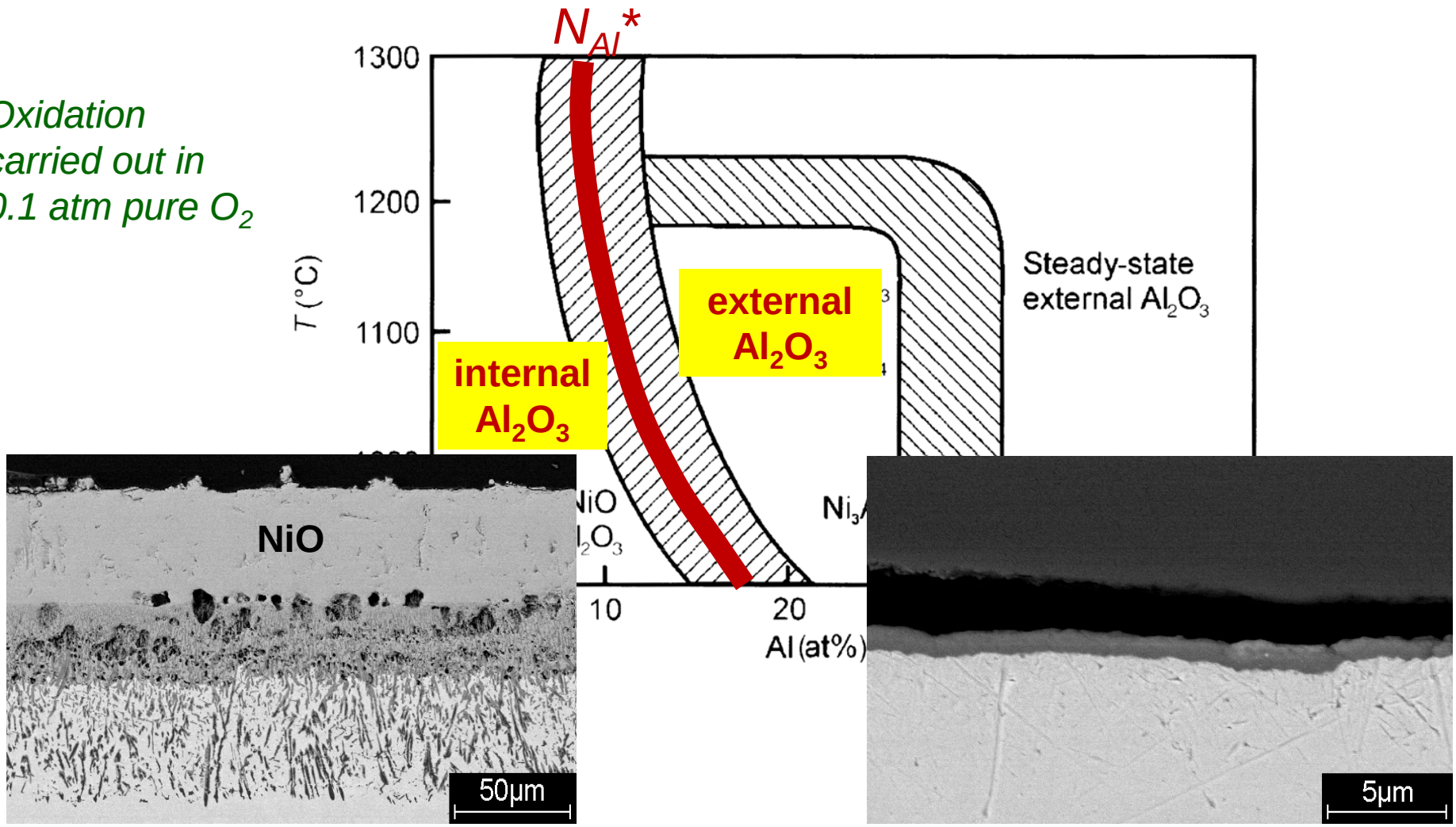
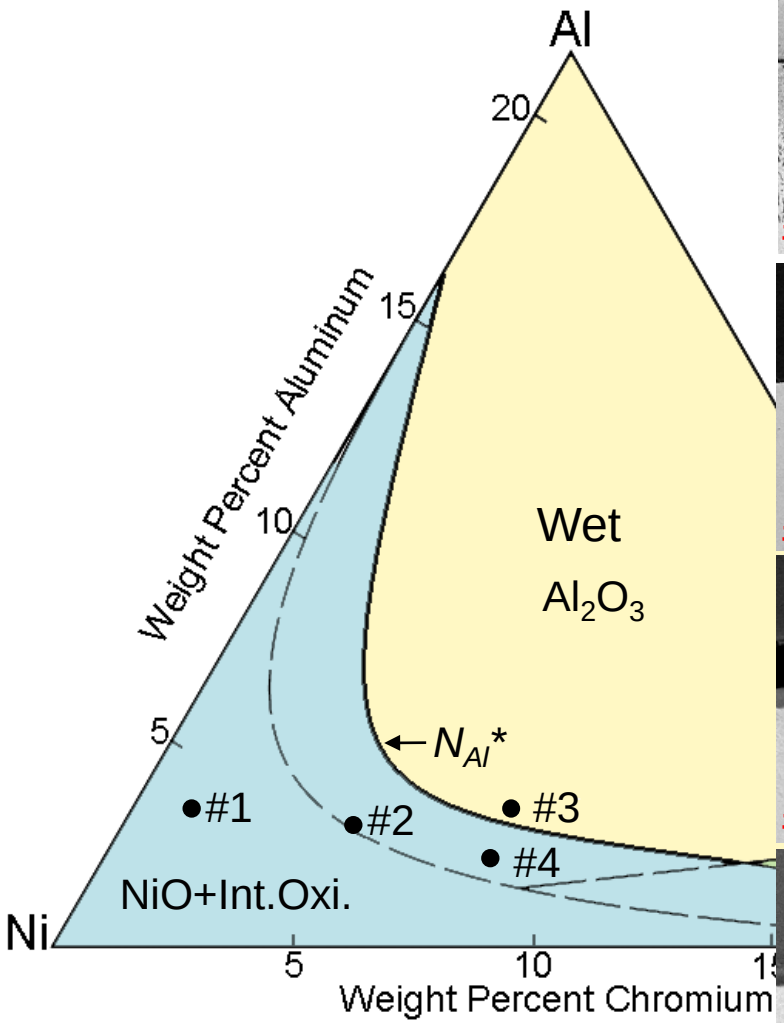
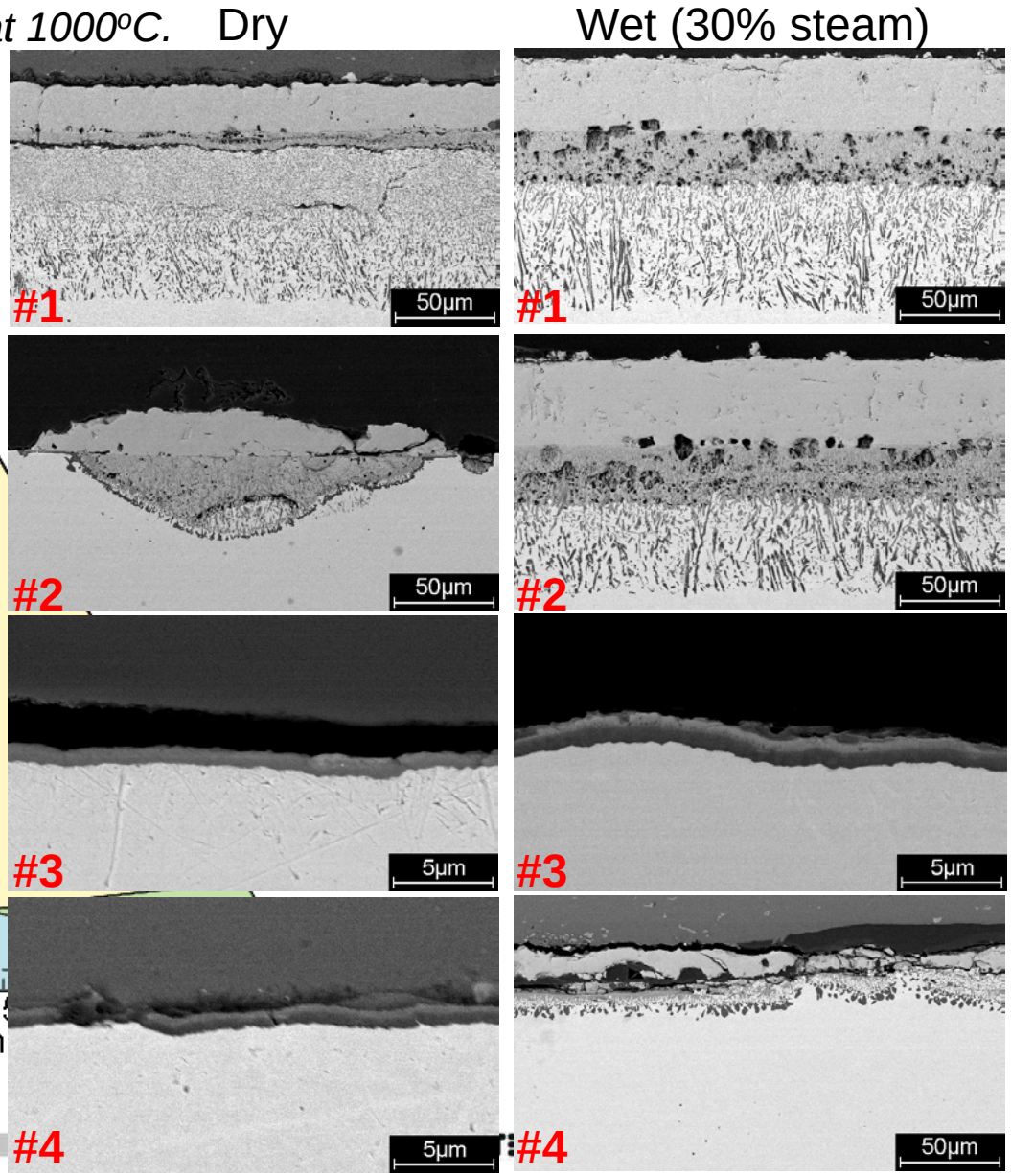



F.S. Pettit, "Oxidation mechanisms for Ni-Al Alloys at temperatures between 900 and 1300°C," *AIME Met. Soc. Trans.*, **239** (1967) 1296.

# Cr and Steam Effects 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.*

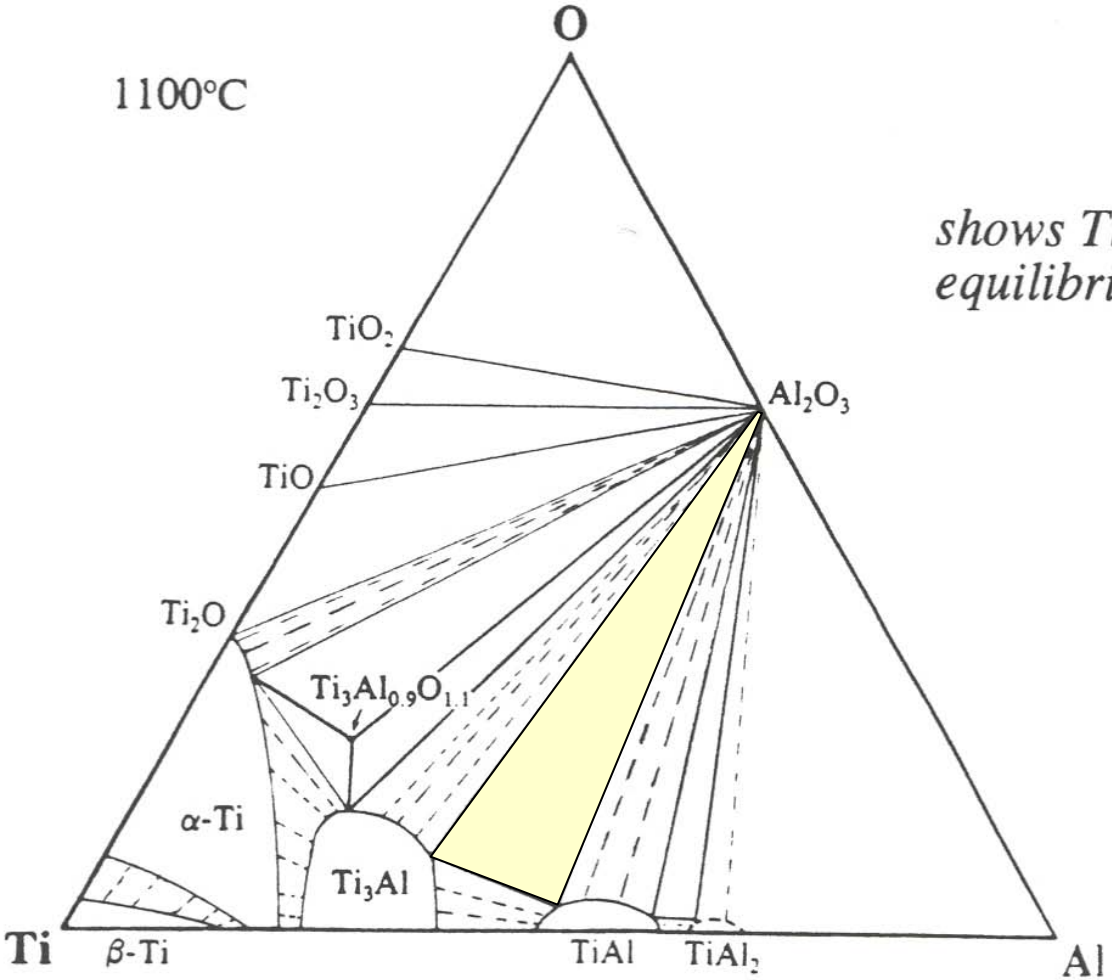





*C.S. Giggins and F.S. Pettit, *J. Electrochem. Soc.*,**118** (1971) 1782

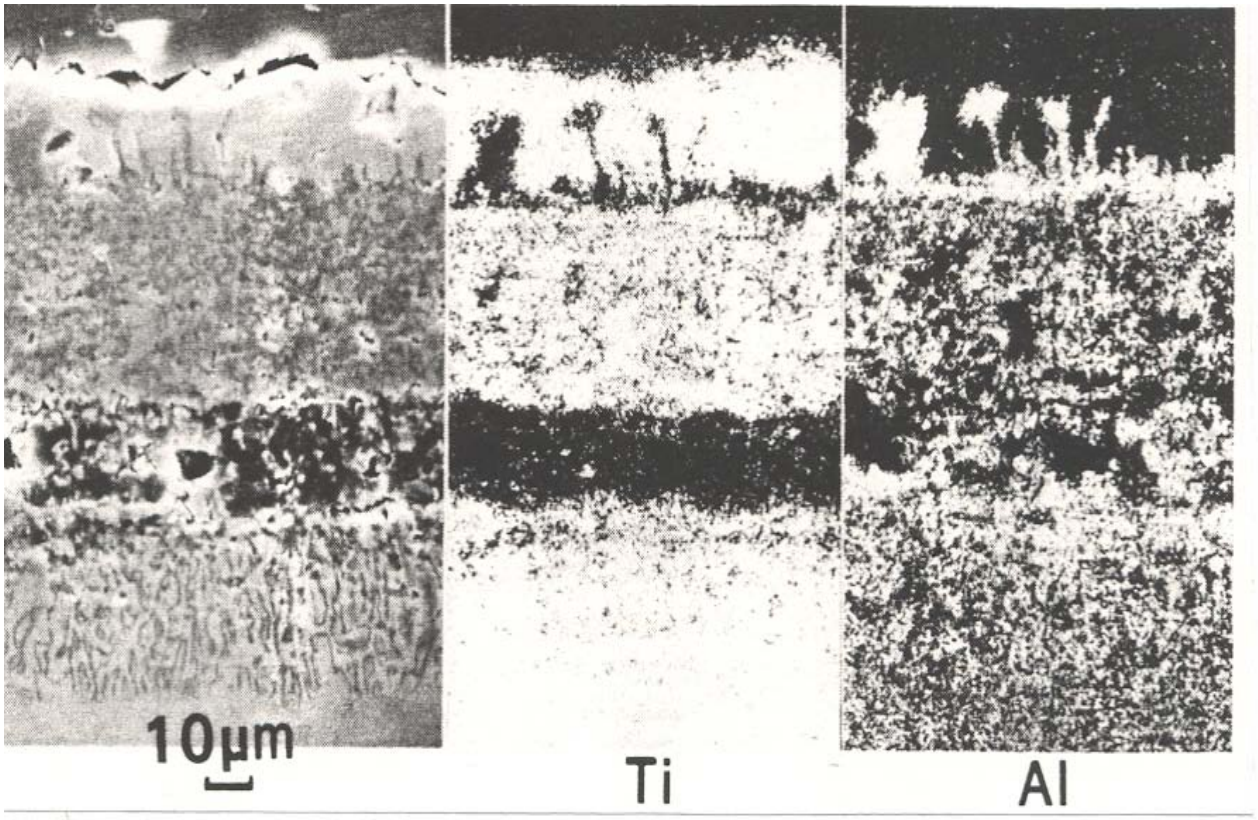
# An Equilibrium Thermodynamic Approach to Alloy Oxidation




*shows $Ti_3Al$ + $TiAl$ + $Al_2O_3$ equilibrium*

# Oxidation of a $Ti_3Al$+TiAl Alloy at 1100°C for 24h in Dry $O_2$

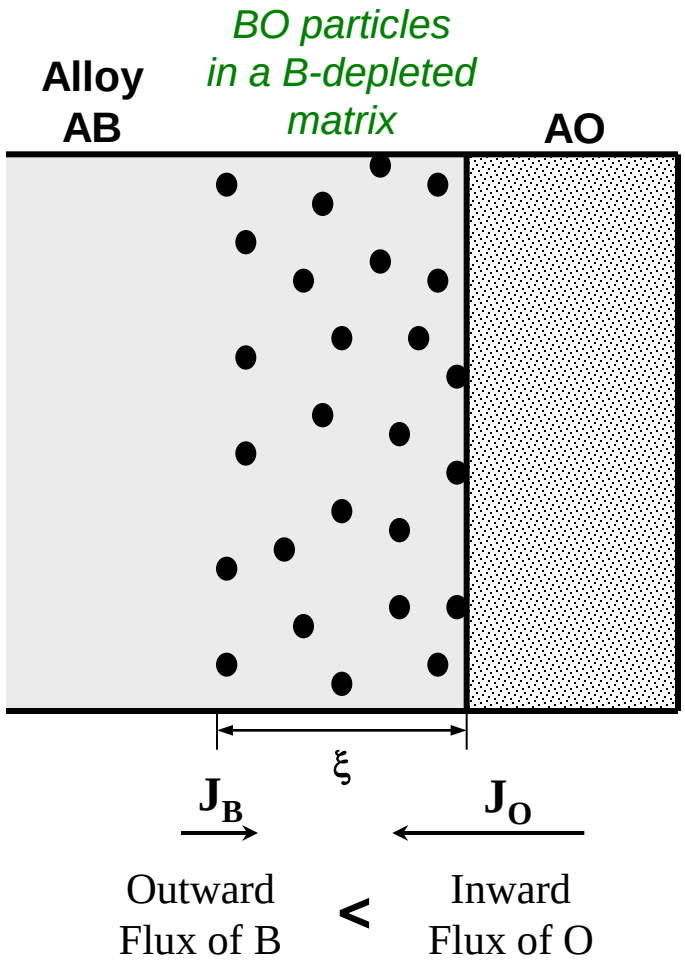
➡ *forms a mixed oxide of $TiO_2$ and $Al_2O_3$*



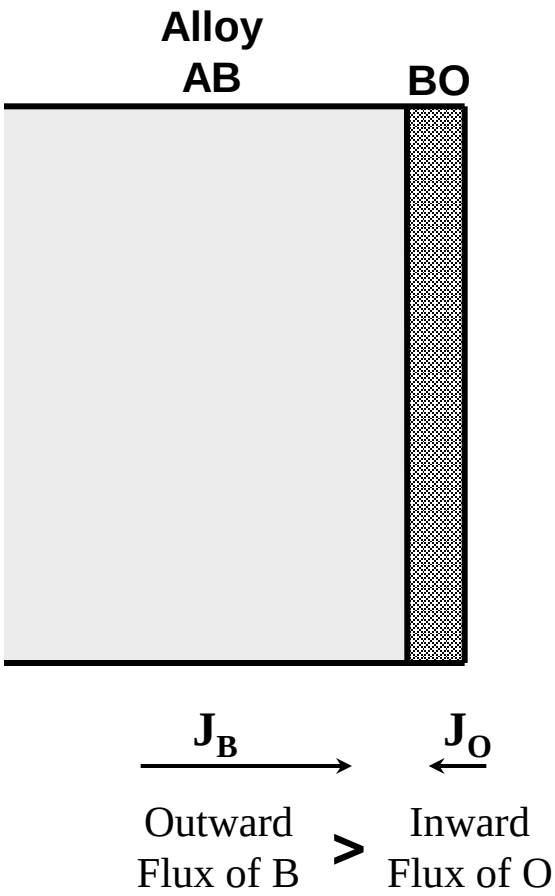

*Kinetic factors dictate the constitution of the scale formed.*

# Limiting Situations for Single-Phase Binary Alloy Oxidation

## Internal BO formation




## External BO formation



# Limiting Theoretical Equation for Single-Phase Binary Alloys

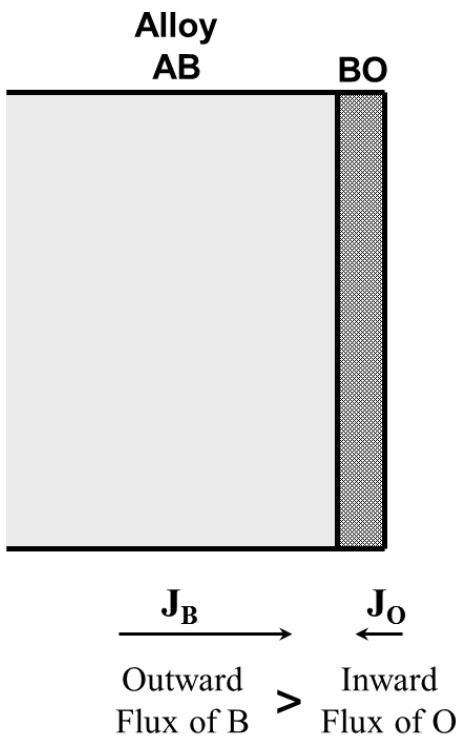
*Critical Concentration of B for the Transition from Internal to External $BO_v$ Formation*

$$N_B^* \geq \left[ f^* \left( \frac{V_{alloy}}{V_{ox}} \right) \pi \frac{N_O^S D_O}{2\nu D_B} \right]^{1/2}$$

$N_o^s D_o$ = 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 the Ni-Al System at "High" $P_{O_2}$

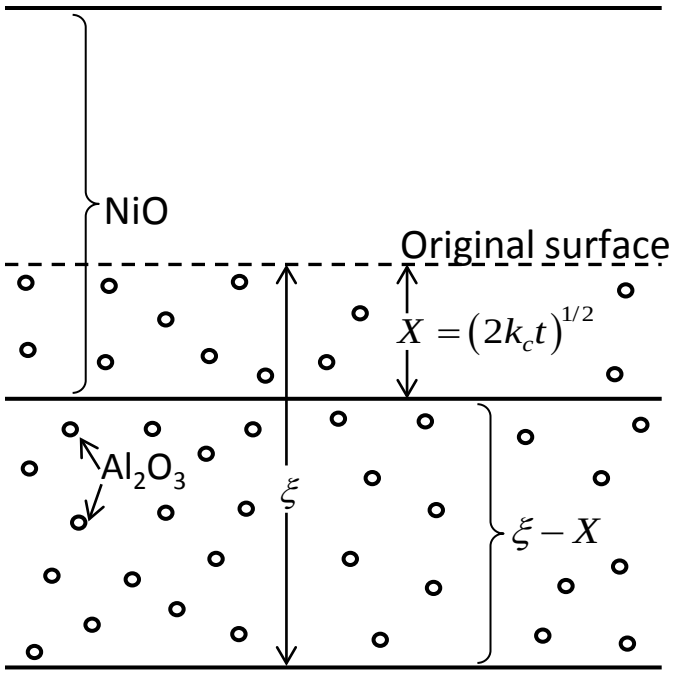
From theoretical analysis[1,2] $N_{Al}^*$ for the transition from internal to external $AlO_{1.5}$ formation is:

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

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

To determine $\gamma$ :

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




(2) Numerically

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

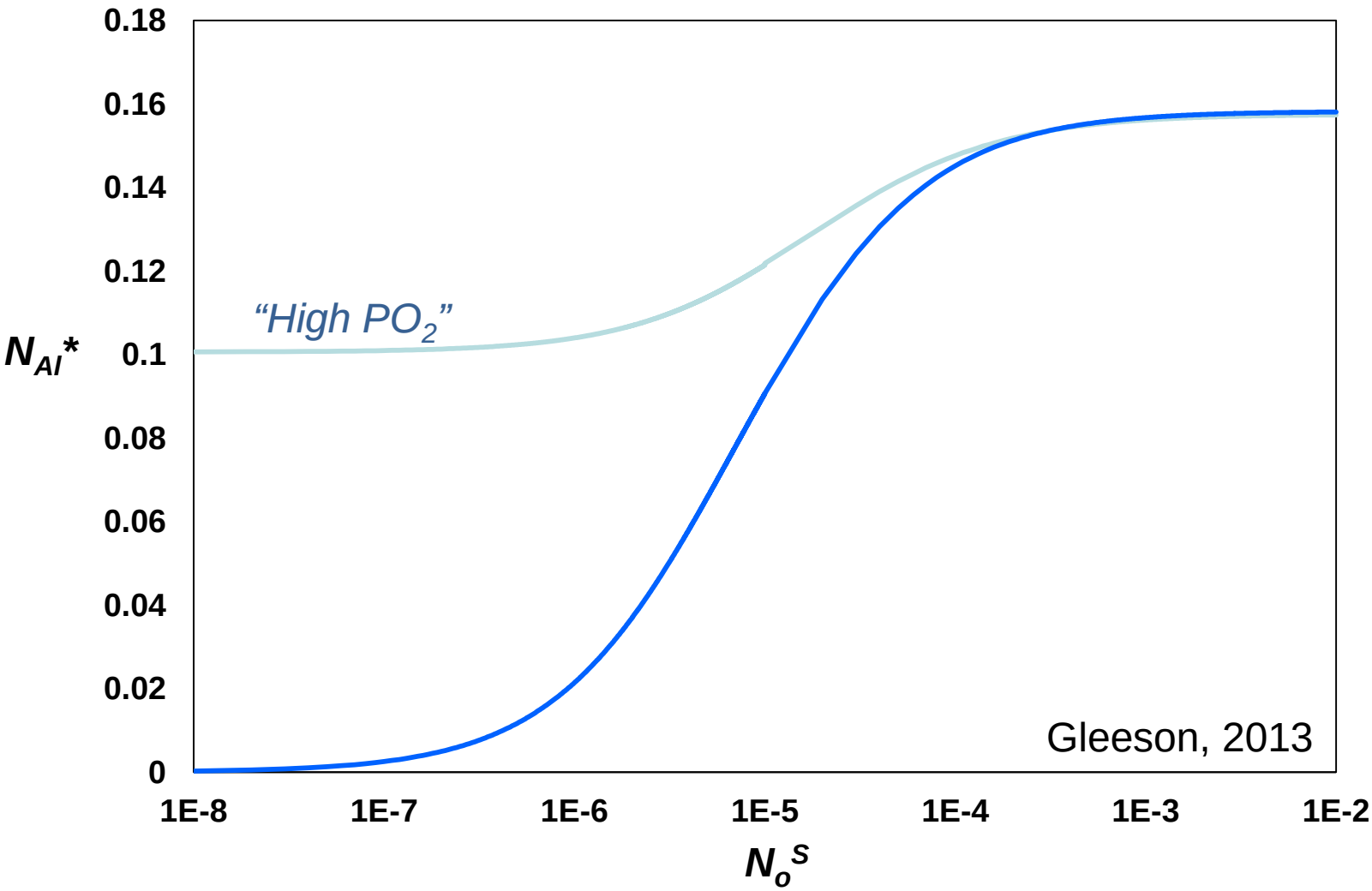
$$\frac{N_O^s}{\nu N_{Al}^0} = \frac{erf(\gamma) - erf(u)}{erf(\gamma)} \frac{G(\gamma)}{F\left(\gamma\varphi^{1/2}\right)}$$

$N_o^S$ = solubility of oxygen on the scale/alloy interface
$N_{Al}^0$ = mole fraction of Al in the bulk alloy
$\nu$ = 1.5 (stoichiometry factor in $AlO_{1.5}$)
$G(r) = \pi^{1/2} r \exp(r^2) erf(r)$



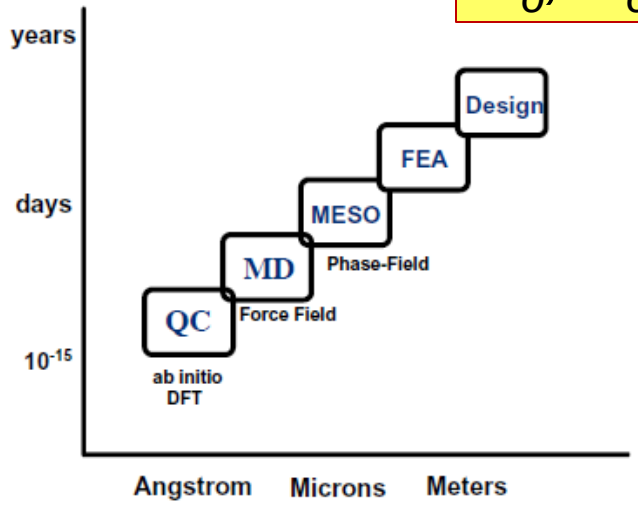

1 C. Wagner, Z.Elektrochem. 63, 772 (1959), F. Maak, Z. Metallkde. 52, 545 (1961)
2 F. Gesmundo and F. Viani, Oxid. Met. 25, 269 (1986)

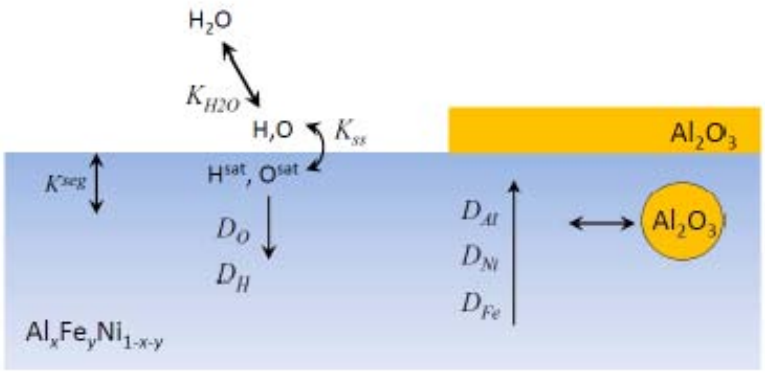
# The occurrence of scaling can affect $N_{Al}$*

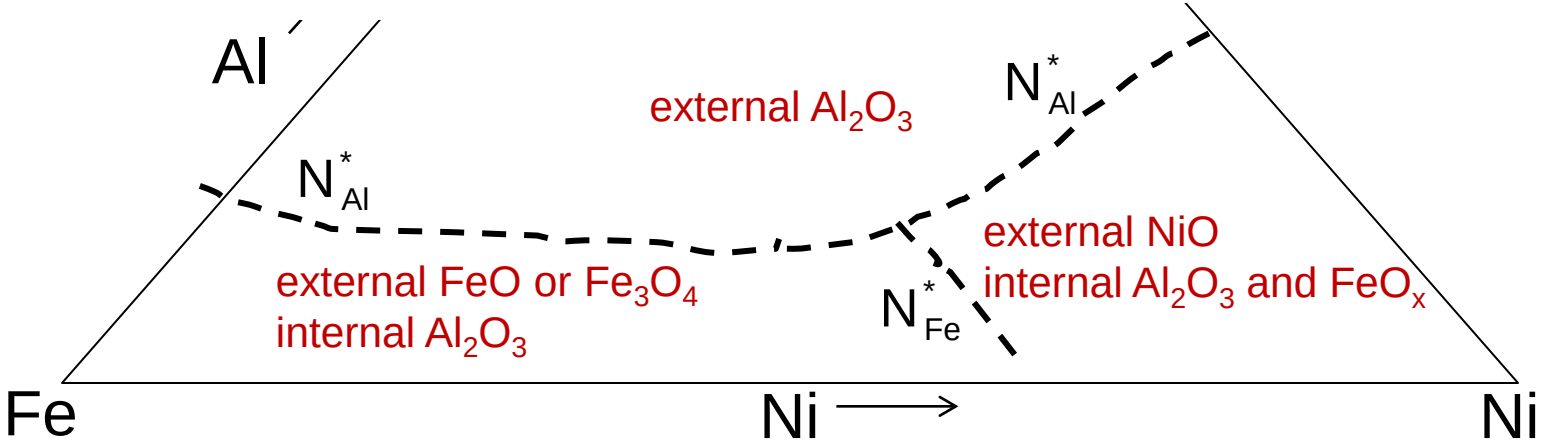


# Multi-scale computational prediction of $N^*_{Al}$

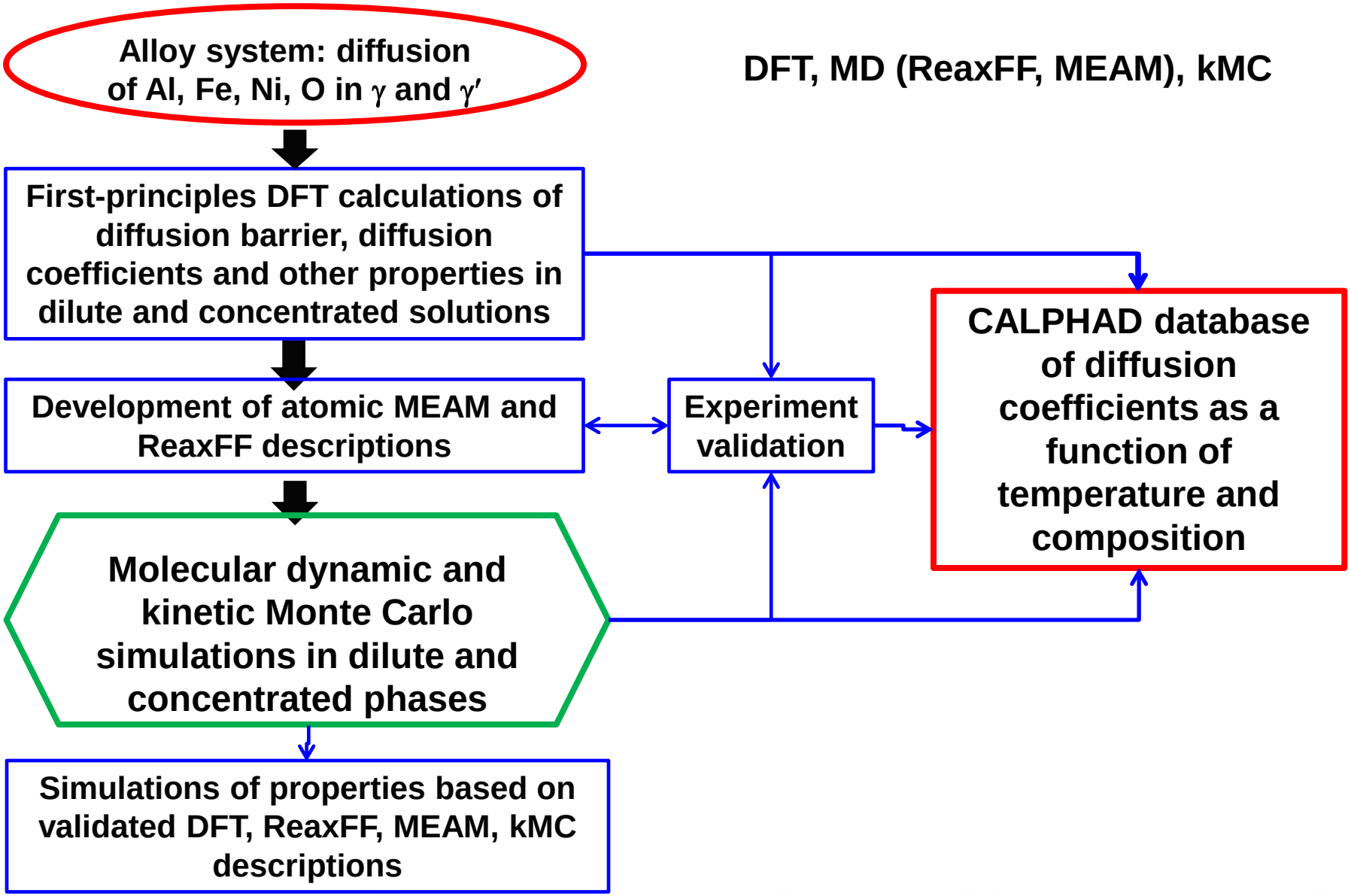
*$D_o$, $N_o$, $D_{Al}$ → alloy composition, $H_2O$, $CO_2$*



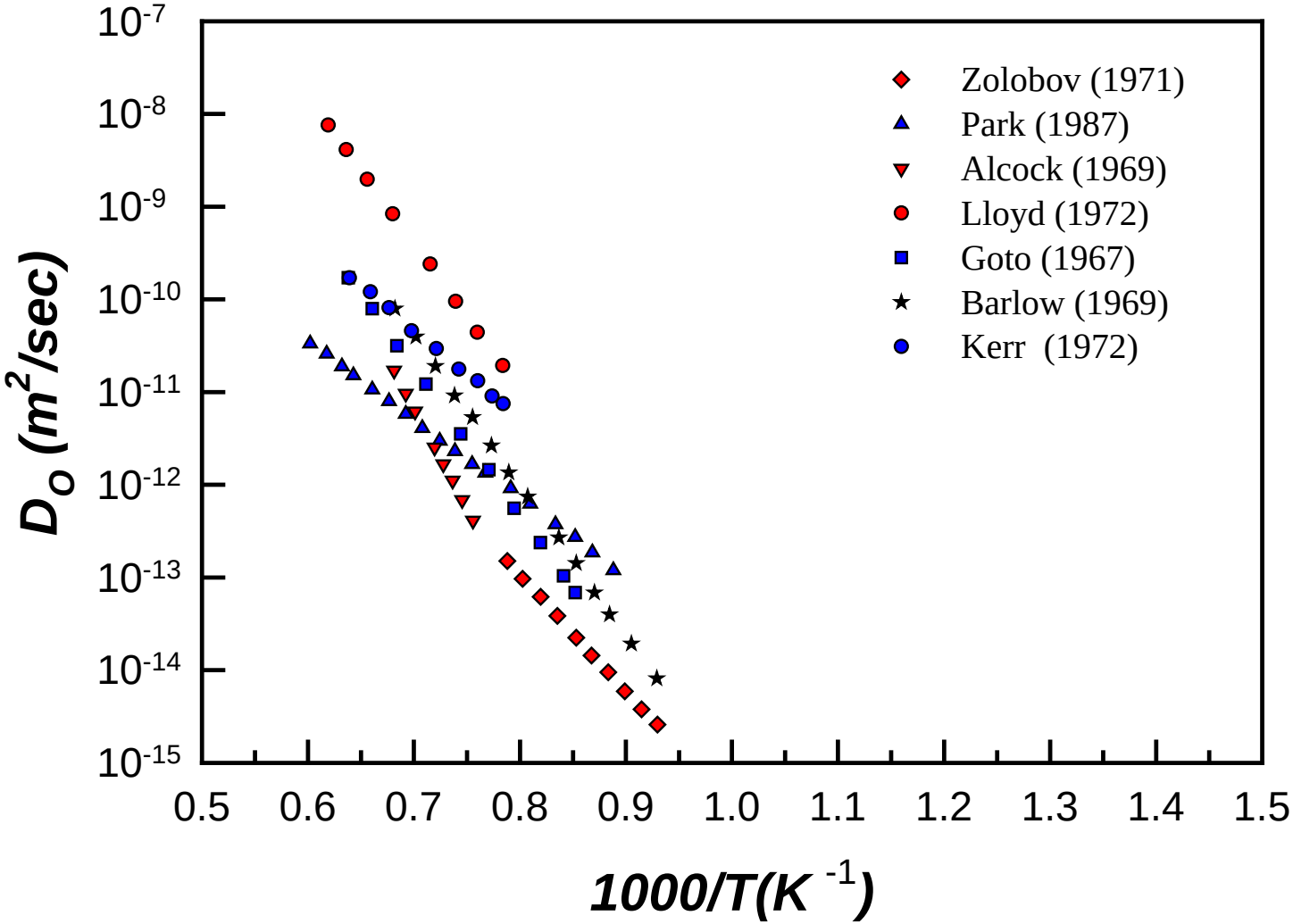



# Computational Framework to Predict Diffusion



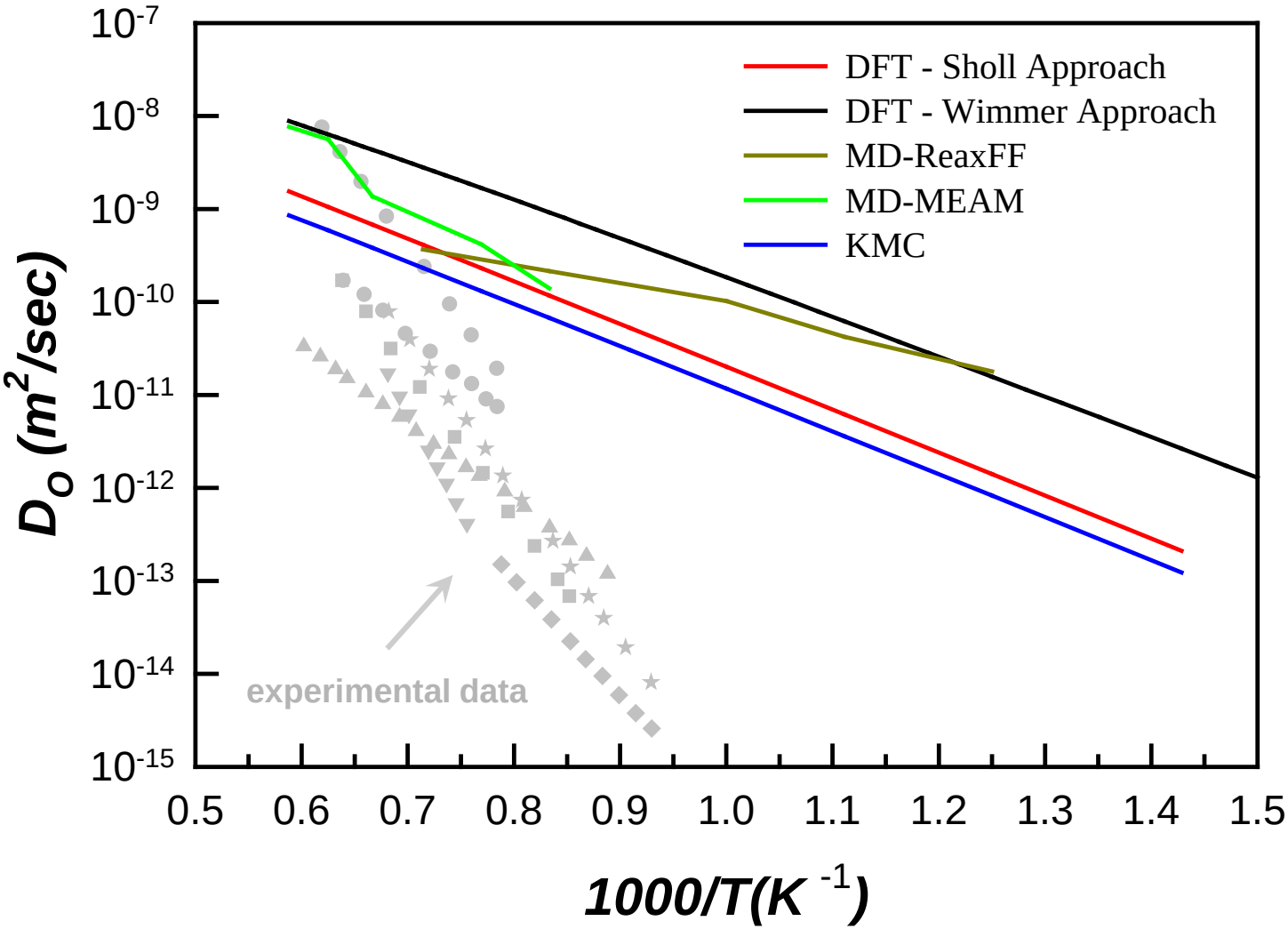
# Simulations to Predict Oxygen Diffusivity in Nickel

$D_o$ from experiments in the literature

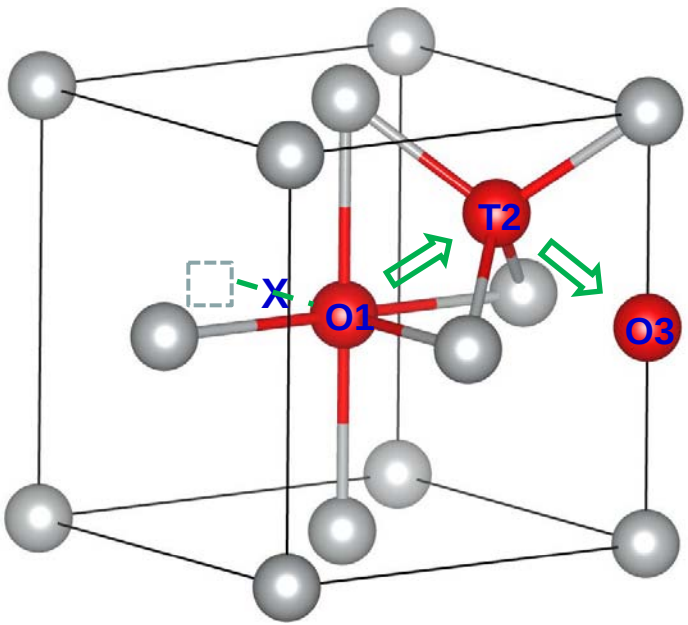


# Simulations to Predict Oxygen Diffusivity in Nickel

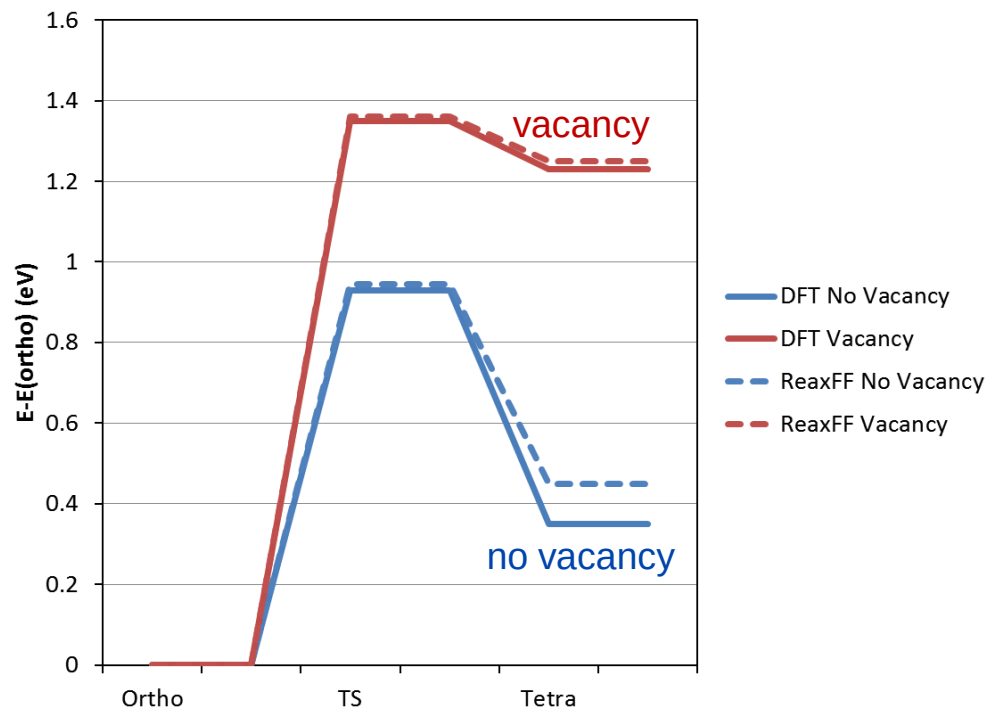
Predictions for $D_O$ in a perfect Ni lattice (i.e., no vacancies)



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



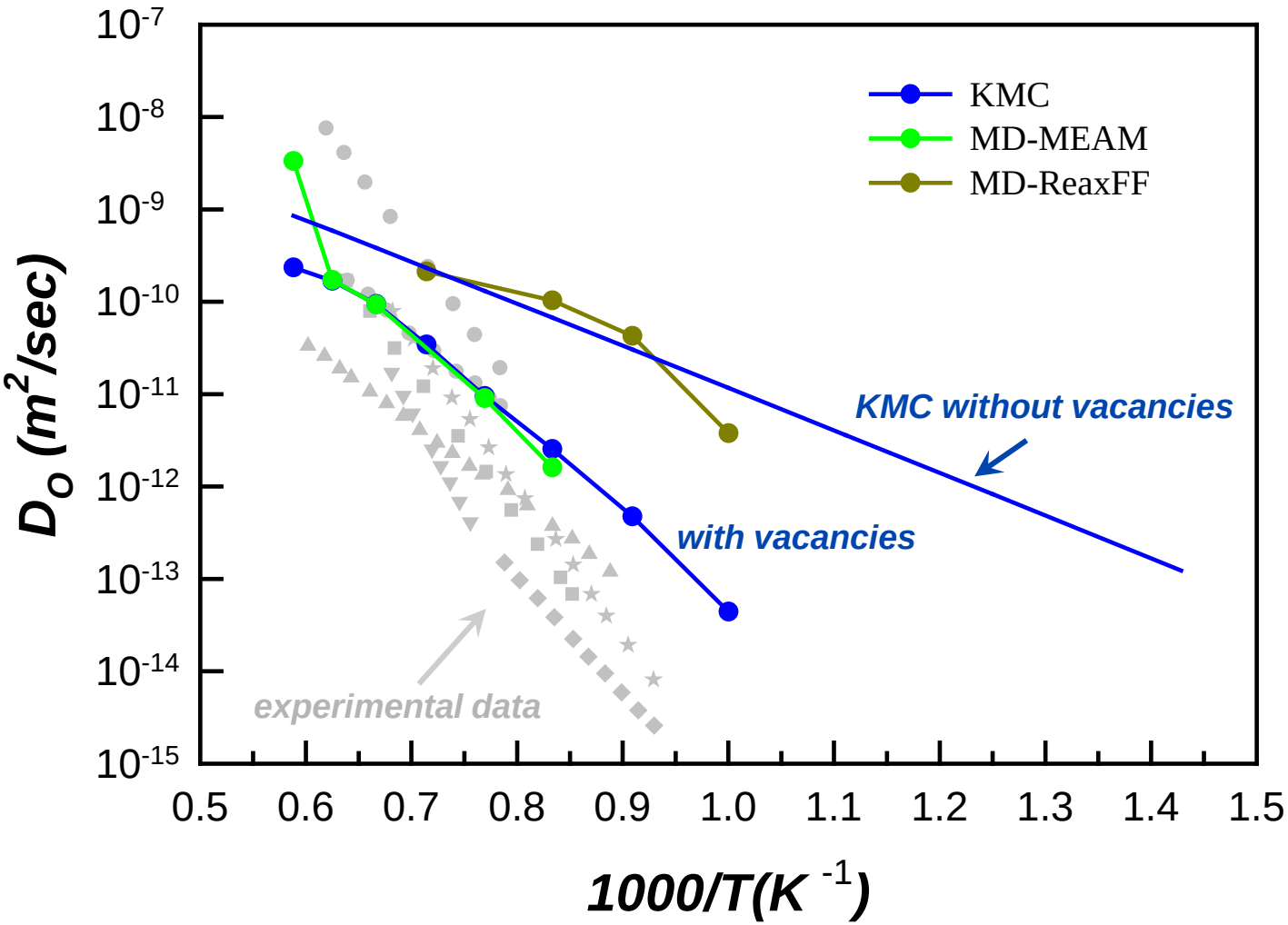

vacancy site



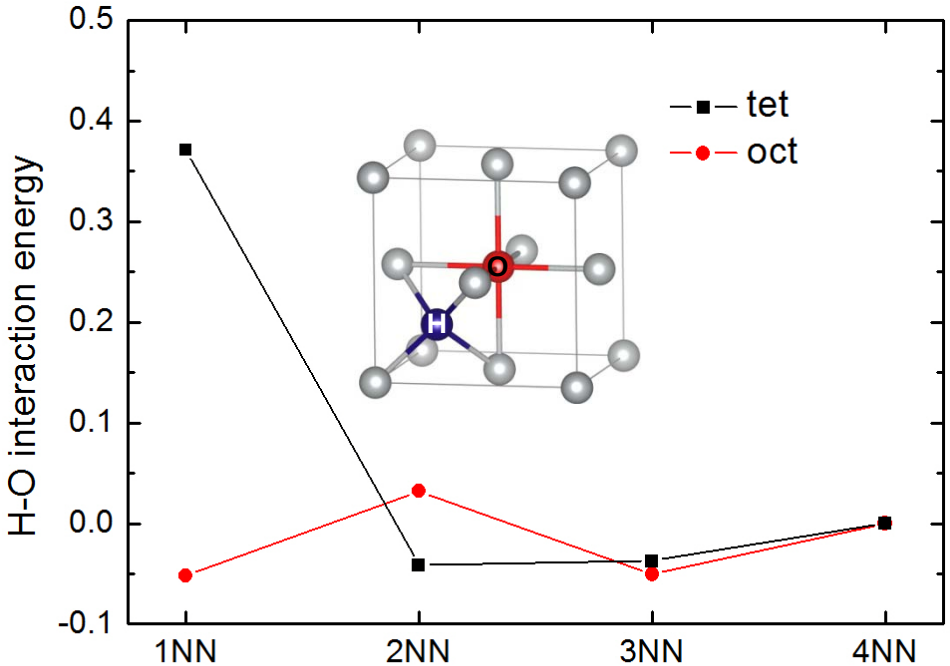

There is a very strong binding energy of ~1.25 eV between oxygen and vacancy. To diffuse away from the vacancy, the oxygen has to overcome a barrier which is 2.1~2.3 times higher than the one without vacancy!

# Simulations to Predict Oxygen Diffusivity in Nickel

*Predictions for $D_O$ in a Ni lattice (incorporating vacancies)*



# The Effect of Hydrogen on Oxygen Diffusion in Nickel




H at various sites with O at the *oct*.

Diffusivities estimated by AIMD at 1500K

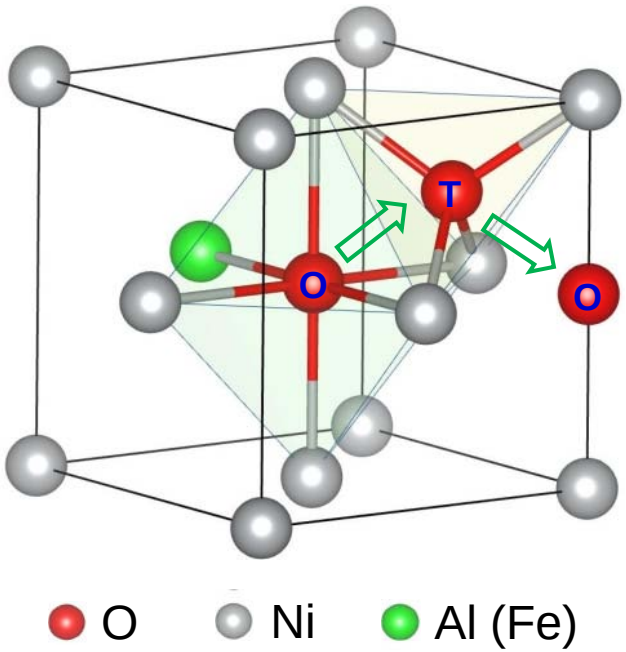
O in pure Ni: $4.3\times10^{-9}$ $m^2/s$

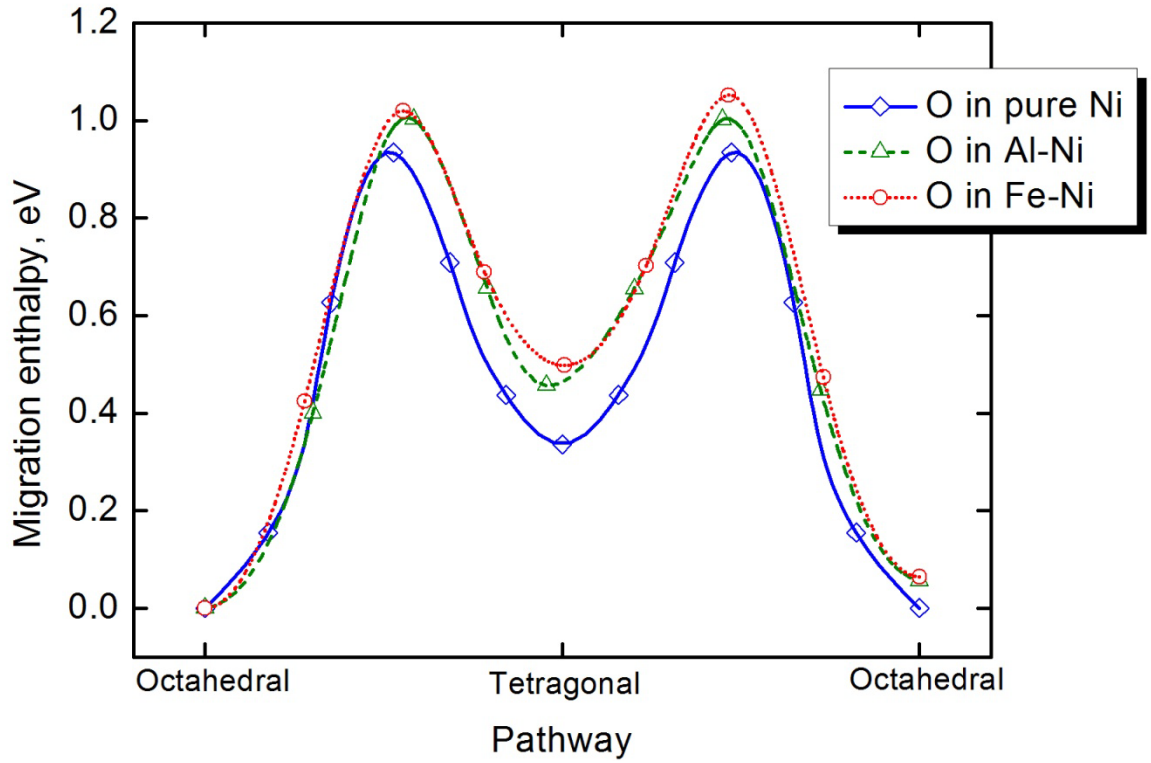
O in H-Ni dilute solution: $6.4\times10^{-9}$ $m^2/s$

.

The binding energy between H and O is found to be very weak, *i.e.* 0.04 eV.
H diffuses very fast compared to O.

# First Principles Approaches to Determine Oxygen Diffusivity in Nickel – *effect of alloying elements*

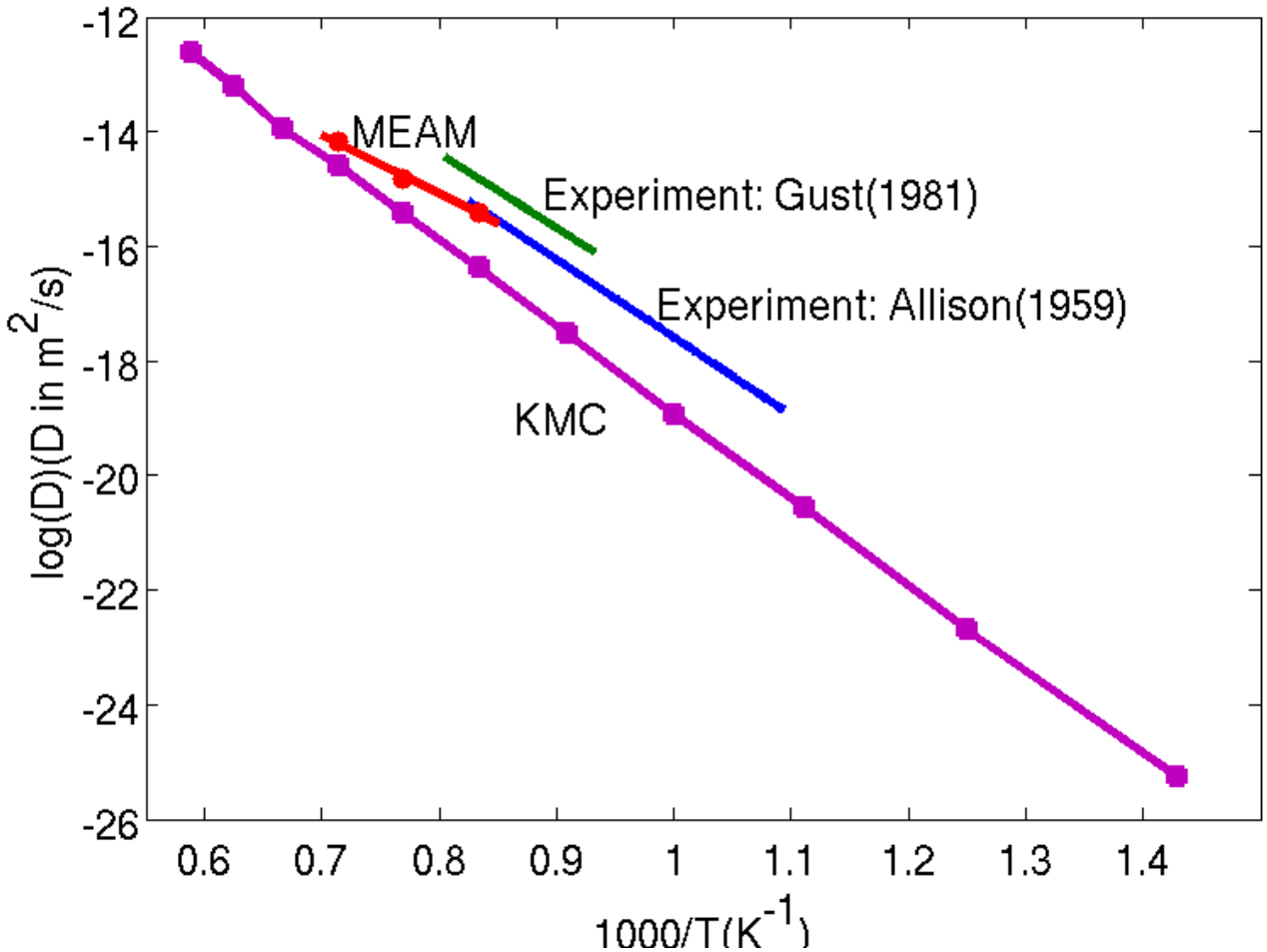



Oxygen diffusion barrier: 0.93 eV (in pure Ni), 1.00 eV (in Al-Ni), 1.05 eV (in Fe-Ni).

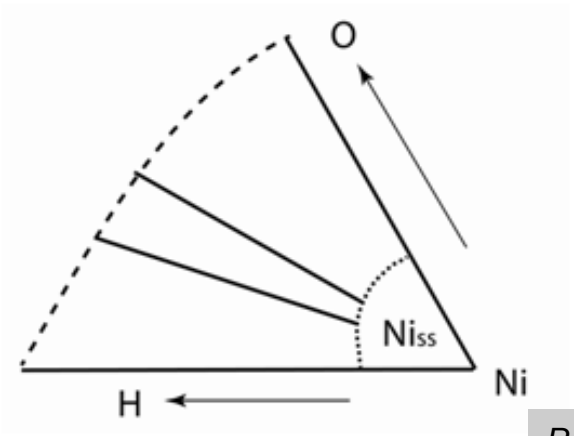
Alloying element Al or Fe only increases the diffusion barrier about 10% !

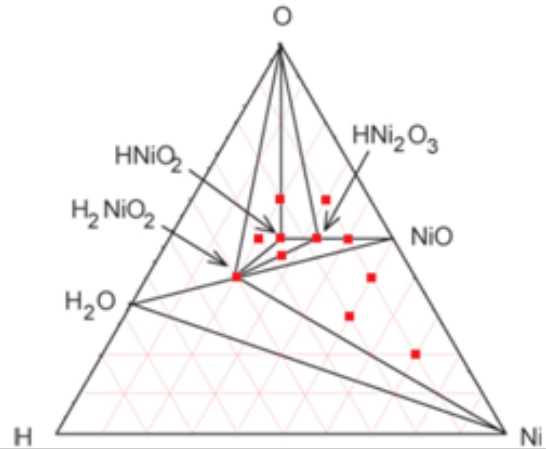
# Molecular Dynamic and kMC Simulations to Determine Al Diffusivity in Ni




[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).

# Ni-O-H Ternary Phase Diagram – Solubility




*RA Huggins, J Power Source 165 (2007) 640*

**Experimental effort**

a) Isotherms: 100°C. Samples are being processed.
b) phase transition and transition temperatures during heating and cooling (DTA or else)
c) Hydrogen solubility measurement using the Sievert method.
d) Hydrogen permeation test.

$$H = E(H_xNi_yO_z) - xE(H_2)/2 - yE(O_2)/2 - zE(Ni)$$

$E(H_2)$ and $E(O_2)$ is the total energy of $H_2$ and $O_2$ molecules in a box respectively.

**Taken from SSUB4 database @25°C)
Unit is kJ/mol of atoms.

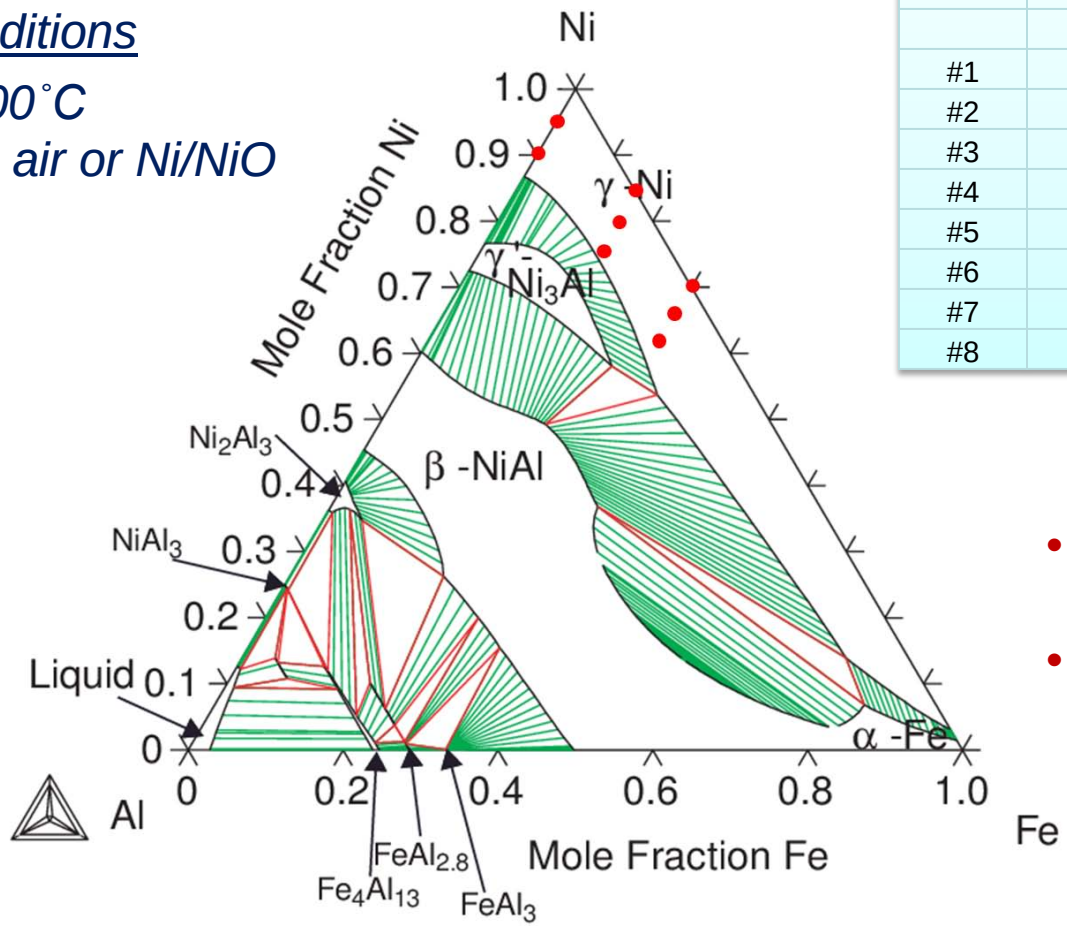
| | CALPHAD** | DFT | DFT-D2 | magnetic state |
|---|---|---|---|---|
| HNiO2 | -97.5 | -91.7 | -94.2 | nonmag |
| Ni(HO)2 | -106.6 | -99.3 | -104.7 | ferromag |
| HNi2O3 | N/A | -103.7 | -107.4 | antiferro |

# Oxidation Behavior of Bulk Fe-Ni-Al Alloys

*Experimental effort*

***Initial test conditions***

*T = 700 - 1000˚C*
*environment: air or Ni/NiO*




| | Atom Percent | | |
|---|---|---|---|
| | Ni | Al | Fe |
| #1 | 85 | 0 | 15 |
| #2 | 70 | 0 | 30 |
| #3 | 95 | 5 | 0 |
| #4 | 80 | 5 | 15 |
| #5 | 65 | 5 | 30 |
| #6 | 90 | 10 | 0 |
| #7 | 75 | 10 | 15 |
| #8 | 60 | 10 | 30 |

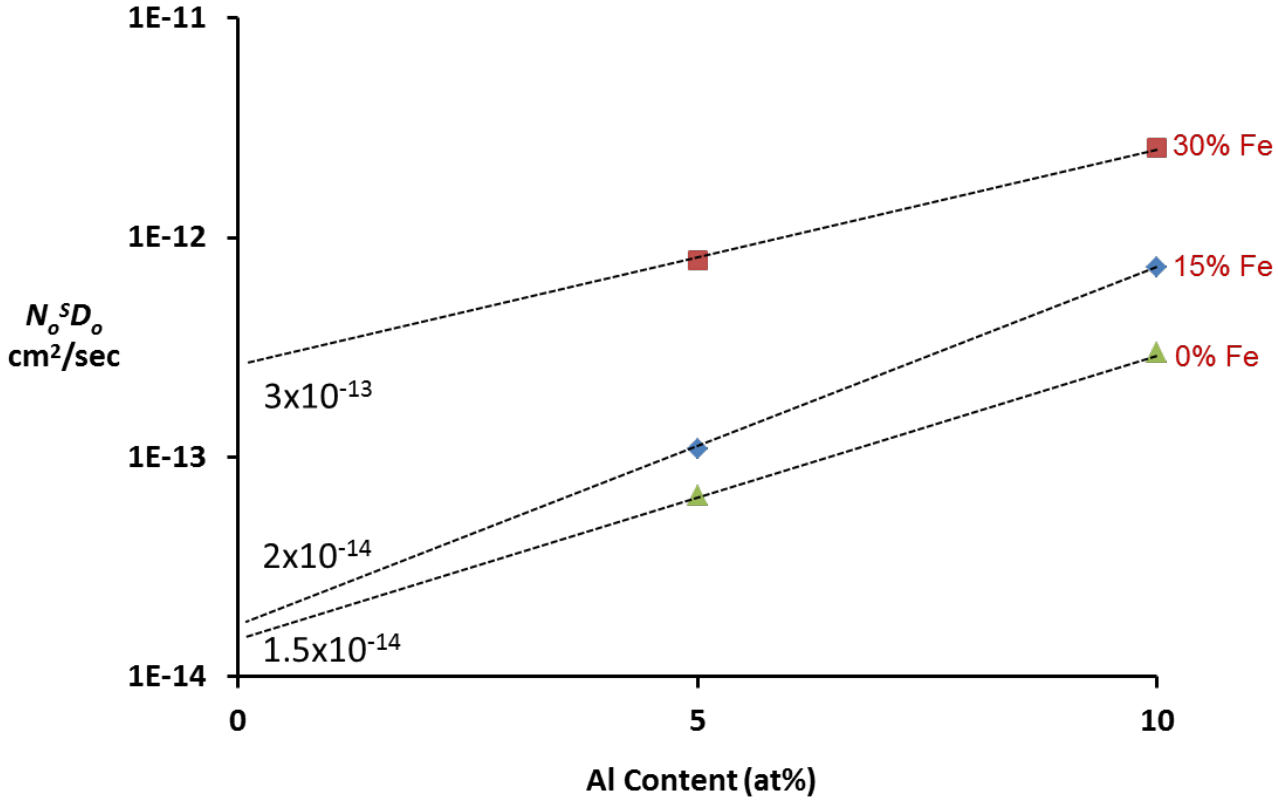
***Output Data***

- *internal oxidation behavior*
- *oxygen permeability, $N_O{}^s D_O$*

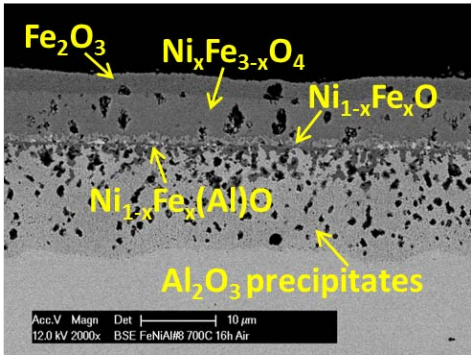
# Oxidation Behavior of Bulk Fe-Ni-Al Alloys

*Experimental effort*

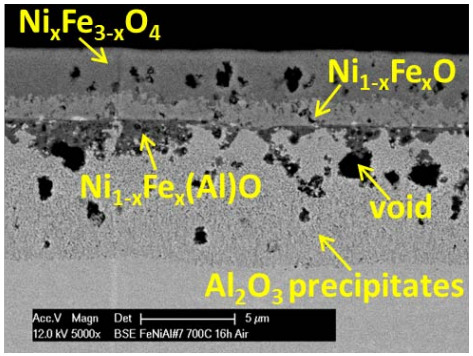
**Example of oxygen permeability measurements: Ni and Ni-Fe alloys at 700°C in air**



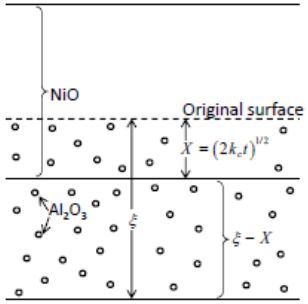

Ni-10Al-30Fe (x2000)




Ni-10Al-15Fe (x5000)



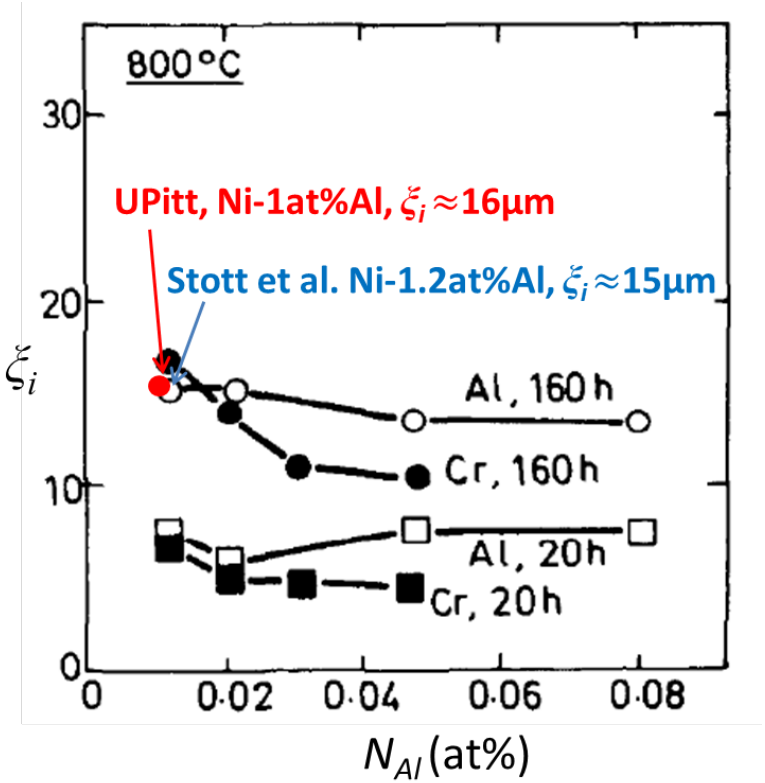

(1) Experimentally: $\xi = 2\gamma (D_O t)^{1/2}$

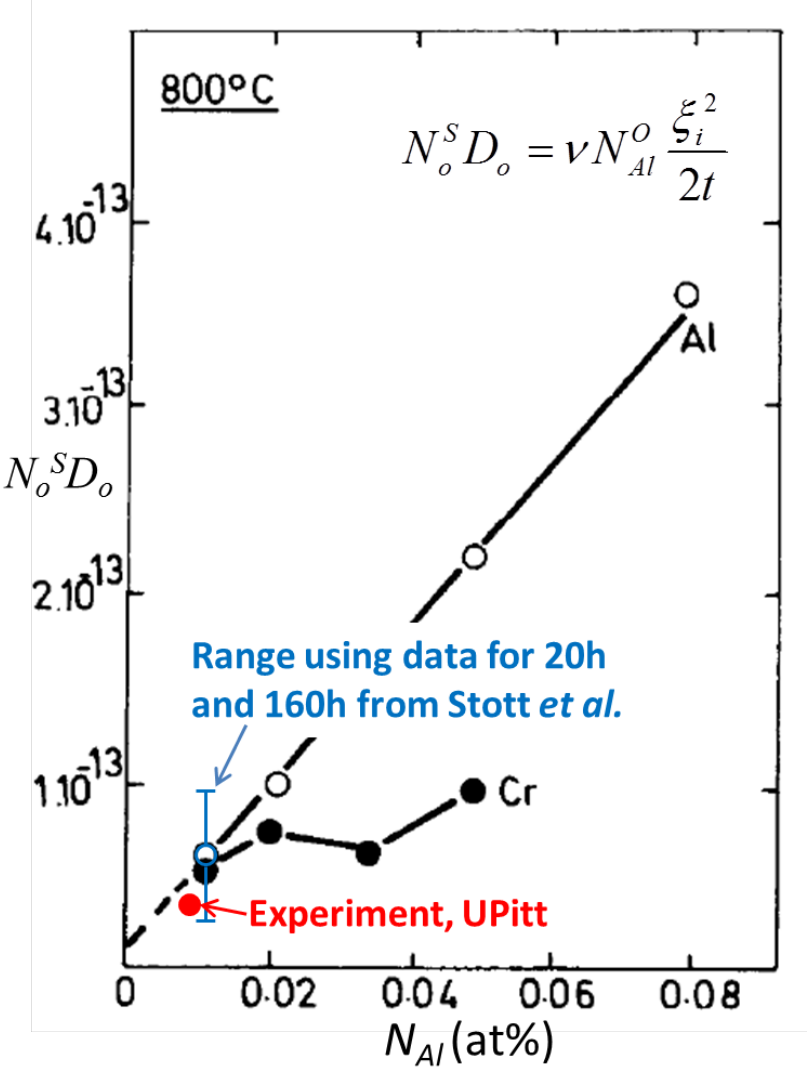


# Oxidation Behavior of Bulk Fe-Ni-Al Alloys

*Experimental effort*

Comparing with the literature





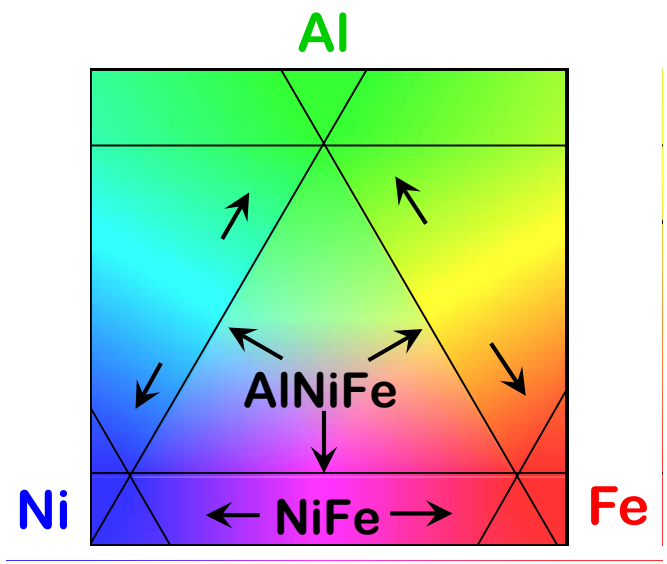



*F.H. Stott, G.C. Wood, D.P. Whittle, B.D. Bastow, Y. Shida and A. Martinez-Villafane, Solid State Ionics, 12, 365, (1984)

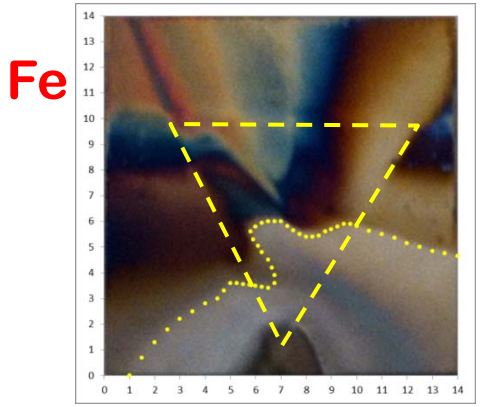
# Composition Spread Alloy Films (CSAFs) to Determine Oxide Maps for the Fe-Ni-Al System

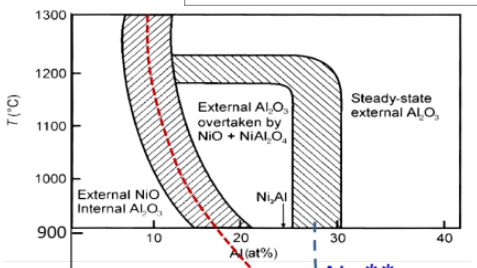
*A. Gellman, CMU*

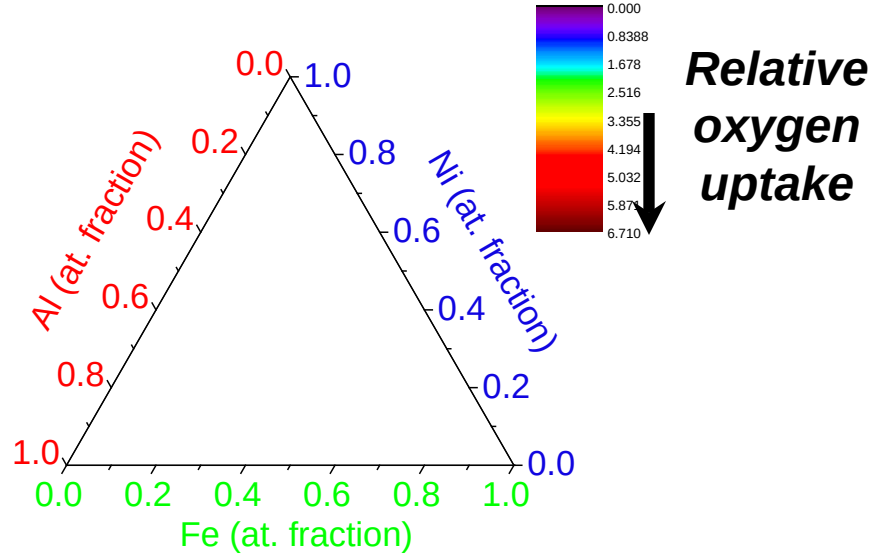
- CSAFs contain all possible compositions of the ternary $Fe_xNi_yAl_{1-x-y}$ ($x = 0 \rightarrow 1$, $y = 0 \rightarrow 1-x$).
- CSAF deposited on Mo using physical vapor deposition tool designed and fabricated at CMU.
- Composition distribution of 100 nm thick $Fe_xNi_yAl_{1-x-y}$ CSAF mapped with EDX.

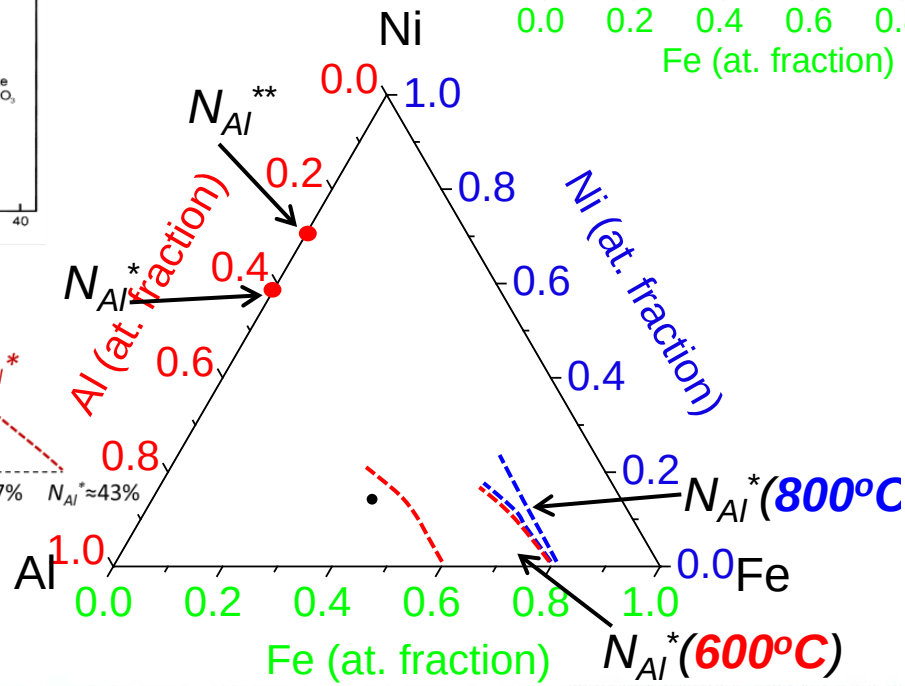


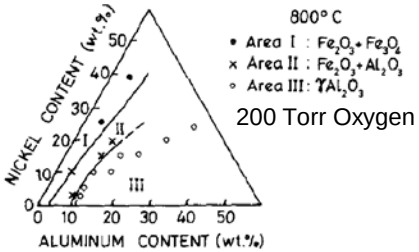
# Oxidation of $Fe_xNi_yAl_{1-x-y}$ CSAF in Air at 427˚C

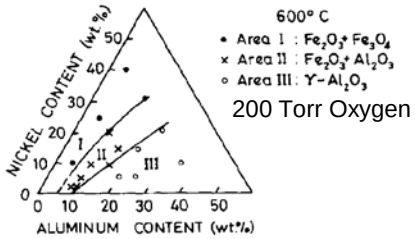


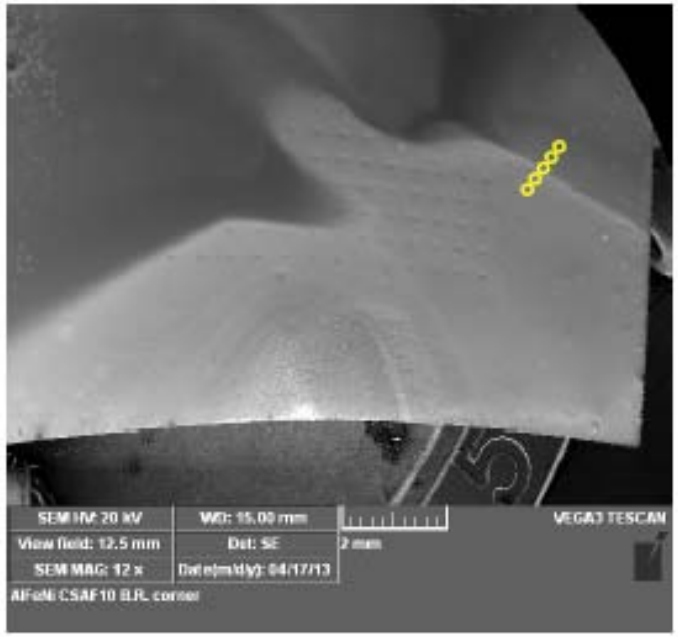





F.S. Pettit, *AIME Met. Soc. Trans.*, **239** (1967) 1296.
M. Sakiyama, P. Tomaszewicz and G. R. Wallwork, *Oxidation of Metals,* Vol. 13, No. 4, 1979

# XPS Depth Profile Across $Al_xNi_{1-x}$ Boundary

## *reveals outer $Al_2O_3$ scale at $N_{Al} \geq 33$ at%*

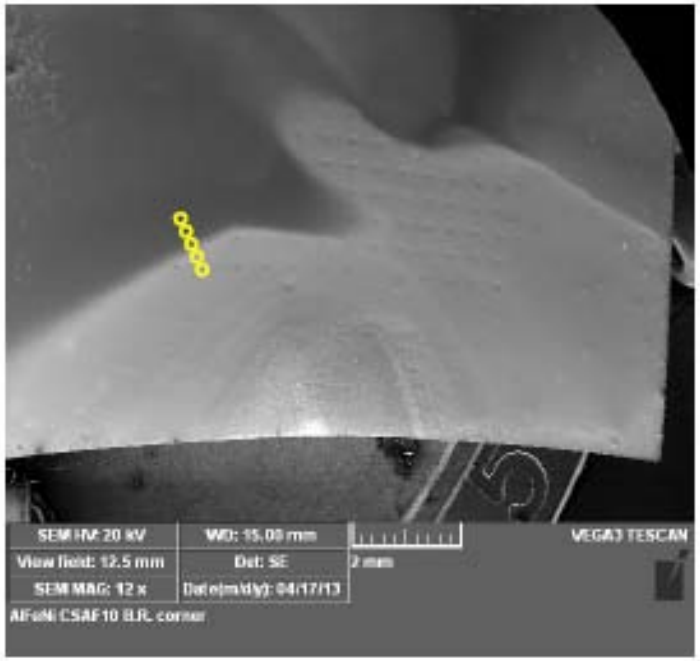



Composition (at%)

| x=Al% |
|---|
| 28% |
| 30% |
| 33% |
| 35% |
| 38% |

# XPS Depth Profile Across $Al_xFe_{1-x}$ Boundary

## *reveals outer $Al_2O_3$ scale at $N_{Al} \geq 65$ at%*




Composition (at%)

**x=Al%**

61%

63%

65%

68%

70%

# Summary

- ***EOS: DFT calculations were used to predict lattice constants, heats of formation, binding energies, barriers to migration (diffusion) for Ni-Al-Fe alloys.***
  - *Over 1000 data sets have been correlated. Data sets necessary for prediction of oxygen solubility and diffusion data.*
- ***DFT, ReaxFF, MEAM and kMC methods used to predict oxygen diffusion in Ni***
  - *Developed ReaxFF parameters for Ni/Al/O systems*
  - *Identified the need for incorporation of vacancies.*
  - *Initiated work on effect of H on O diffusion in Ni.*
  - *Initiated work on effect Al, Fe on O diffusion in Ni.*

# Summary

- ***CALPHAD, DFT used to predict phase diagrams → solubility parameters***
- ***Targeted validation experiments for oxygen permeability initiated***
- ***CSAF high throughput experimental method under development.***

- ***<u>Next Step:</u>***

  ***Predict $N^*_{Al}$***