Measured Activities of Al and Ni in γ-(Ni) and γ′-$(Ni)_3Al$ in the Ni-Al-Pt System

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Abstract
Adding Pt to Ni-Al coatings is critical to achieving the required oxidation protection of Ni-based superalloys, but the nature of the "Pt effect" remains unresolved. This research provides a fundamental part of the answer by measuring the influence of Pt on the activities of Al and Ni in γ-(Ni), γ'-$(Ni)_3Al$ and liquid in the Ni-Al-Pt system. Measurements have been made at 25 compositions in the Ni-rich corner over the temperature range, T = 1400 – 1750 K, by the vapor pressure technique with a multiple effusion-cell mass spectrometer (*multi-cell KEMS*). These measurements clearly show adding Pt (for $X_{Pt} < 0.25$) decreases a(Al) while increasing a(Ni). This solution behavior supports the idea that Pt increases Al transport to an alloy / Al_2O_3 interface and also limits the interaction between the coating and substrate alloys in the γ-(Ni) + γ'-$(Ni)_3Al$ region. This presentation will review the progress of this study.

measured *a*(Al) and *a*(Ni) in γ-(Ni) and γ′-(Ni)$_3$Al in the Ni-Al-Pt System

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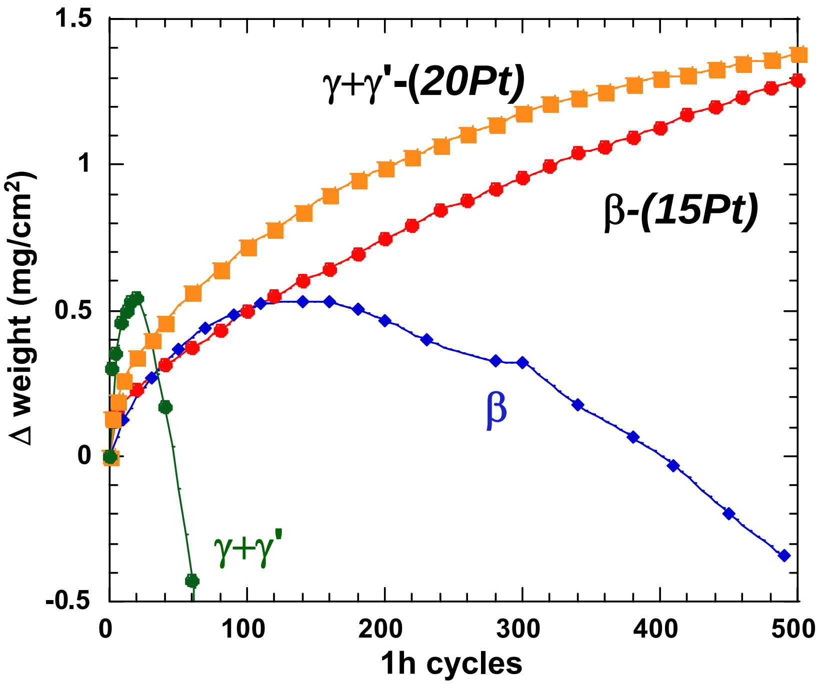
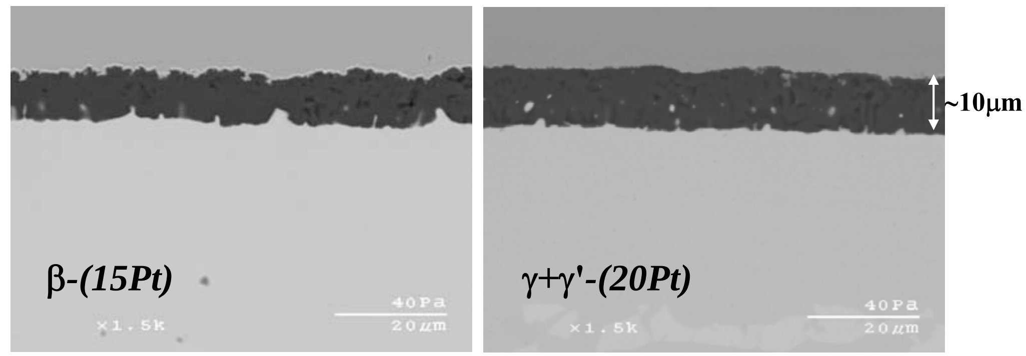
motivation

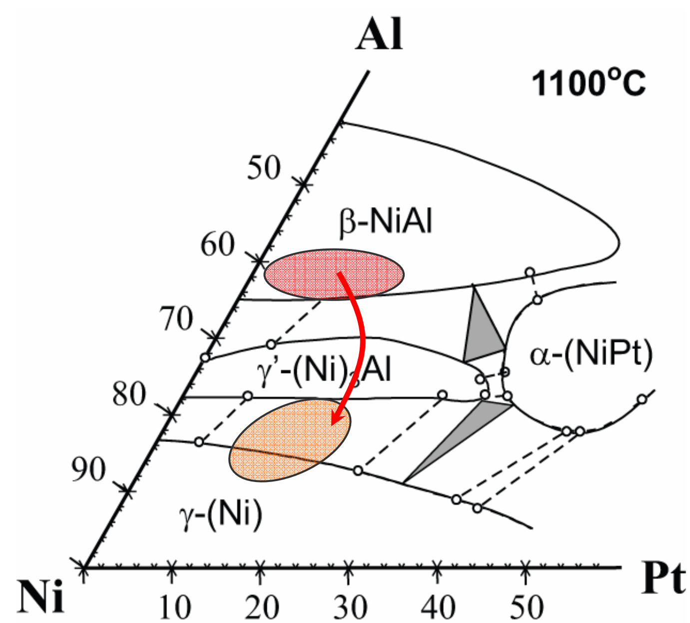


cyclic oxidation at 1150˚C in air



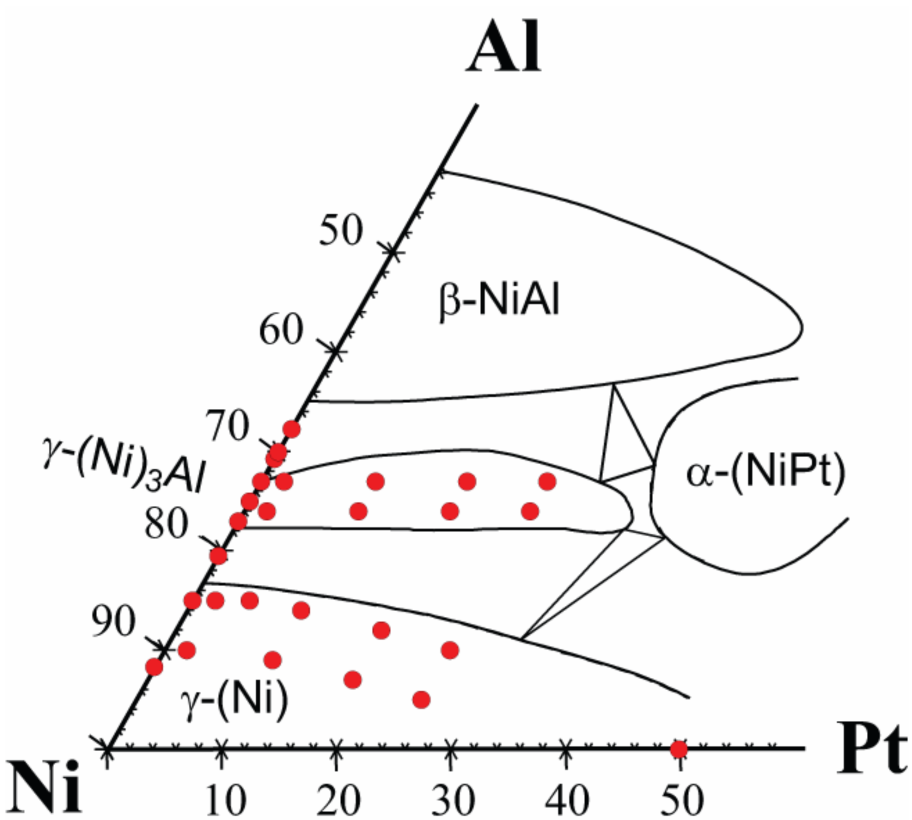
protective Al_2O_3 formation

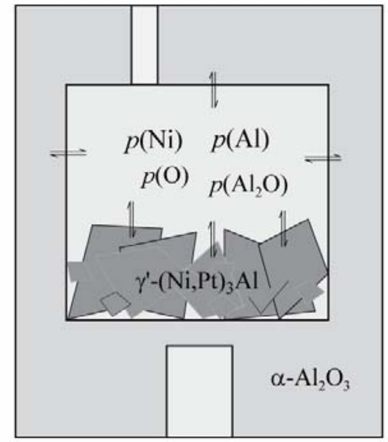
β-(Pt) coatings → γ + γ′-(Pt) coating / alloy



S. Hayashi, S. Ford, D. Young, D. Sortelet, M. Besser, B. Gleeson, *Acta Materialia*, 2005, 53, 3319.

measured alloy compositions





Knudsen effusion-cell

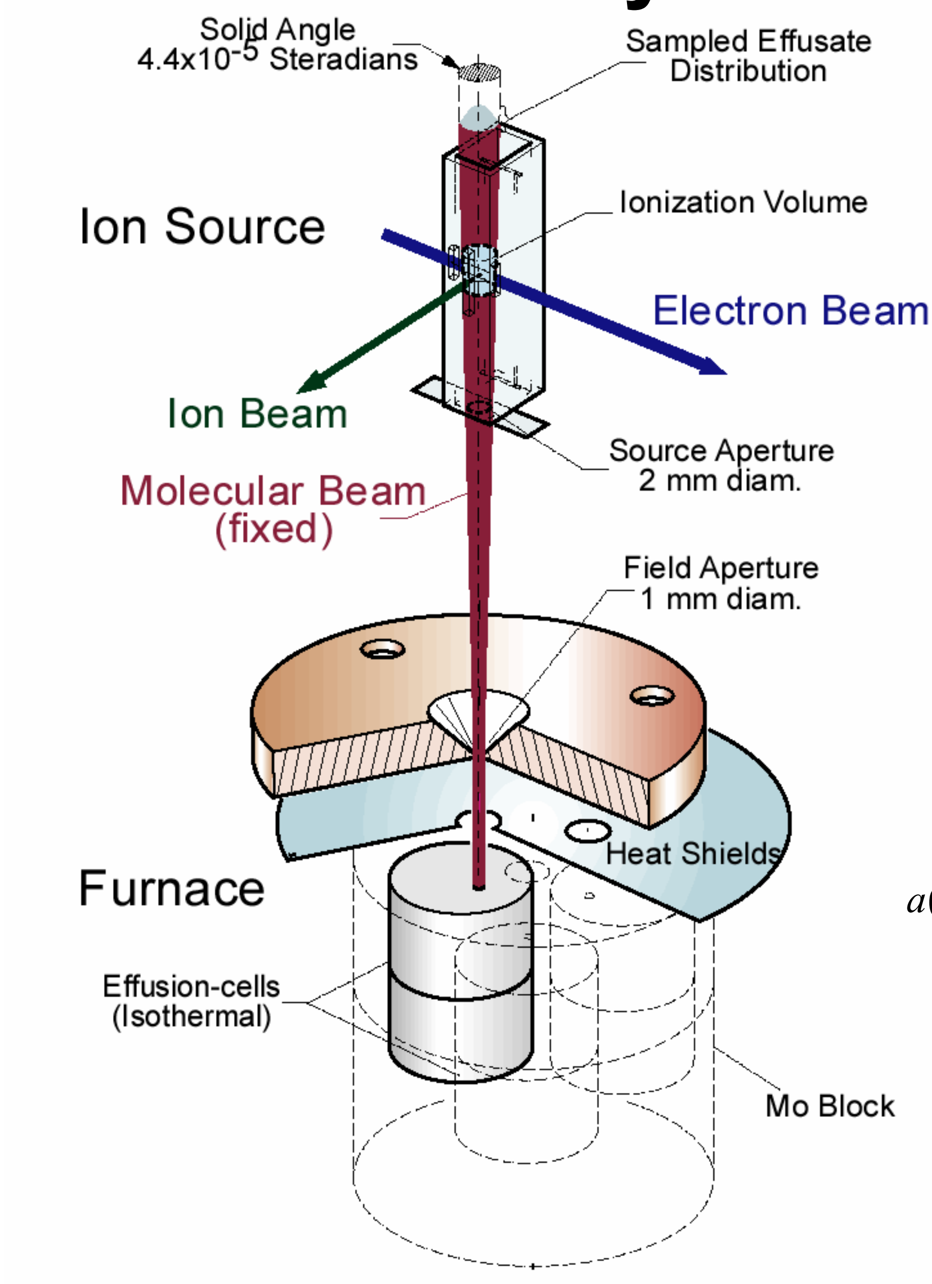
	[illegible]	[illegible]	[illegible]
	50.0	~	50.0
	76.8	23.2	~
γ′	75.0	25.0	~
	73.7	27.3	~
	73.6	24.3	2.0
	65.8	24.2	10.0
	57.9	24.0	18.1
	51.1	23.8	25.1
	70.8	27.2	2.0
	63.8	26.4	9.8
	54.9	27.0	18.1
	48.1	26.7	25.2

(at.% ± 0.5)

γ-(Ni), γ′-(Ni,Pt)$_3$Al and *L* equilibrium with Al_2O_3

→ Ni-Al-Pt-O system

thermodynamic measurements



multi-cell *KEMS*

pressure measurement

$$p(\mathrm{i}) = I_{ik}^{+}T \big/ S_{ik}$$

activity measurement

$$a(\mathrm{i}) = \frac{p(\mathrm{i})}{p^{\mathrm{o}}(\mathrm{i})} = \frac{I_{\mathrm{i}}}{I_{\mathrm{i}}^{\mathrm{o}}}$$

$$a(\mathrm{i}) = \frac{p(\mathrm{i})}{\cancel{p^{\circ}(\mathrm{Au})}} \cdot \left[\frac{\cancel{p^{\circ}(\mathrm{Au})}}{p^{\circ}(\mathrm{i})} \right] = \frac{I_{\mathrm{i}}}{I_{\mathrm{Au}}^{\circ}} \cdot \boxed{\frac{\mathrm{S}_{\mathrm{Au}}}{\mathrm{S}_{\mathrm{i}}}} \cdot \frac{g(R)}{g(A)} \cdot \boxed{\left[\frac{p^{\circ}(\mathrm{Au})}{p^{\circ}(\mathrm{i})} \right]}$$

(i = Ni, Al, Al_2O)

routine experiment… easy

reference states / reaction enthalpies

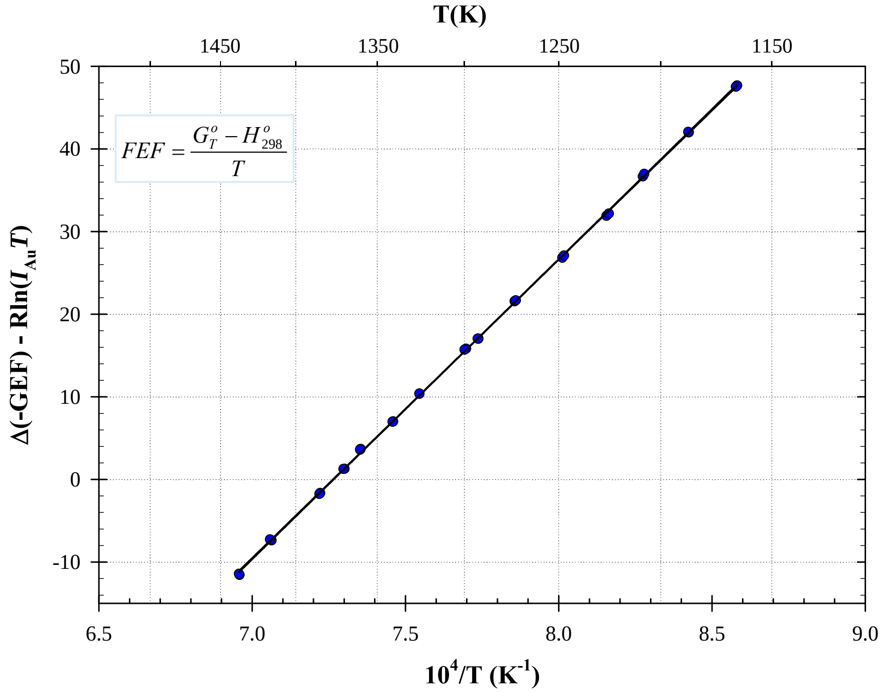
reference state	reaction (298K)	measured ($kJmol^{-1}$)	IVTAN ($kJmol^{-1}$)
{ Au(s,l) + C }	Au(s,l) = Au(g)	363.5±2.8 367.0±1.3*	367.0±0.9
{ Ni(s) + Al_2O_3 }	Ni(s) = Ni(g)	428.3±2.6	428.0±8.0
{ Al(l) + Al_2O_3 }	Al(s) = Al(g)	341.0±2.2	330.0±3.0
	4/3Al(s) + 1/3Al_2O_3(s) = Al_2O(g)	414.2±3.6	409.9±55
	2Al(s) + 3O(g) = Al_2O_3(s)	~	-3083.2 ±5
	2Al(g) + O(g) = Al_2O(g)	-1075.5±9.0	-1057.8±20.0
	4Al(g) + Al_2O_3(s) = 3Al_2O(g)	~	~

* 3rd law measurements

- pure-Al data is wrong,… use my second law data
- Au(s,l) ref. ➞ *T* and *p*(i) standards, good check of experiment
- measure 2 alloys in single experiment

sensitivity of measurements?

Au(s,l) = Au(g)



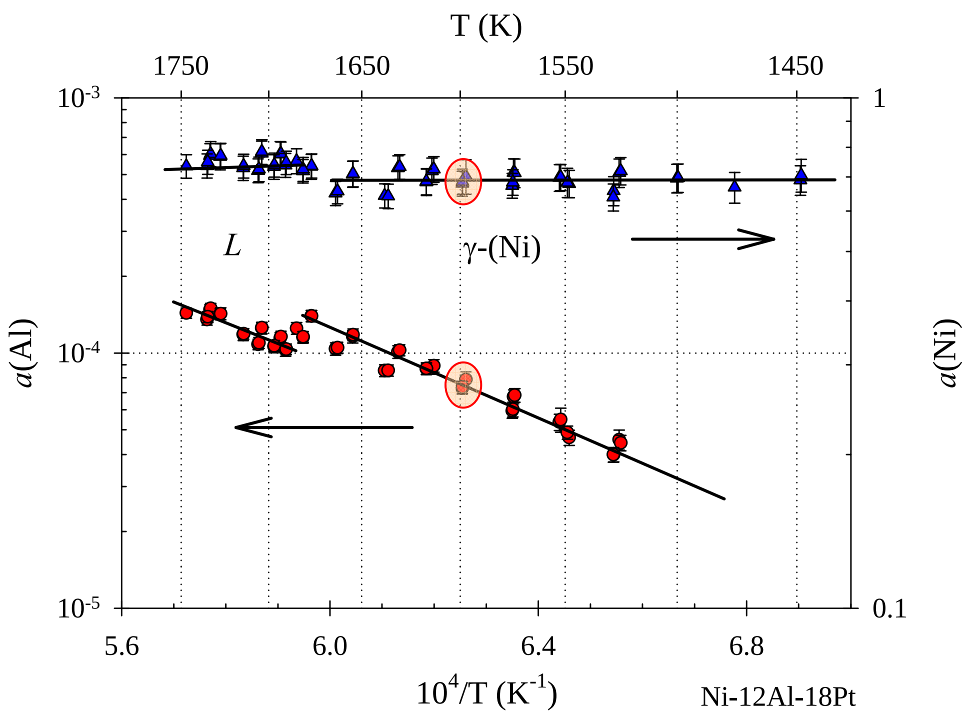
$$\Delta_{sub}H^o_{298}(\text{Au}) = \frac{d\left[\Delta(-FEF) - R\ln I_{\text{Au}}T\right]}{d\,1/T} = 362.2 \pm 1.7 k\text{Jmol}^{-1}$$

= 6.018 ± **0.029** eV/atom

$$\Delta_{sub}H^o_{298}(\text{Au}) = T\left[\Delta(-FEF) - R\ln p(\text{Au})\right] = 366.3 \pm 0.8 k\text{Jmol}^{-1}$$

= 6.086 ± **0.013** eV/atom

xNi + yAl + zPt = γ-(NiAlPt)



$$\Delta_{mix}\overline{G}^{\gamma}_{\text{Al}} = RT\ln a(\text{Al}) = -124.4 \pm 0.8 k\text{Jmol}^{-1}$$

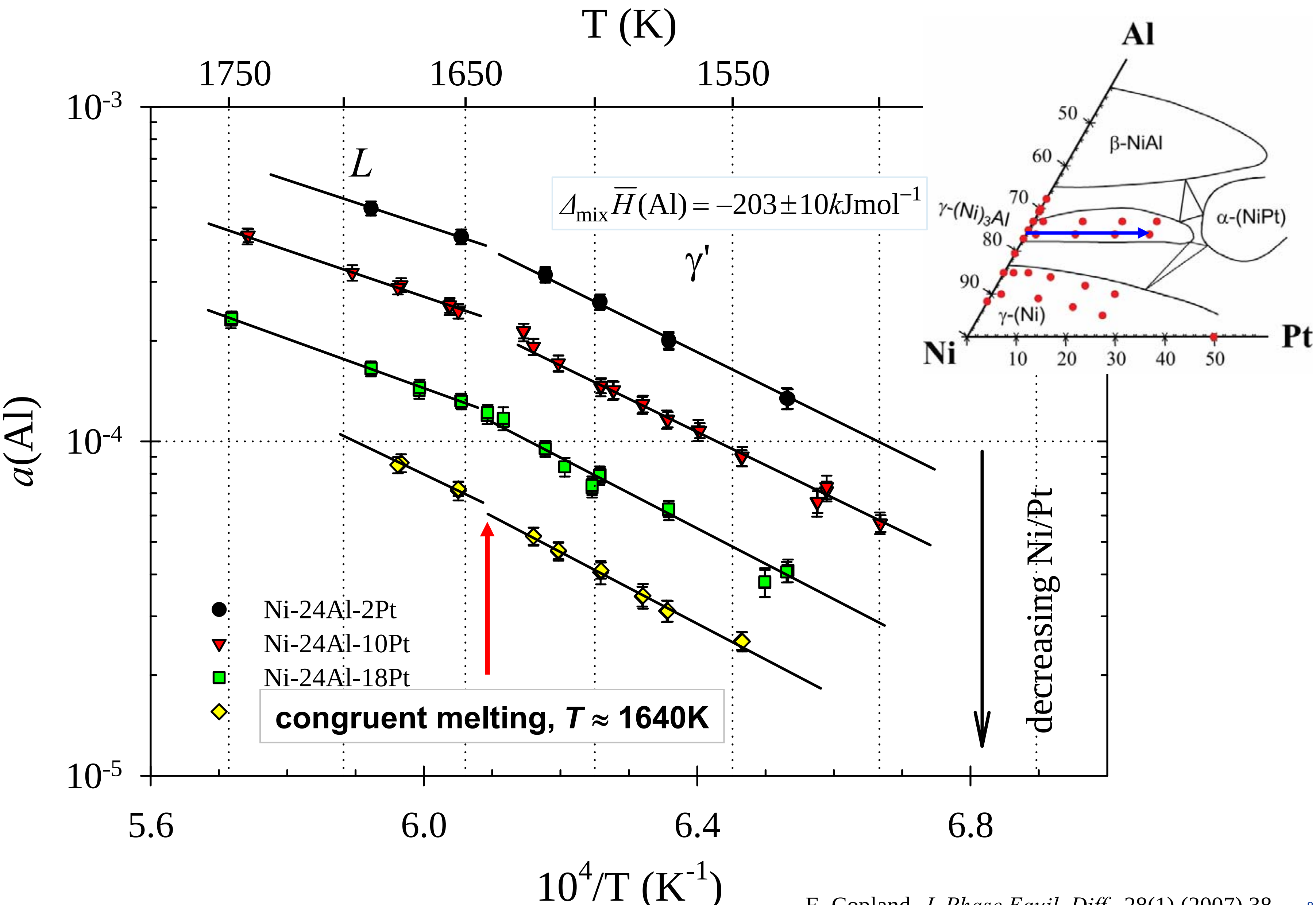
= -2.10 ± **0.015** eV/atom

$$\Delta_{mix}\overline{G}^{\gamma}_{\text{Ni}} = RT\ln a(\text{Ni}) = -4.5 \pm 0.9 k\text{Jmol}^{-1}$$

= -0.08 ± **0.015** eV/atom

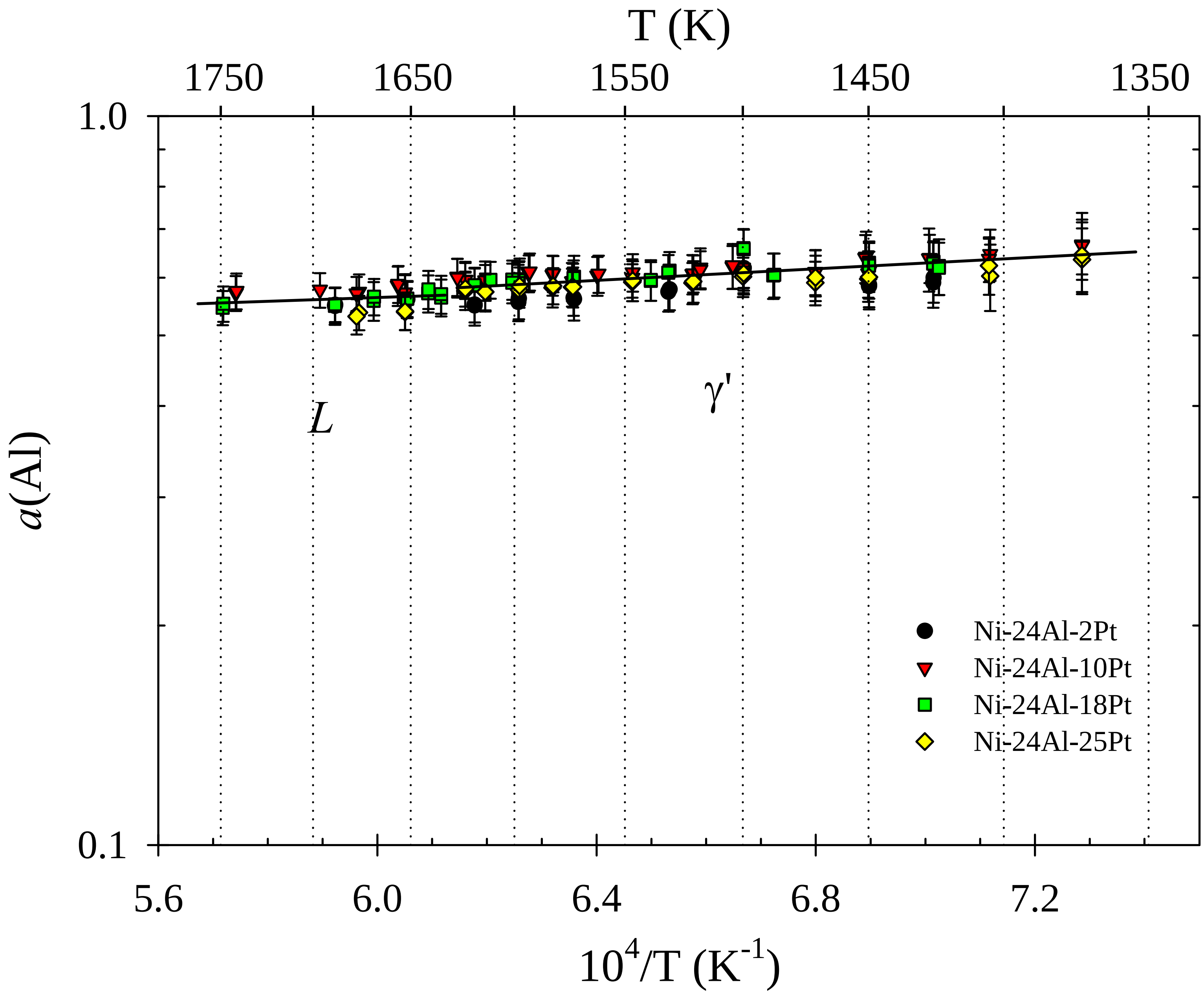
R. C. Paule, J. Mandel: NBS Special Publication 260-19, 1970.

a(Al) vs 1/*T* in Ni-24Al-XPt

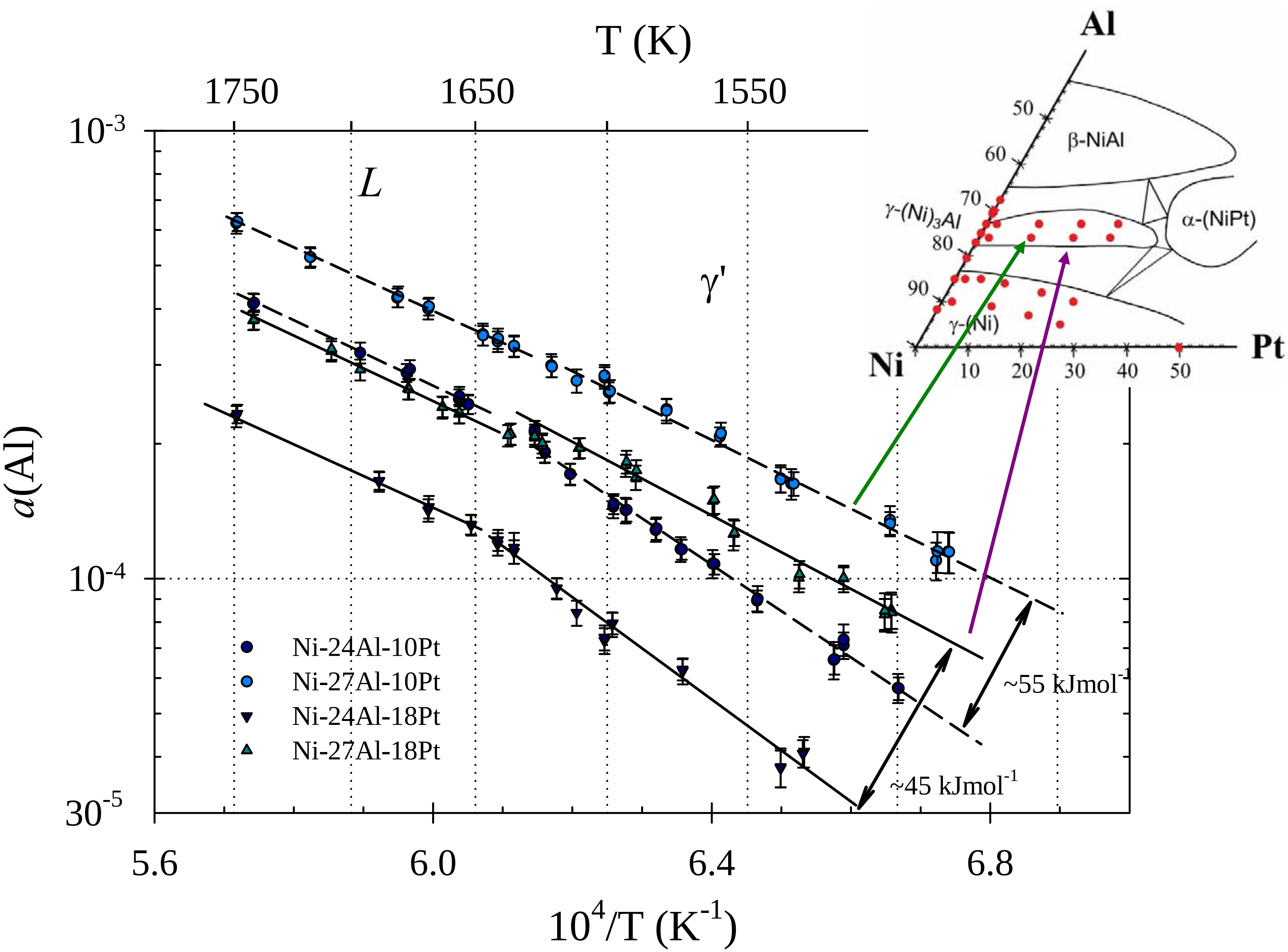


E. Copland, *J. Phase Equil. Diff.*, 28(1) (2007) 38

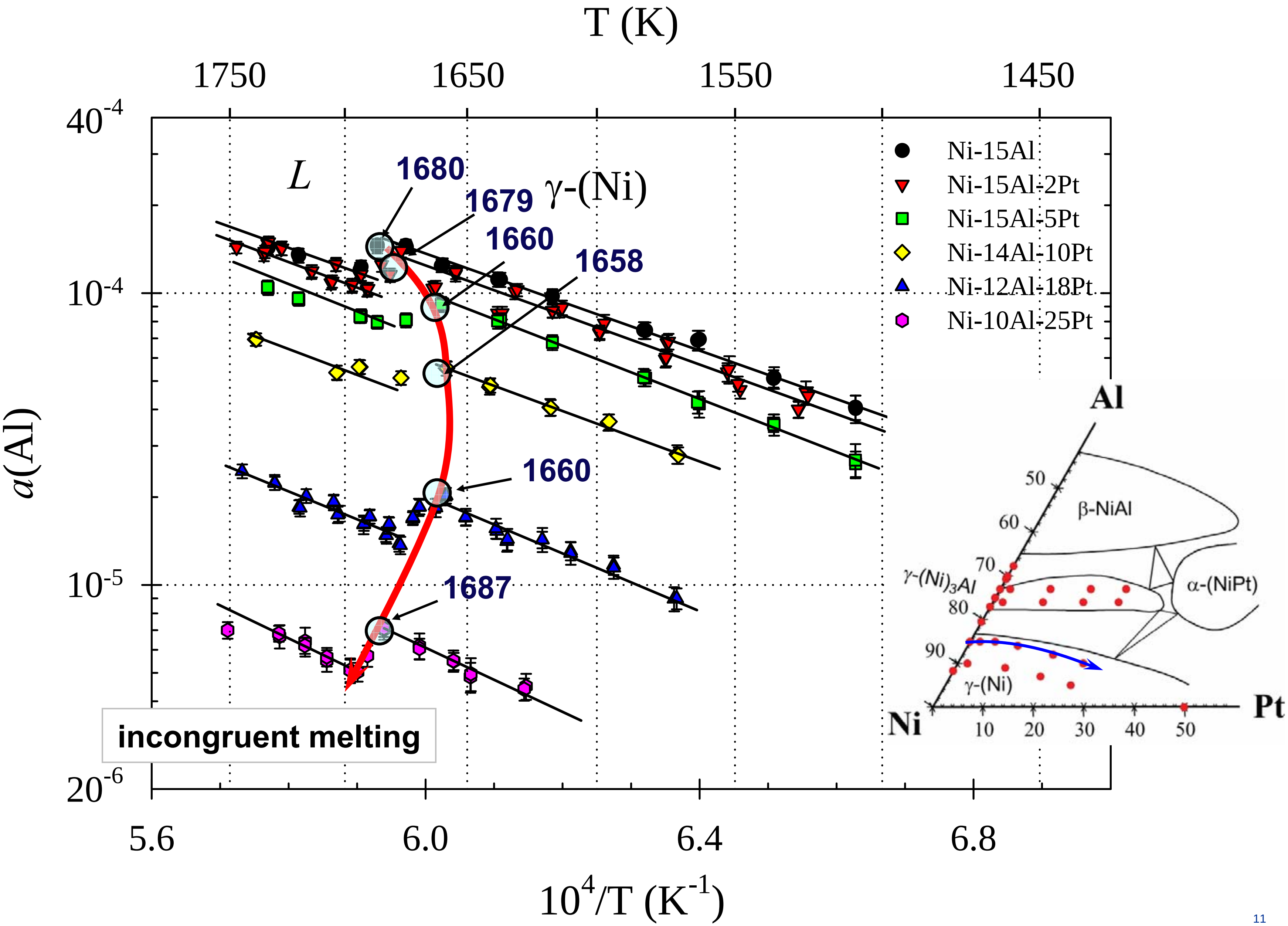
a(Ni) vs 1/T in Ni-24Al-XPt



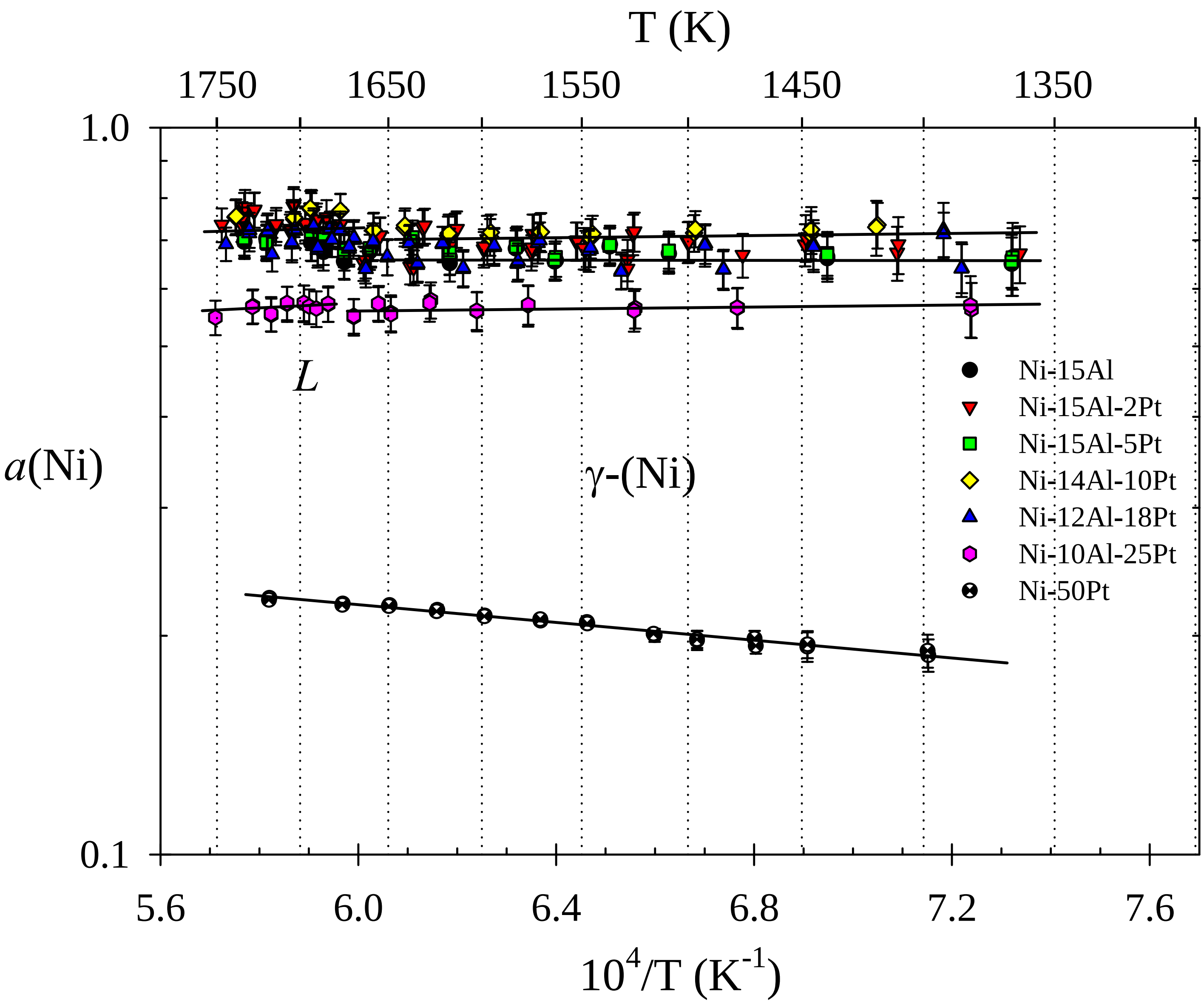
hypo- / hyper-stoichiometric γ´



a(Al) vs 1/*T* in γ-(Ni)



a(Ni) vs 1/*T* in γ-(Ni)



"interaction parameter formalism"

$$a(i) = \gamma(i) X_i \big|_{X_j/X_k}$$

$$\ln \gamma_{\text{solvent}} = -\frac{1}{2}\left(\varepsilon_{\text{AlAl}} X_{\text{Al}}^2 + \varepsilon_{\text{PtPt}} X_{\text{Pt}}^2 + \varepsilon_{\text{AlPt}} X_{\text{Al}} X_{\text{Pt}}\right)$$

$$\ln \gamma_{\text{i}} / \gamma_{\text{i}}^{o} = \ln \gamma_{\text{solvent}} + \varepsilon_{\text{iAl}} X_{\text{Al}} + \varepsilon_{\text{iPt}} X_{\text{Pt}} \quad {}_{\text{i=Al,Pt}}$$

$$\varepsilon_{\text{ij}} = \left(\partial \ln \gamma_{\text{i}} / \partial X_{\text{j}}\right)_{\text{solvent}}$$

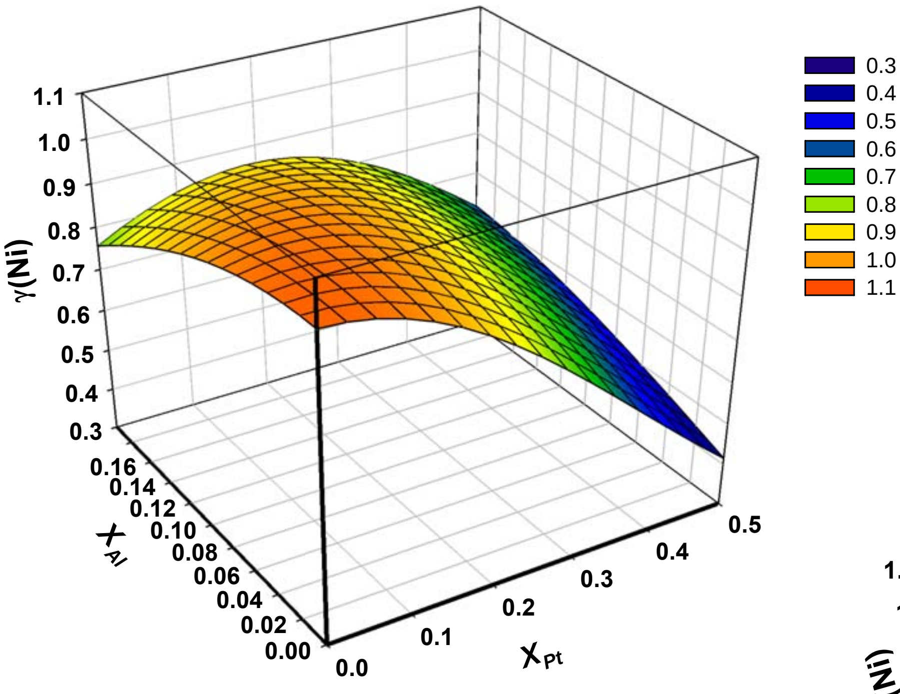
coefficients at 1550K	
$\ln\gamma_{Al}^{o}$	-9.84±0.07
$\ln\gamma_{Pt}^{o}$	*-5.0*
ε_{AlAl}	14.57±0.55
ε_{PtPt}	7.03±0.4
ε_{PtAl}	-13.70±2.7

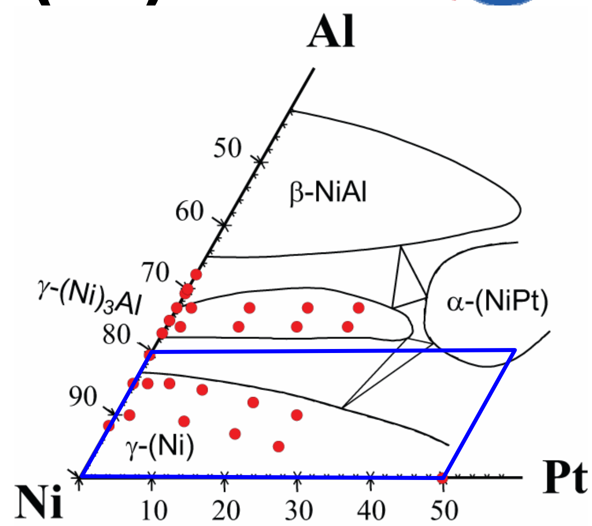
- **need a function to understand / observe the solution behavior…**
- **computational thermo → *GEF*(X_i,*T*), but are problems (Ni-Al and Al-ref)**
- **use interaction parameter formalism (origin: Wagner, Lupis & Darken)**
  - **Pelton & Bale modified to work at finite concentrations**
  - **measured *a*(Ni) and *a*(Al),… predict *a*(Pt)**

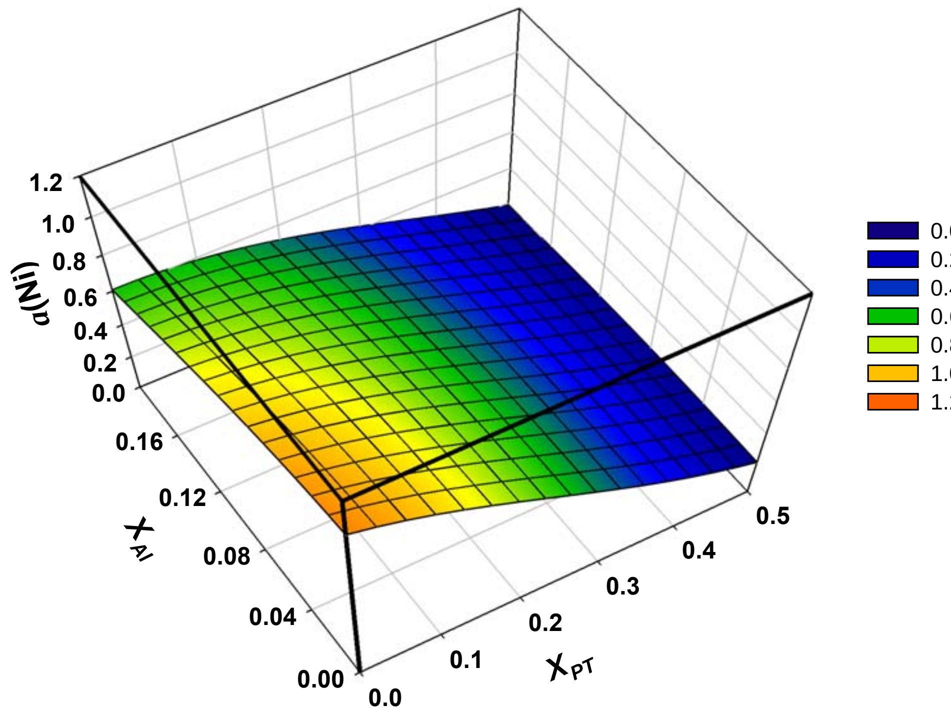
A. Pelton, C. Bale *Met. Trans. A*, (1986), 17A, 1211

γ_{Ni}, a(Ni) surfaces in γ-(Ni)

***T* = 1550 K**

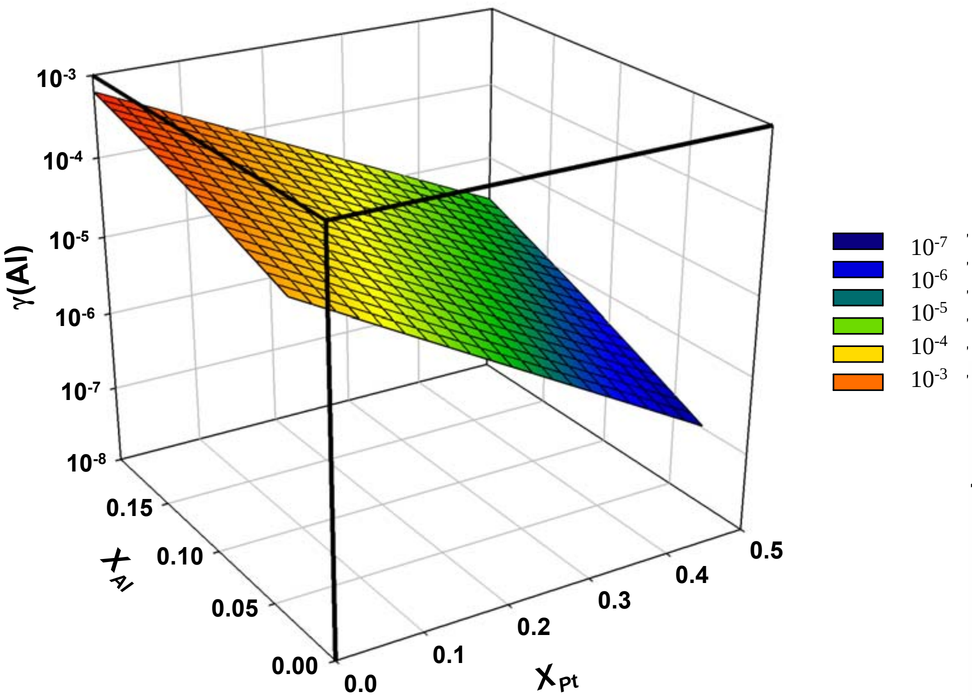




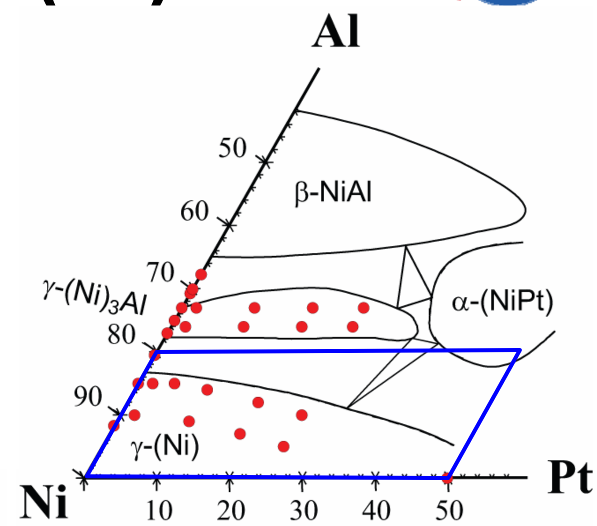


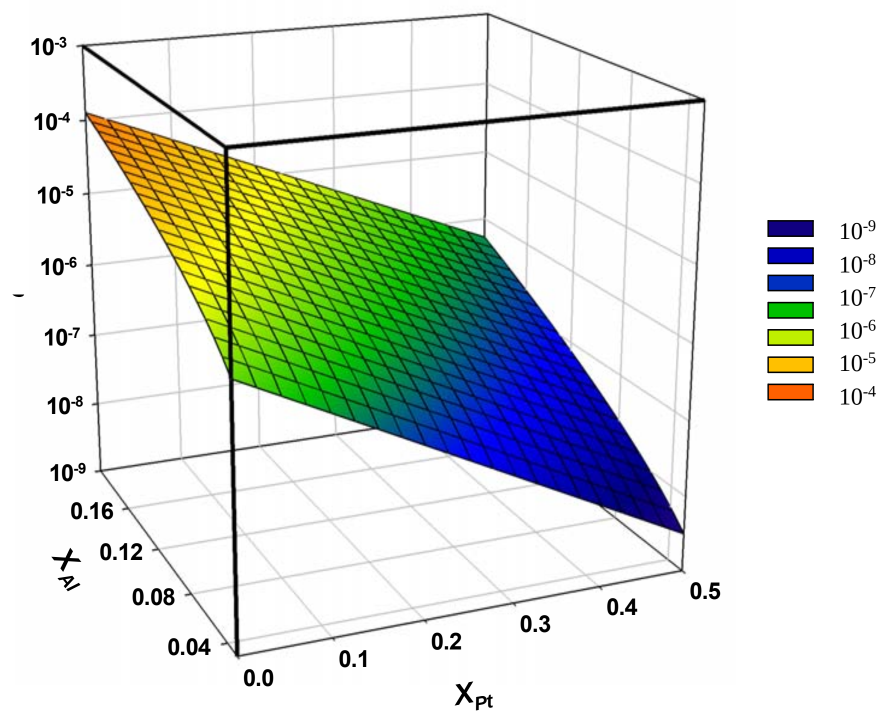
- **a(Ni) remains high with Pt addition… more pronounced in γ´-(Ni)$_3$Al**
- **limits ΔG for J_{Ni} → γ + γ´(Pt) coating**
- **exclusive Al_2O_3-layer not due to ↓ a(Ni)**

γ_{Al}, *a*(Al) surfaces in γ-(Ni)



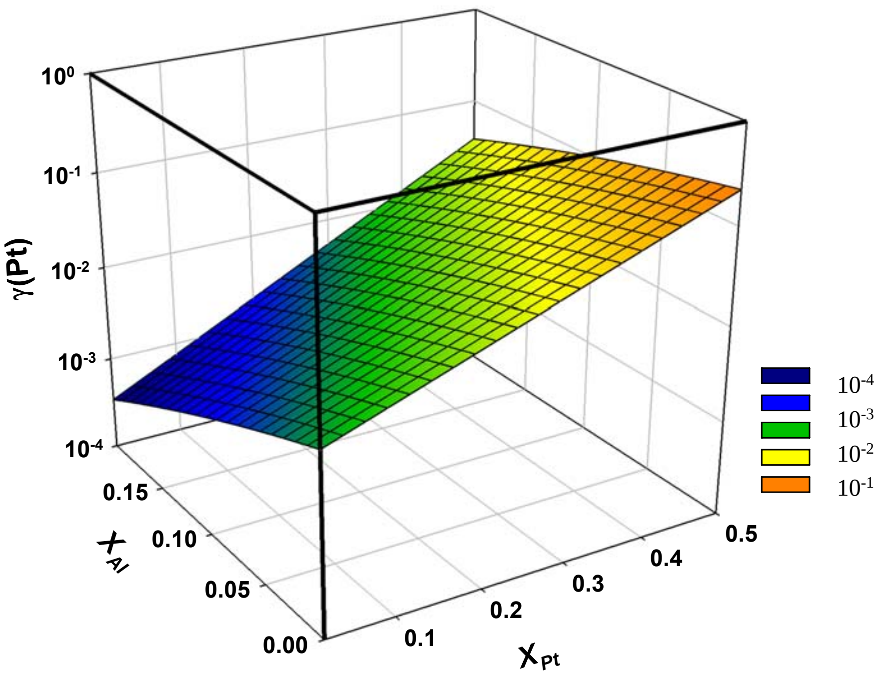
T = 1550 K



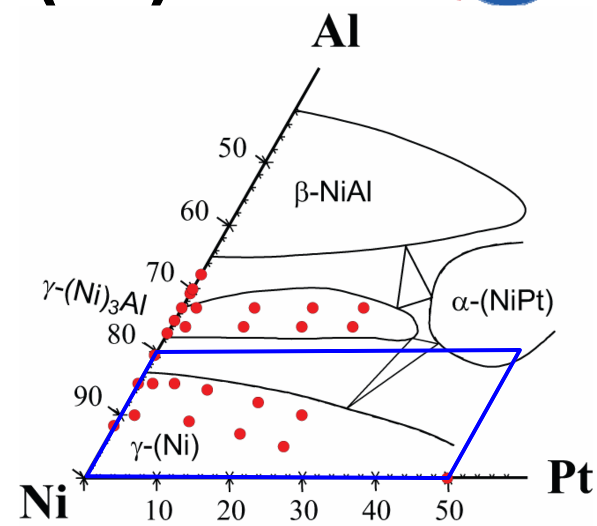


- *a*(Al) strong influence Al, Pt $\varepsilon_{AlAl} \approx - \varepsilon_{PtAl}$
- ↓ *a*(Al) doesn't destabilize Al_2O_3
- Pt enrichment: ΔG for $J_{Al} \rightarrow$ alloy/Al_2O_3

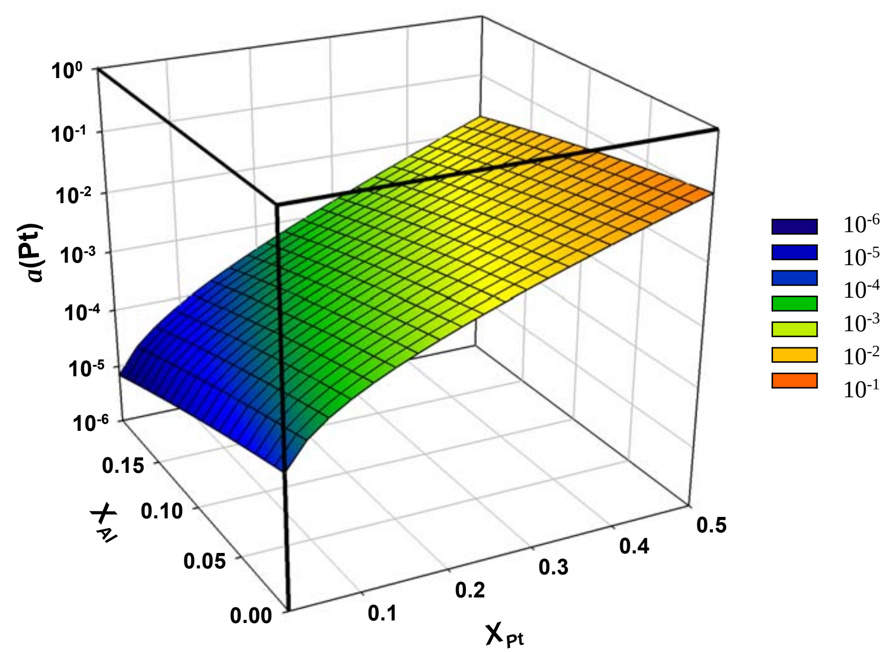
γ_{Pt}, a(Pt) surfaces in γ-(Ni)



T = 1550 K



- *a*(Al) and *a*(Ni), Gibbs-Duhem → *a*(Pt)
- Pt behavior ≈ - Al behavior
- ~



summary

- a(Al), a(Ni) measured at 25 comp. in Ni-corner of Ni-Al-Pt
  - ↪ T = 1400 – 1750 K in γ-(Ni), γ′-$(Ni)_3Al$ and *L*
  - ↪ Pt addition: a(Al) reduced, a(Ni) ~ constant
- ***thermodynamic measurements are easy!*** **(2 ~ 4 alloys / week)**
  - ↪ must closely consider state of the system (Al_2O_3)
- future work:
  - ↪ calculate γ-(Ni) / *L*, γ-(Ni) / γ′-$(Ni)_3Al$ phase boundaries
  - ↪ show activities are as good as phase equilibria
  - ↪ introduce Al_2O_3 and O to data analysis

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