

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 $a(\text{Al})$ while increasing $a(\text{Ni})$. This solution behavior supports the idea that Pt increases Al transport to an alloy / Al₂O₃ 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.



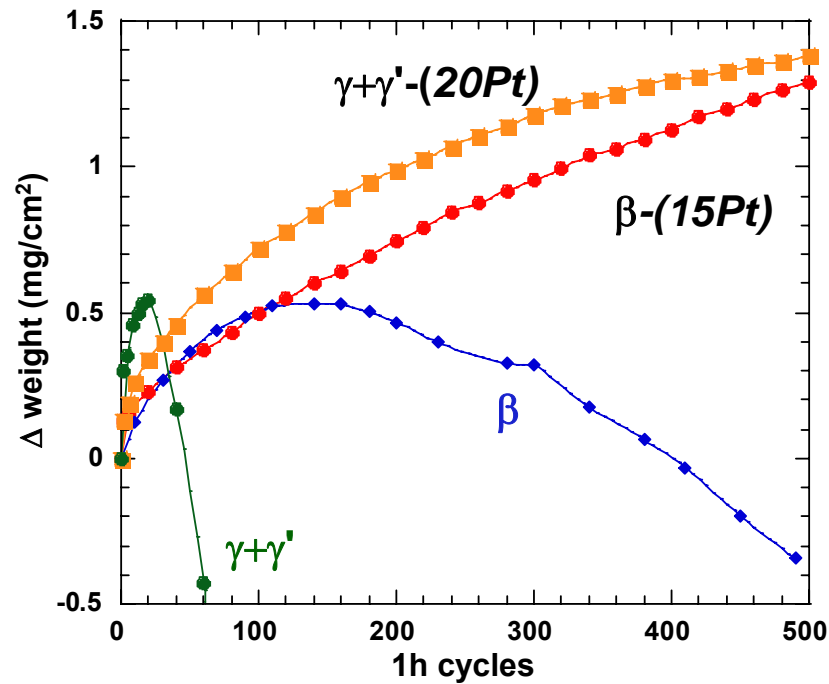
measured $a(\text{Al})$ and $a(\text{Ni})$ in $\gamma\text{-(Ni)}$ and $\gamma'\text{-(Ni)}_3\text{Al}$ in the Ni-Al-Pt System

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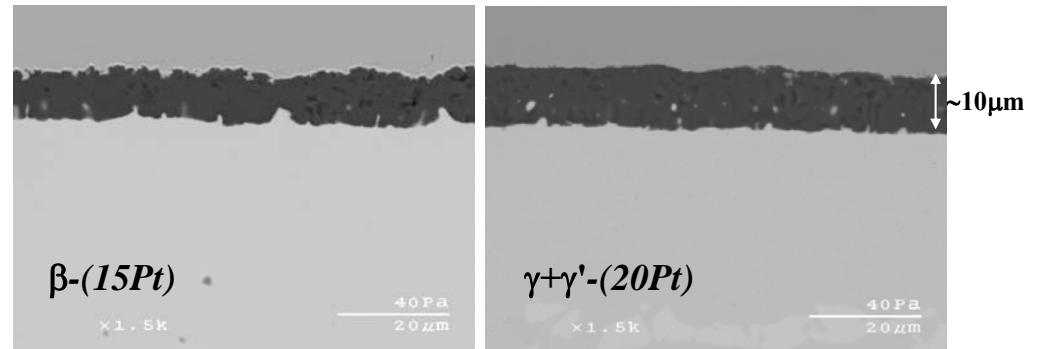
MS&T 2007: 9/19/2007 – COBO Center Detroit, Michigan, USA

motivation

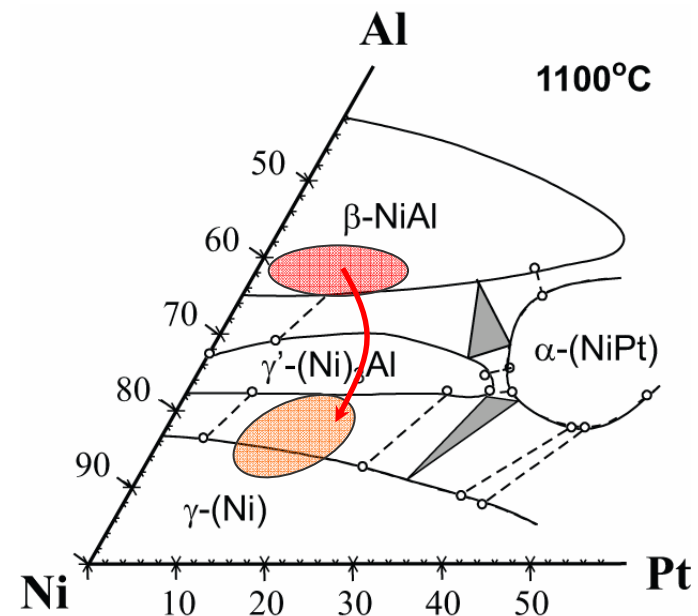


cyclic oxidation at 1150°C in air

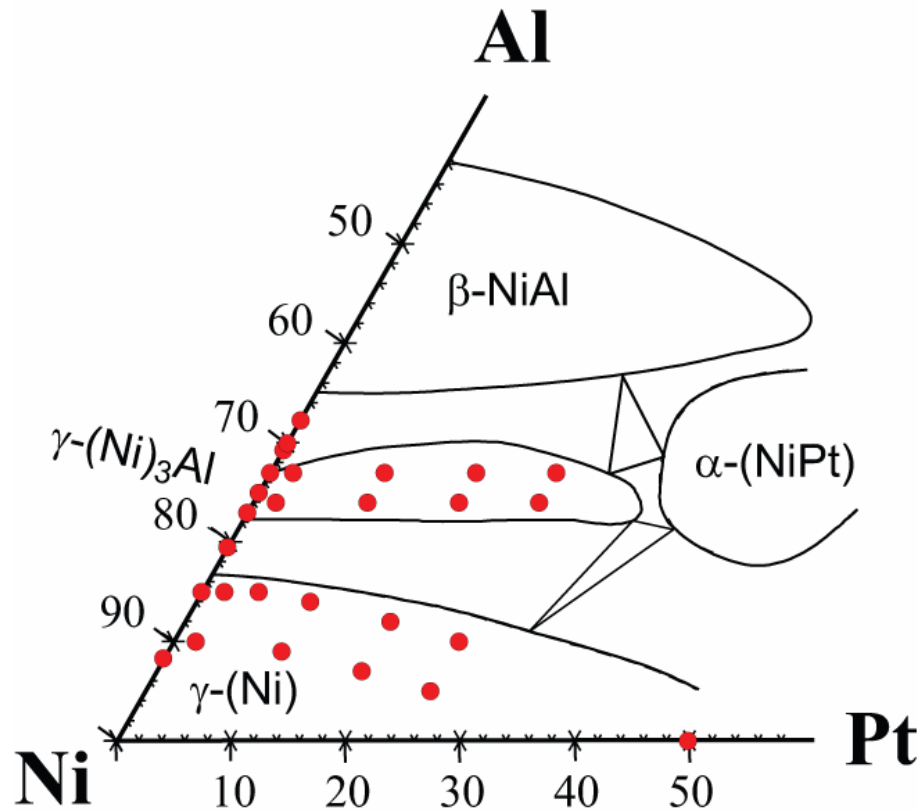
β -(Pt) coatings \rightarrow $\gamma + \gamma'$ -(Pt) coating / alloy



protective Al₂O₃ formation

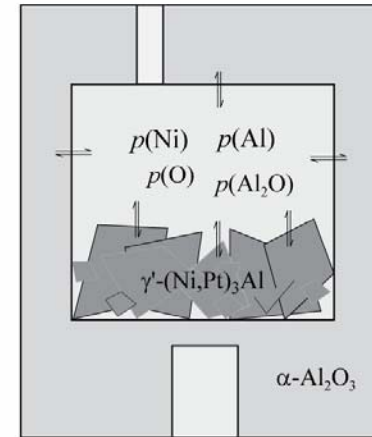


measured alloy compositions



γ -(Ni), γ' -(Ni,Pt)₃Al and L equilibrium with Al₂O₃

→ Ni-Al-Pt-O system



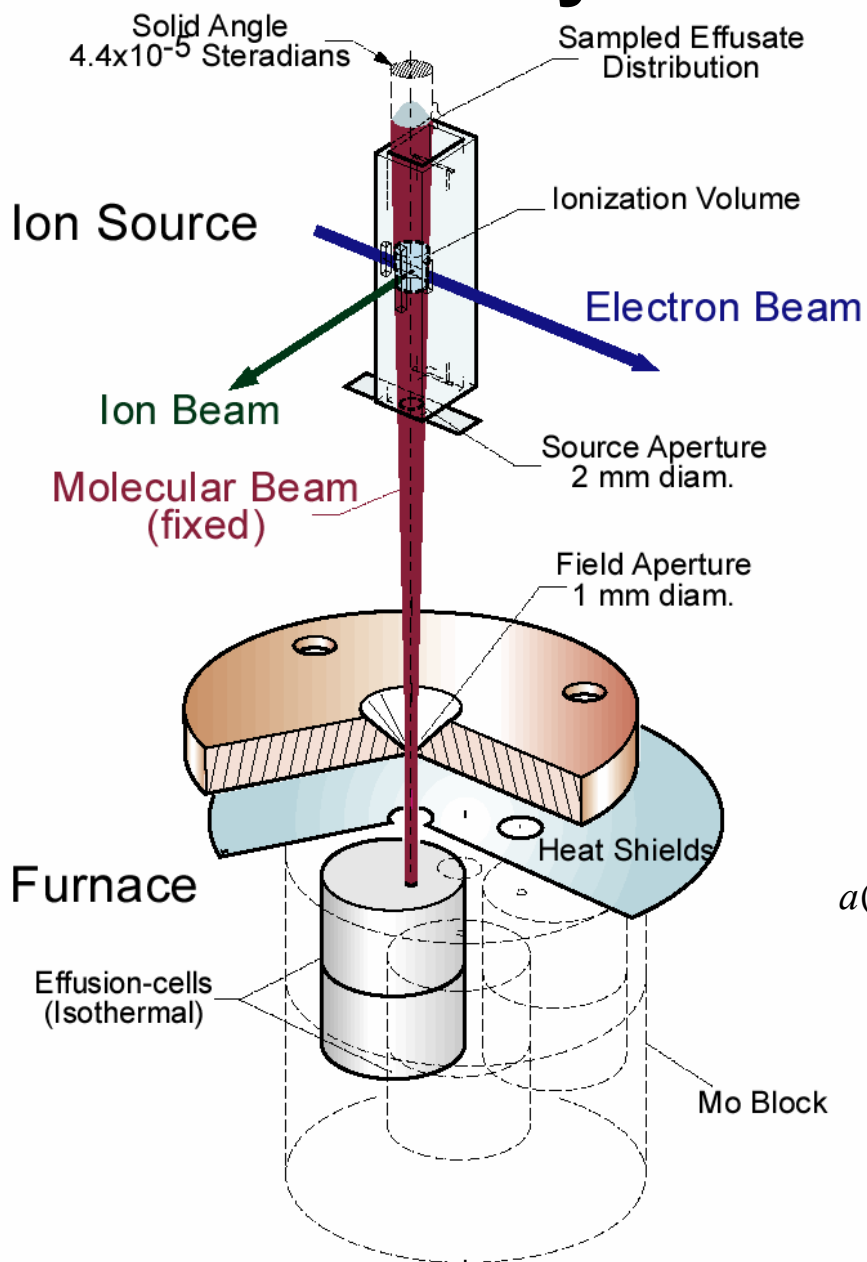
Knudsen effusion-cell

	50.0	~	50.0
γ'	76.8	23.2	~
	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.% \pm 0.5)



thermodynamic measurements



multi-cell *KEMS*

pressure measurement

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

activity measurement

$$a(i) = \frac{p(i)}{p^\circ(i)} = \frac{I_i}{I_i^\circ}$$

$$a(i) = \frac{p(i)}{\cancel{p^\circ(\text{Au})}} \cdot \left[\frac{\cancel{p^\circ(\text{Au})}}{p^\circ(i)} \right] = \frac{I_i}{I_{\text{Au}}^\circ} \cdot \boxed{\frac{S_{\text{Au}}}{S_i}} \cdot \frac{g(R)}{g(A)} \cdot \boxed{\frac{p^\circ(\text{Au})}{p^\circ(i)}}$$

(i = Ni, Al, Al₂O)

routine experiment... easy

reference states / reaction enthalpies

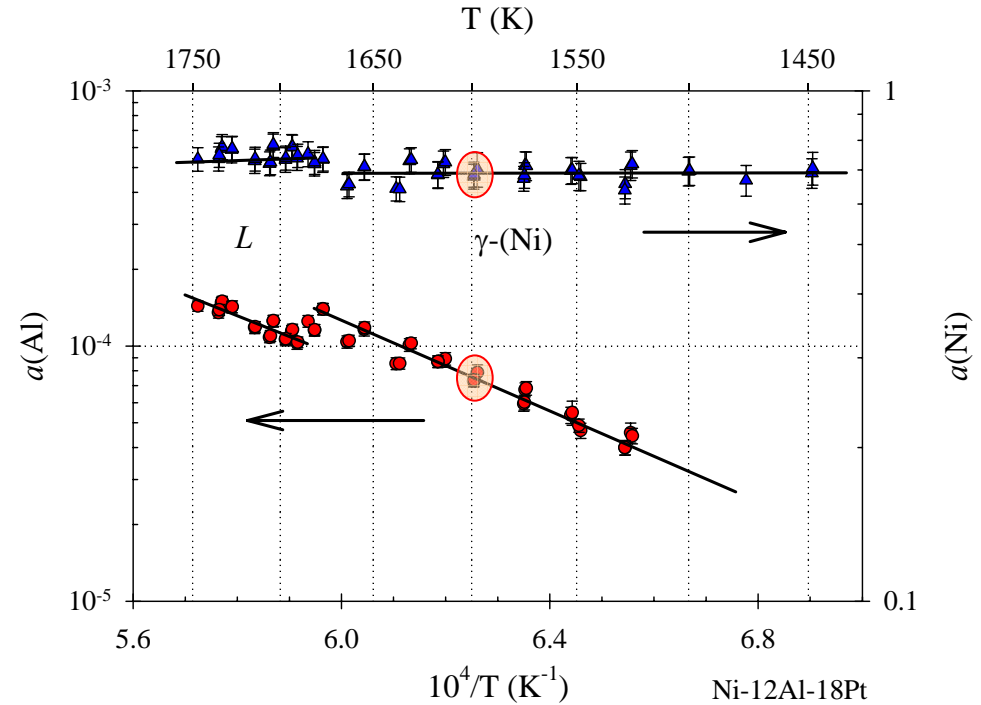
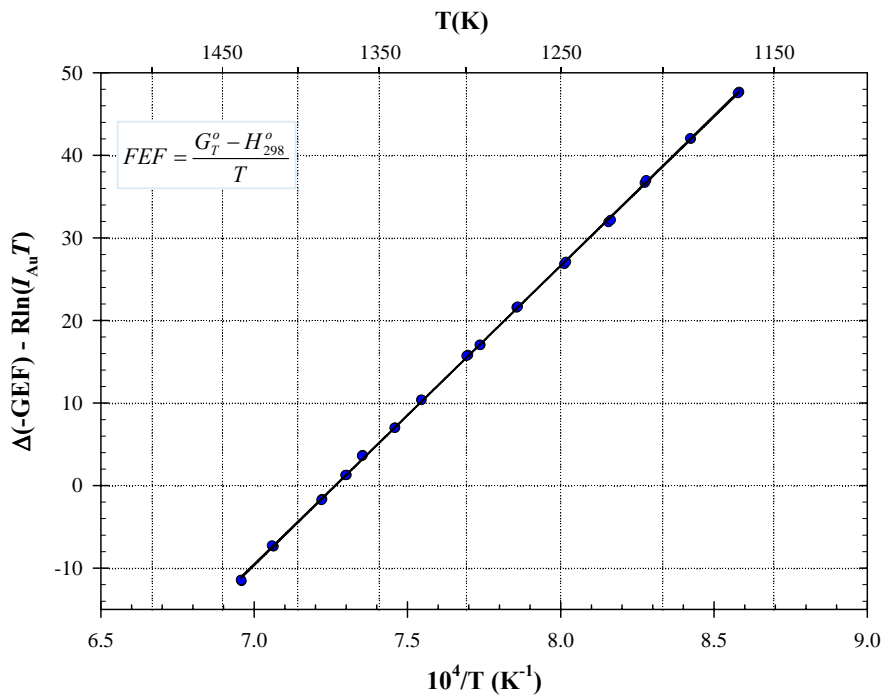
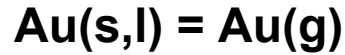


reference state	reaction (298K)	measured (kJmol ⁻¹)	IVTAN (kJmol ⁻¹)
{ Au(s,l) + C }	Au(s,l) = Au(g)	363.5±2.8 367.0±1.3*	367.0±0.9
{ Ni(s) + Al ₂ O ₃ }	Ni(s) = Ni(g)	428.3±2.6	428.0±8.0
{ Al(l) + Al ₂ O ₃ }	Al(s) = Al(g)	341.0±2.2	330.0±3.0
	4/3Al(s) + 1/3Al ₂ O ₃ (s) = Al ₂ O(g)	414.2±3.6	409.9±55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



$$\Delta_{sub} H_{298}^o(\text{Au}) = \frac{d[\Delta(-FEF) - R \ln I_{\text{Au}} T]}{d(1/T)} = 362.2 \pm 1.7 \text{ kJmol}^{-1}$$

$$= 6.018 \pm 0.029 \text{ eV/atom}$$

$$\Delta_{sub} H_{298}^o(\text{Au}) = T[\Delta(-FEF) - R \ln p(\text{Au})] = 366.3 \pm 0.8 \text{ kJmol}^{-1}$$

$$= 6.086 \pm 0.013 \text{ eV/atom}$$

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

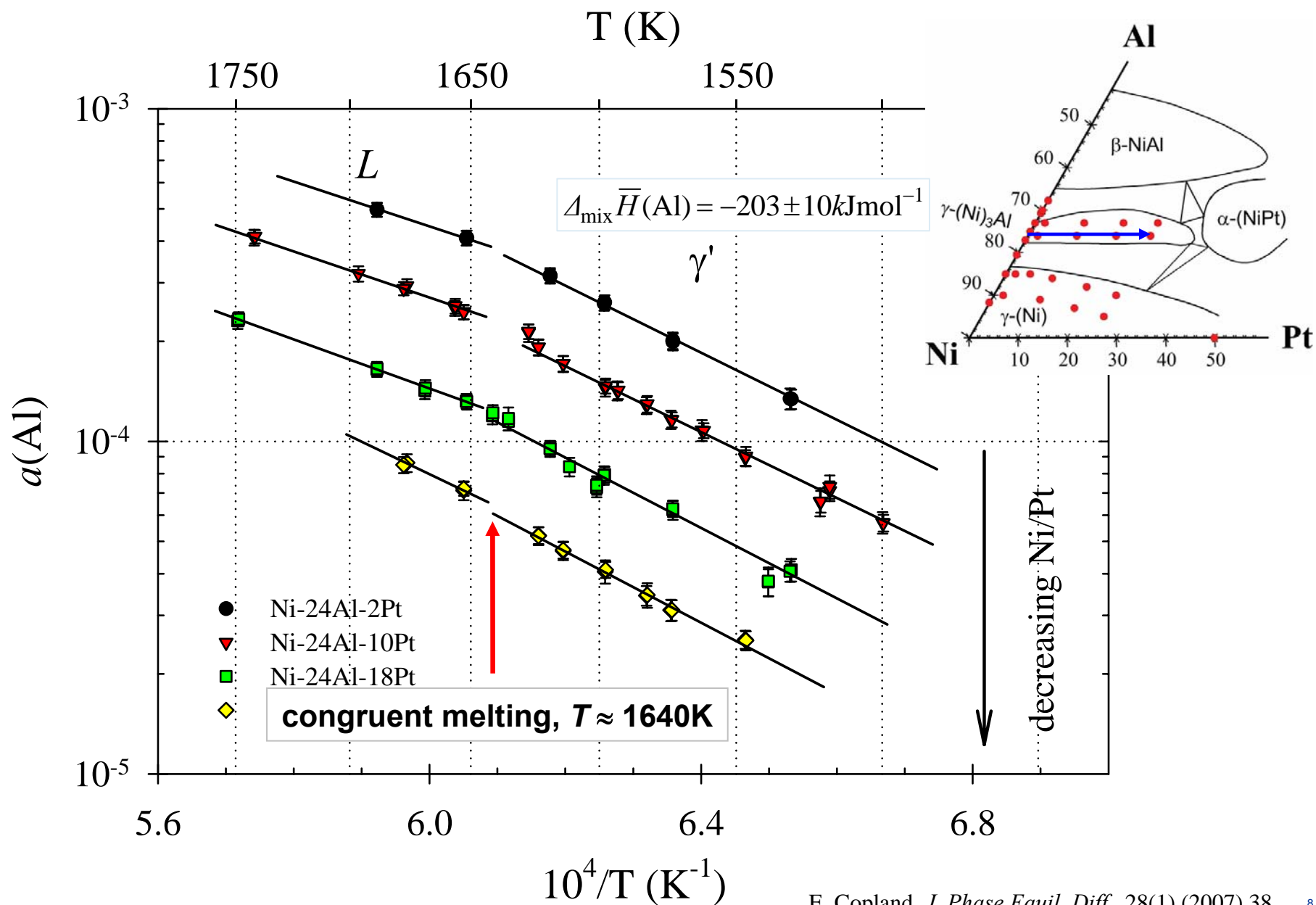
$$= -2.10 \pm 0.015 \text{ eV/atom}$$

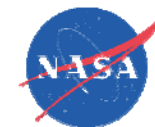
$$\Delta_{mix} \bar{G}_{\text{Ni}}^{\gamma} = RT \ln a(\text{Ni}) = -4.5 \pm 0.9 \text{ kJmol}^{-1}$$

$$= -0.08 \pm 0.015 \text{ eV/atom}$$

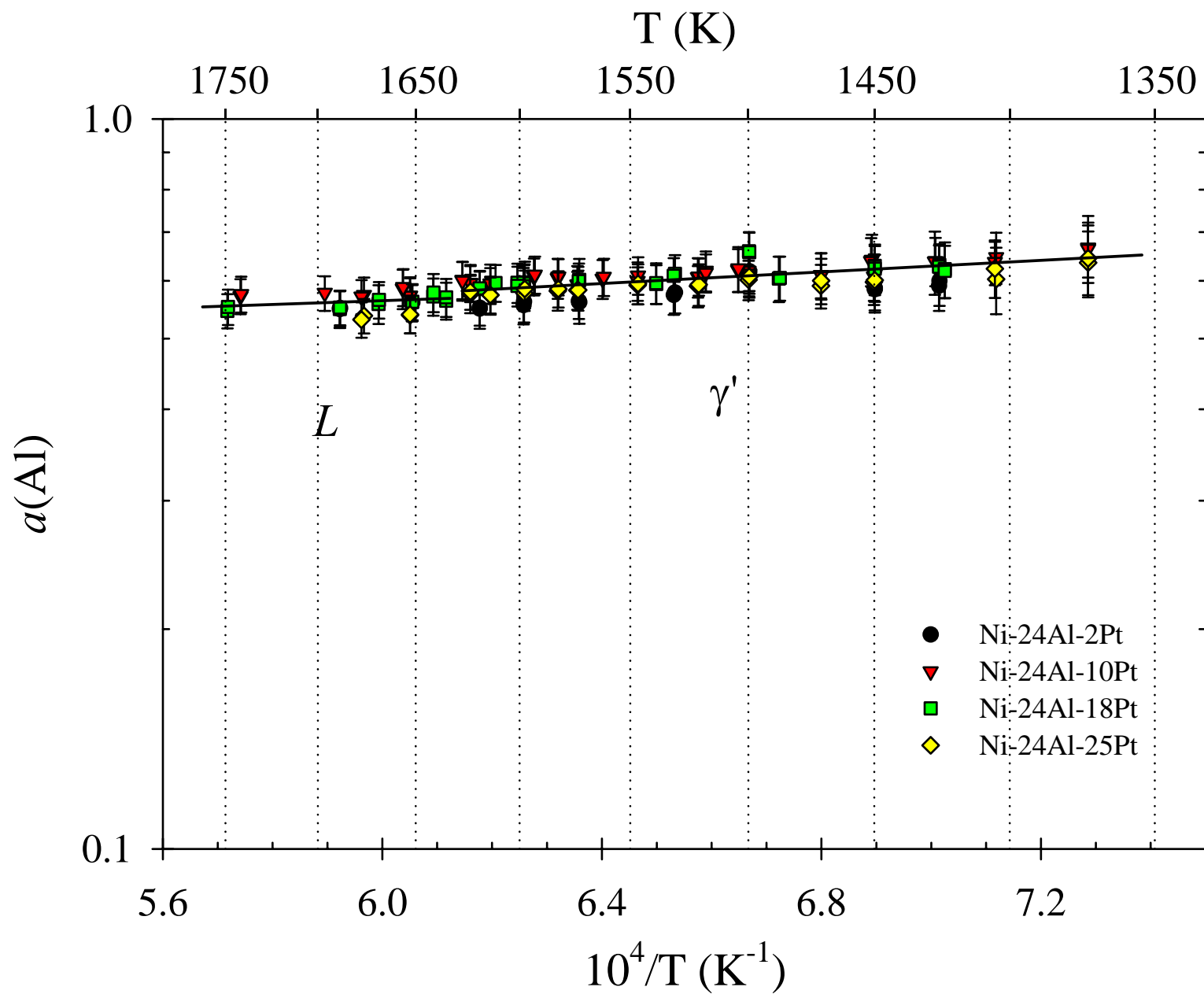


$a(\text{Al})$ vs $1/T$ in Ni-24Al-XPt

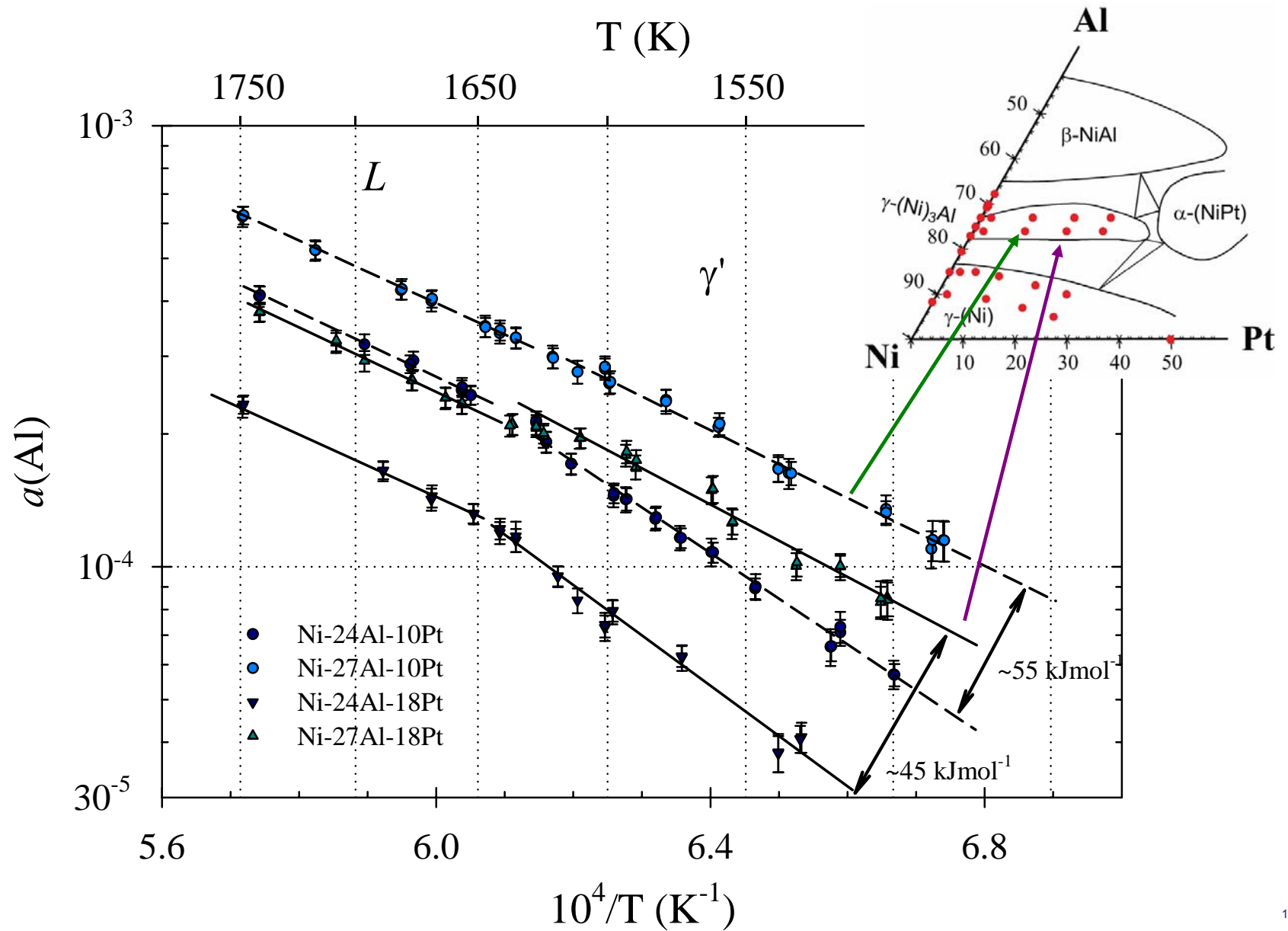




$a(\text{Ni})$ vs $1/T$ in Ni-24Al-XPt

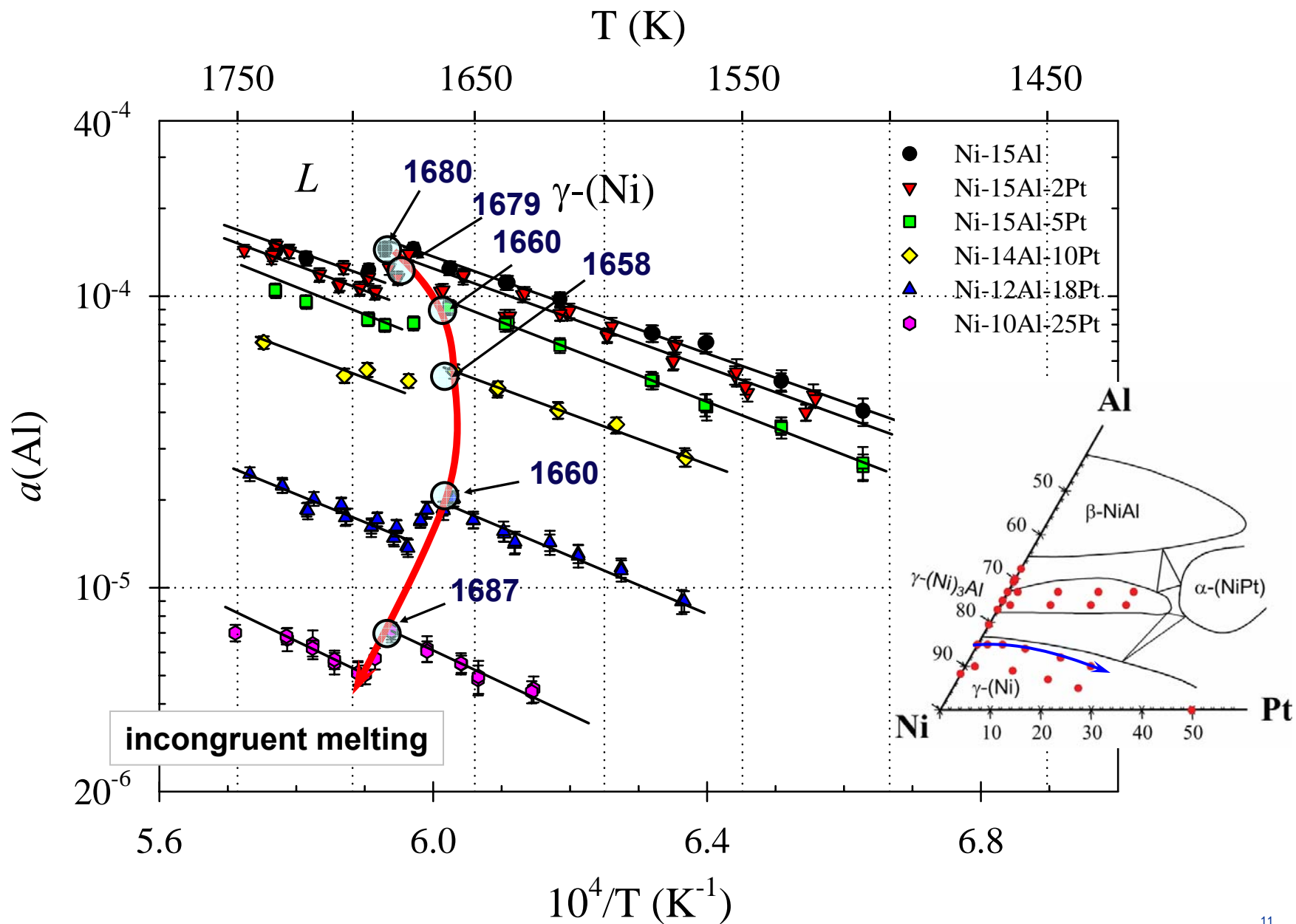


hypo- / hyper-stoichiometric γ'



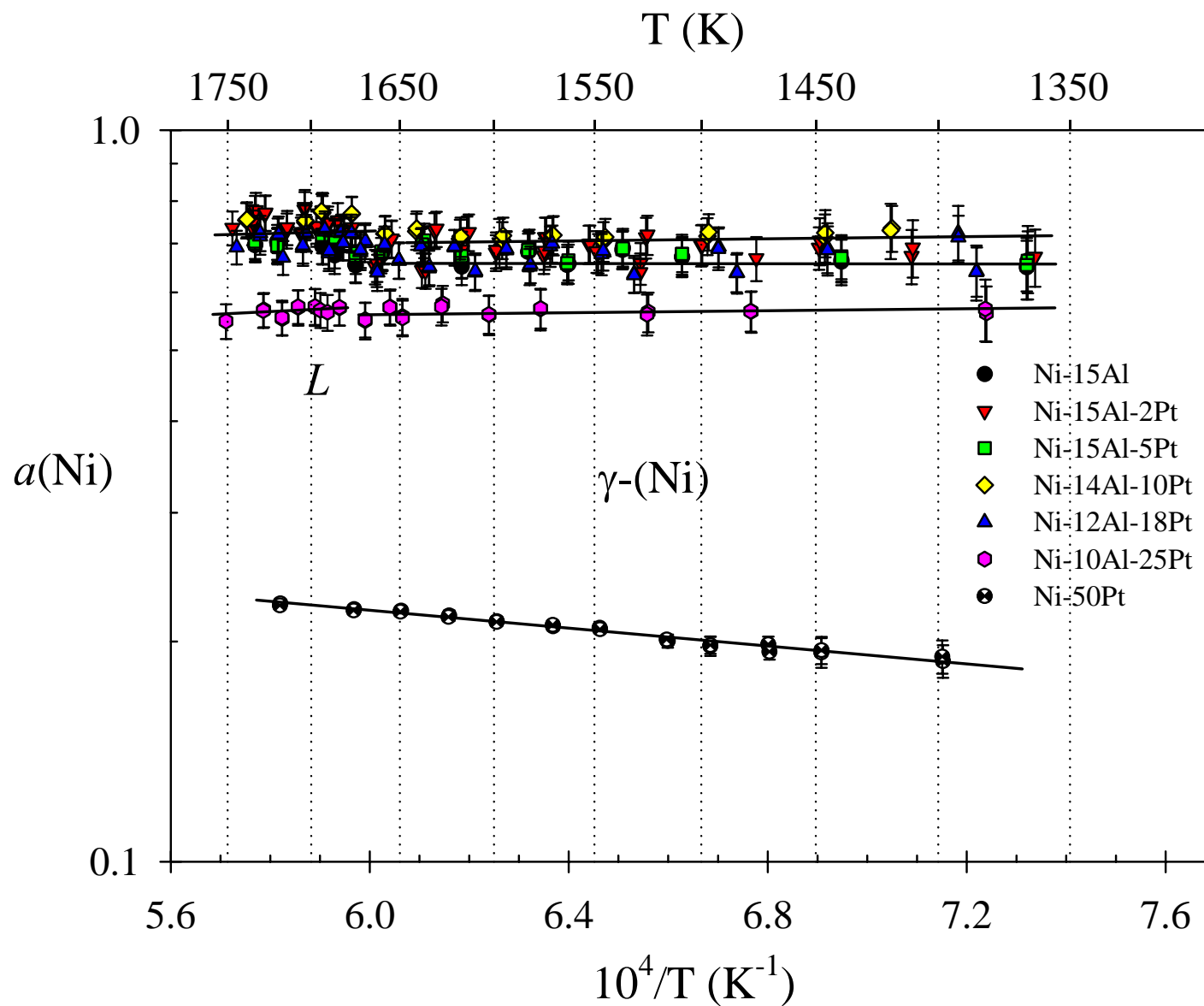


$a(\text{Al})$ vs $1/T$ in γ -(Ni)





$a(\text{Ni})$ vs $1/T$ in γ -(Ni)



“interaction parameter formalism”



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

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

$$\ln \gamma_i / \gamma_i^0 = \ln \gamma_{\text{solvent}} + \epsilon_{i\text{Al}} X_{\text{Al}} + \epsilon_{i\text{Pt}} X_{\text{Pt}} \quad i=\text{Al,Pt}$$

$$\epsilon_{ij} = \left(\partial \ln \gamma_i / \partial X_j \right)_{\text{solvent}}$$

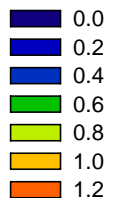
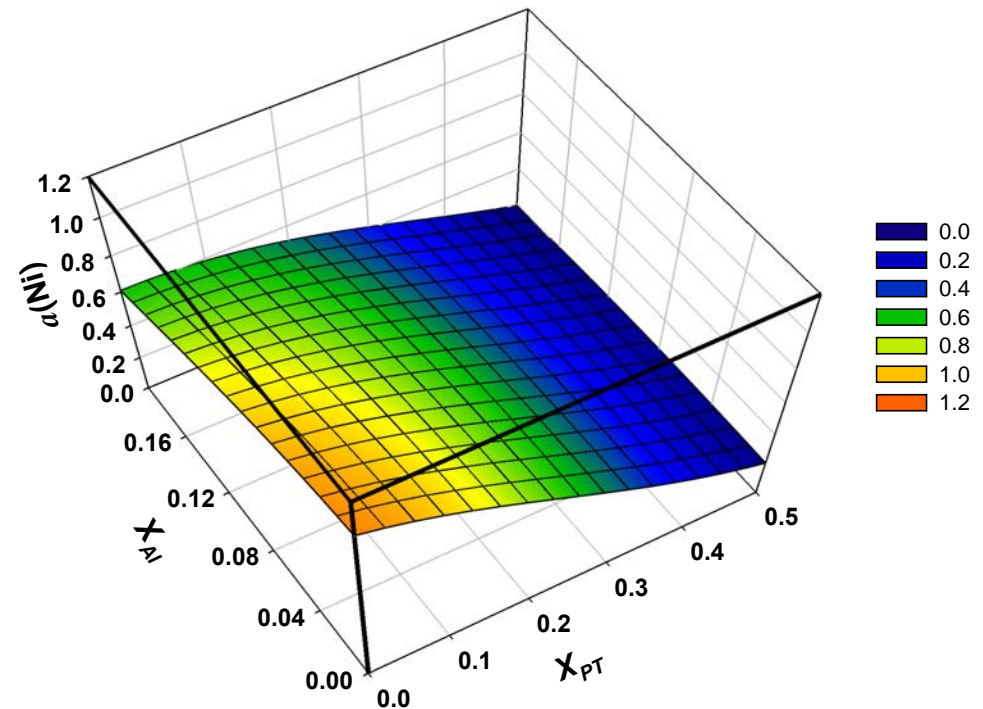
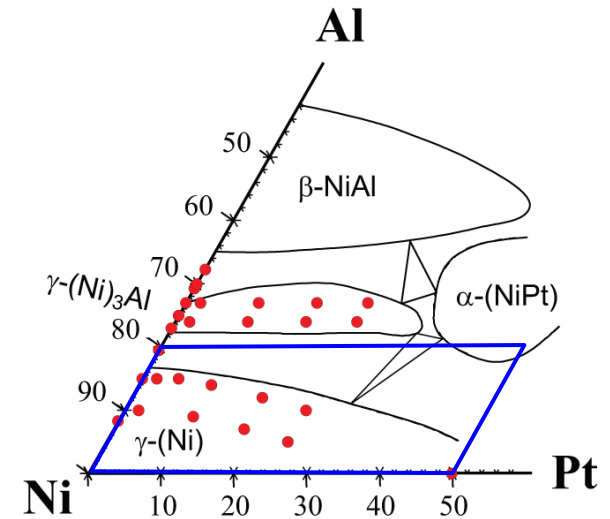
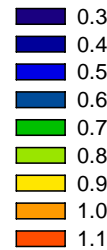
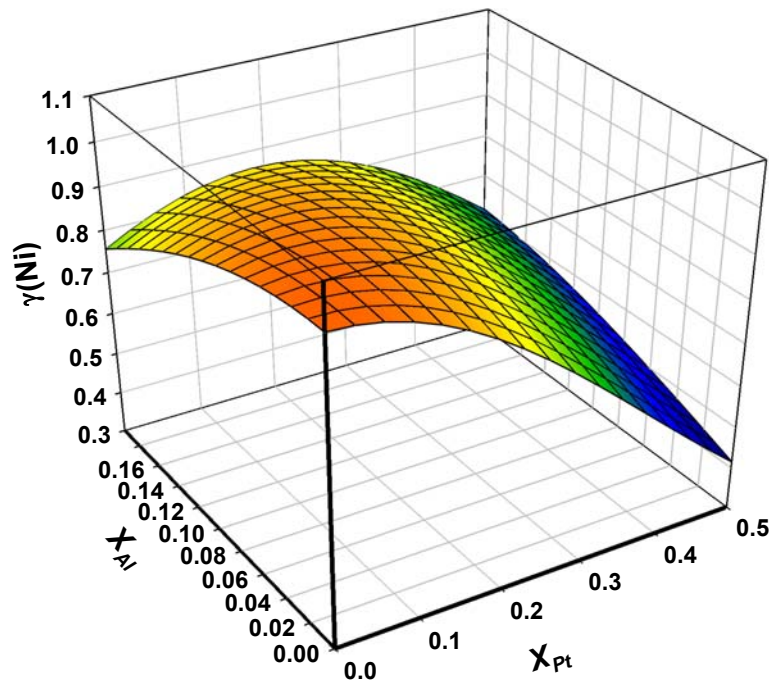
coefficients at 1550K	
$\ln \gamma_{\text{Al}}^0$	-9.84±0.07
$\ln \gamma_{\text{Pt}}^0$	-5.0
ϵ_{AlAl}	14.57±0.55
ϵ_{PtPt}	7.03±0.4
ϵ_{PtAl}	-13.70±2.7

- 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 $a(\text{Ni})$ and $a(\text{Al})$,... predict $a(\text{Pt})$



γ_{Ni} , $a(\text{Ni})$ surfaces in γ -(Ni)

$T = 1550 \text{ K}$

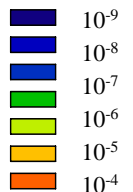
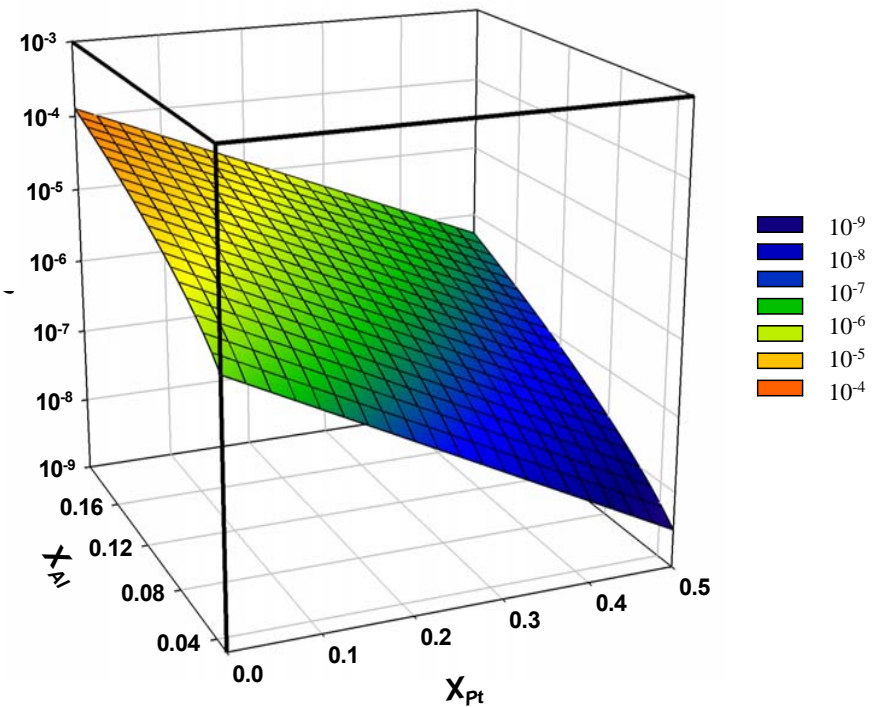
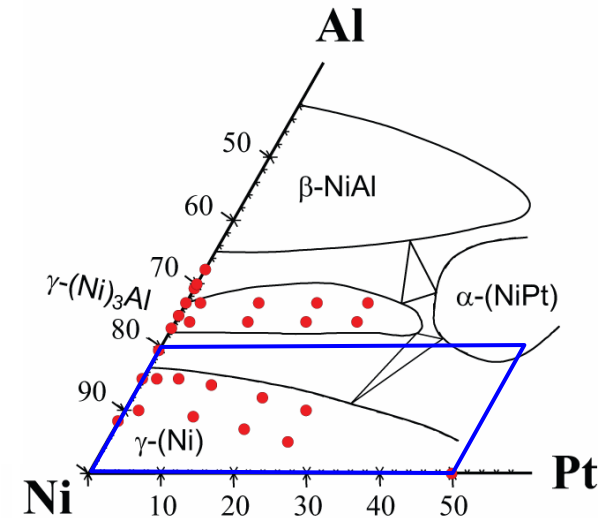
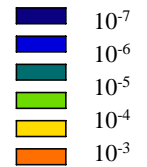
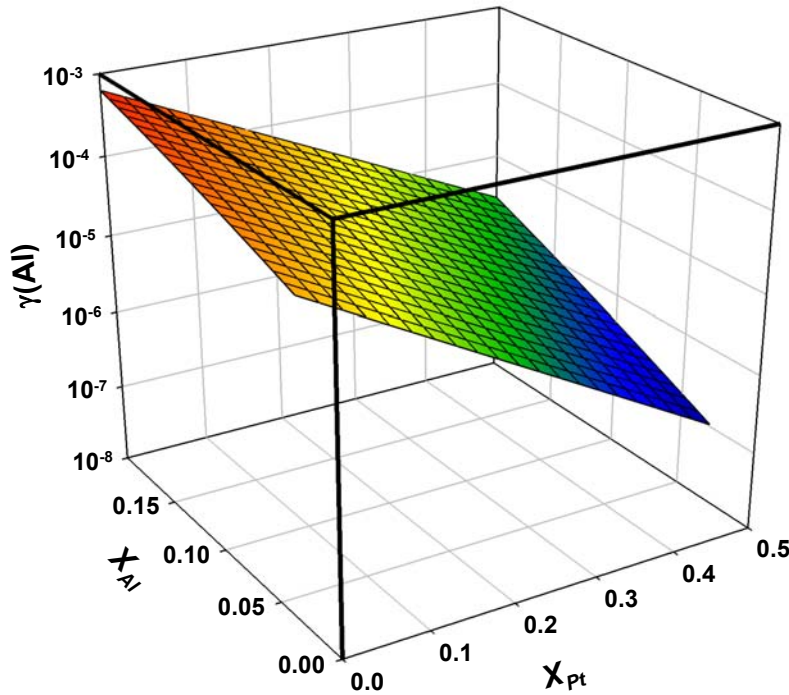


- $a(\text{Ni})$ remains high with Pt addition... more pronounced in γ' -(Ni)₃Al
- limits ΔG for $J_{\text{Ni}} \rightarrow \gamma + \gamma'(\text{Pt})$ coating
- exclusive Al_2O_3 -layer not due to $\downarrow a(\text{Ni})$



γ_{Al} , $a(Al)$ surfaces in γ -(Ni)

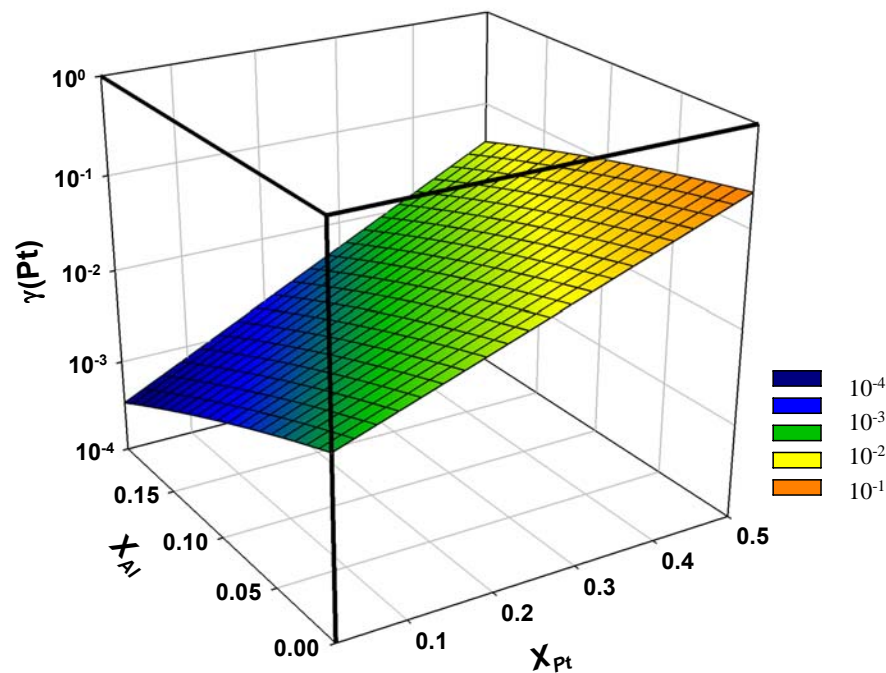
$T = 1550 \text{ K}$



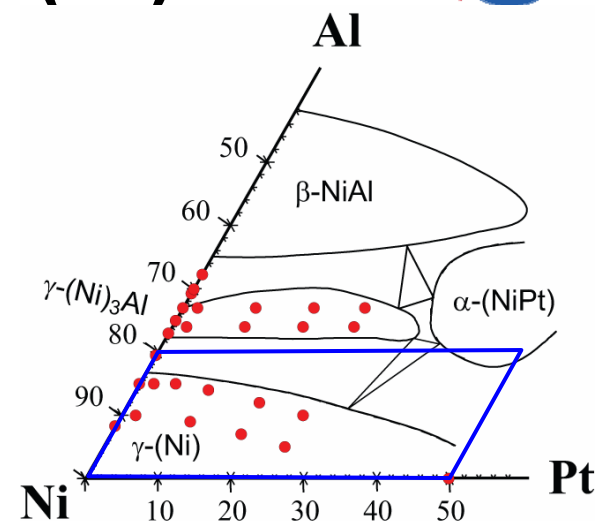
- $a(Al)$ strong influence Al, Pt $\epsilon_{AlAl} \approx -\epsilon_{PtAl}$
- $\downarrow a(Al)$ doesn't destabilize Al_2O_3
- Pt enrichment: ΔG for $J_{Al} \rightarrow \text{alloy}/Al_2O_3$



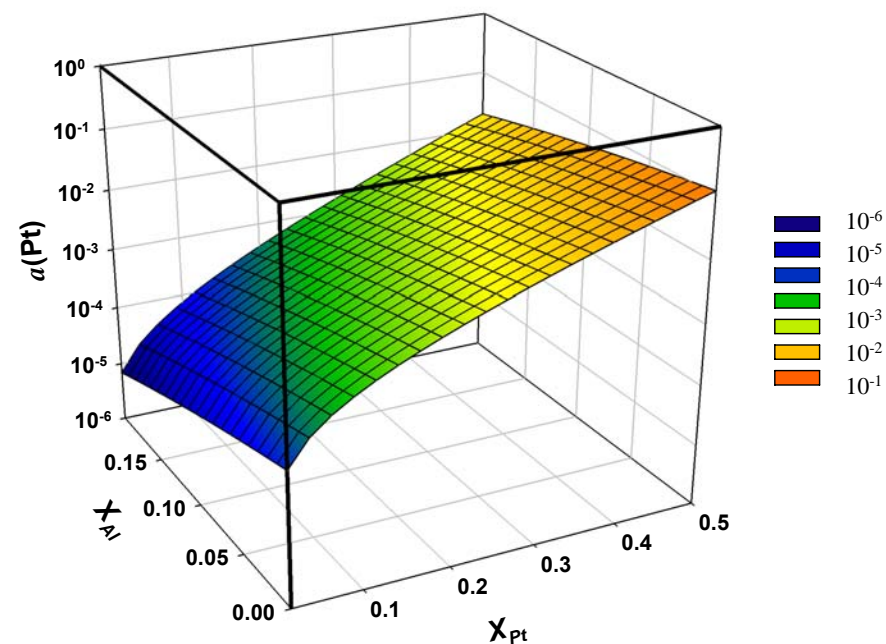
γ_{Pt} , $a(Pt)$ surfaces in γ -(Ni)



$T = 1550$ K



- $a(Al)$ and $a(Ni)$, Gibbs-Duhem $\rightarrow a(Pt)$
- Pt behavior \approx - Al behavior
- \sim





summary

- $a(\text{Al})$, $a(\text{Ni})$ measured at 25 comp. in Ni-corner of Ni-Al-Pt
 - ↳ $T = 1400 - 1750$ K in $\gamma\text{-(Ni)}$, $\gamma'\text{-(Ni)}_3\text{Al}$ and L
 - ↳ Pt addition: $a(\text{Al})$ reduced, $a(\text{Ni}) \sim \text{constant}$
- *thermodynamic measurements are easy!* (2 ~ 4 alloys / week)
 - ↳ must closely consider state of the system (Al_2O_3)
- future work:
 - ↳ calculate $\gamma\text{-(Ni)} / L$, $\gamma\text{-(Ni)} / \gamma'\text{-(Ni)}_3\text{Al}$ phase boundaries
 - ↳ show activities are as good as phase equilibria
 - ↳ introduce Al_2O_3 and O to data analysis



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