Partial Thermodynamic Properties of γ'-$(Ni,Pt)_3Al$

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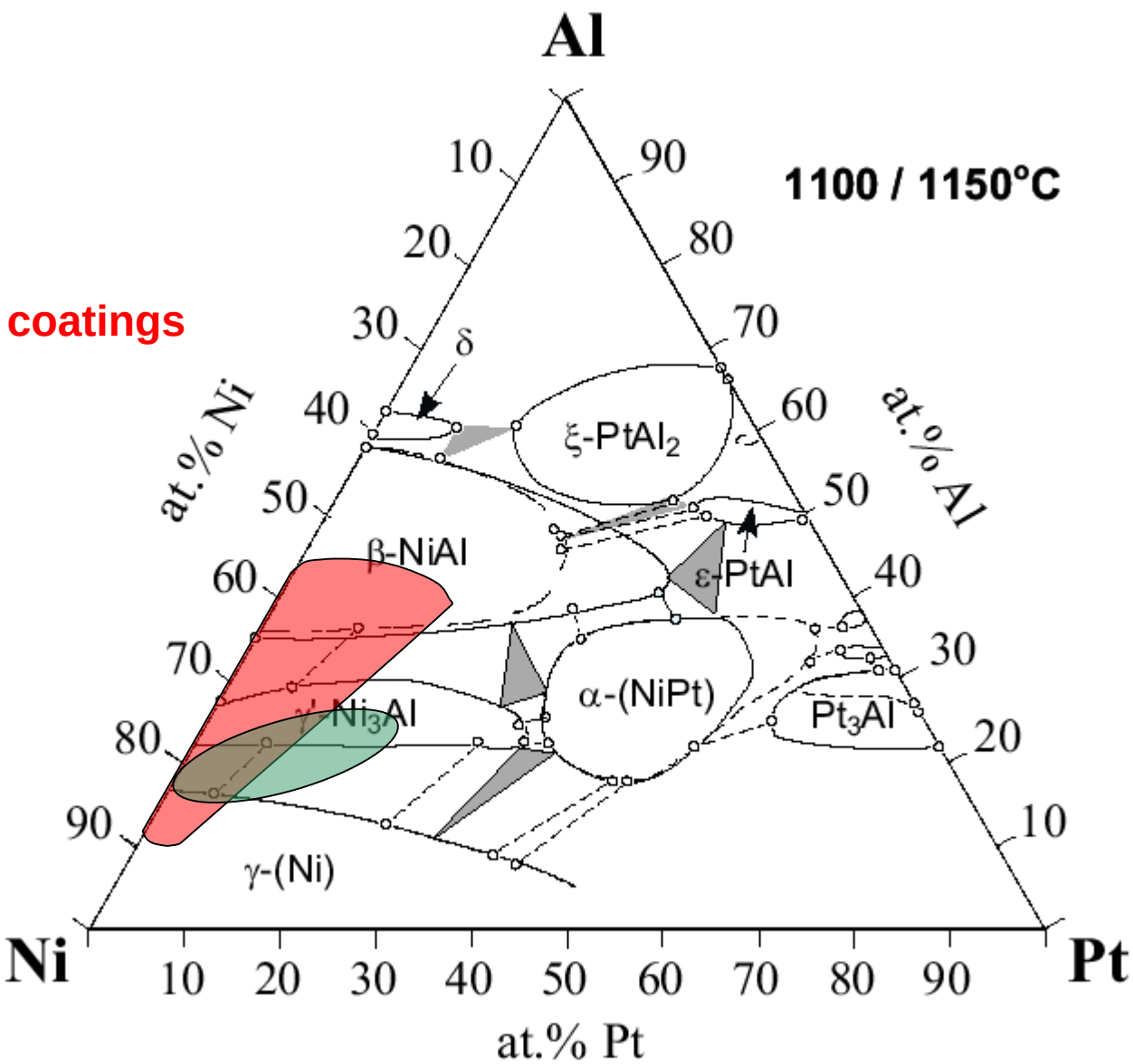
outline

- Ni-Al-Pt phase diagram / scope of study
- partial thermodynamic property measurements
  - ➥ "vapor pressure" technique, multi-cell *KEMS*
  - ➥ Al_2O_3 container: Ni-Al-Pt $\Leftrightarrow$ Ni-Al-Pt-O
  - ➥ reference states: { Al(l) + Al_2O_3 } and { Ni(s) + Al_2O_3 }
- a(Al) and a(Ni) in γ'-$(Ni,Pt)_3Al$
  - ➥ X_{Al} = 0.24 (*hypo-stoich.*); X_{Pt} = 0.02 – 0.25
  - ➥ X_{Al} = 0.27 (*hyper-stoich.*); X_{Pt} = 0.02 – 0.25
- summarize influence of Pt on Al and Ni
- diffusion profile question…

Ni-Al-Pt

Pt - aluminide coatings

γ′ + γ coatings



S. Hayashi, *et al.*, *Acta Materialia.* 461-462, (2005), 213

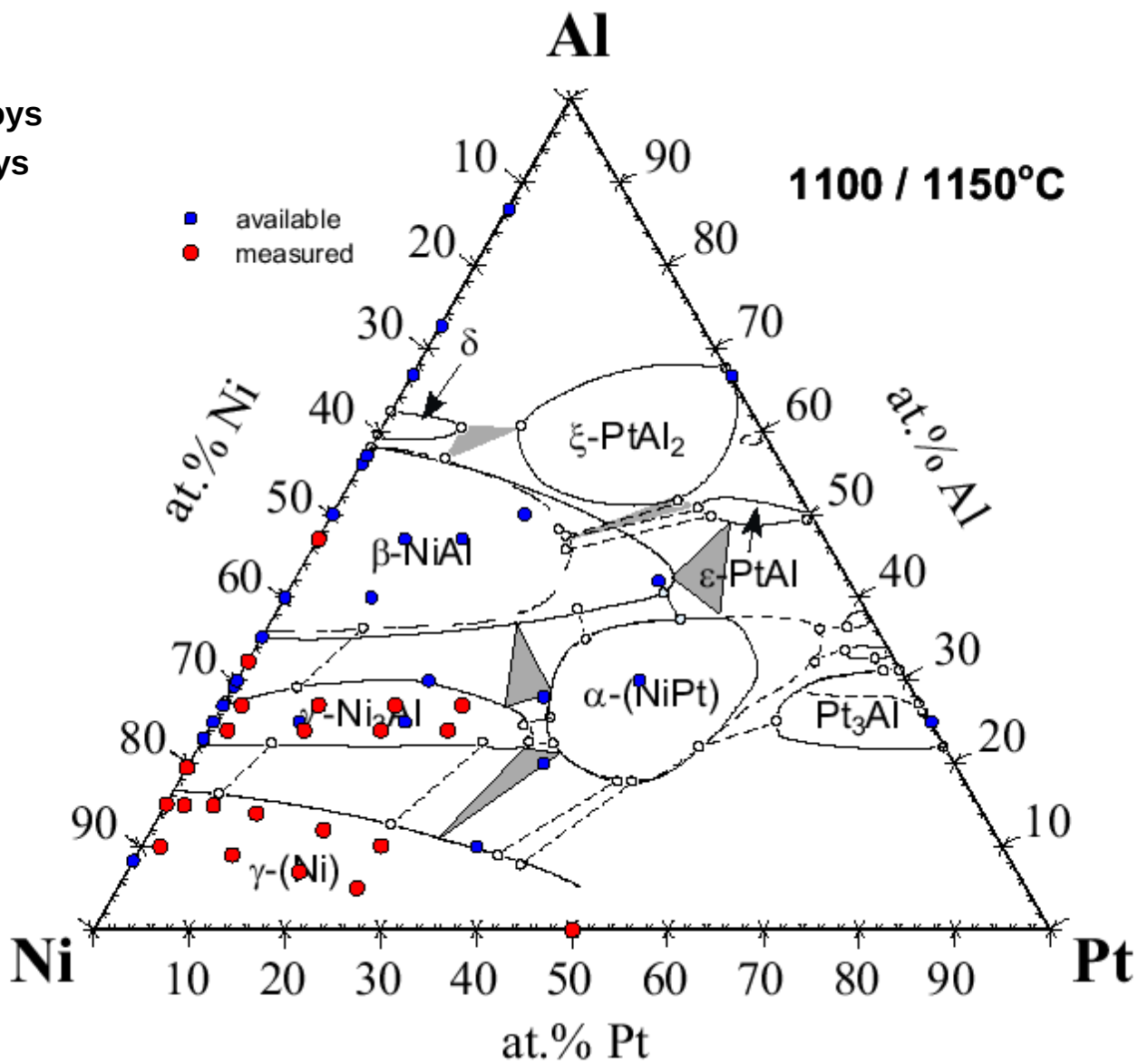
scope of work

- investigate “Pt effect”… multi-component diffusion
- accurate thermodynamic description of Ni-Al-Pt-X
  - ➥ routine thermodynamic properties measurements
  - ➥ integrate experimental and modeling approach
- initial focus: Ni-Al-Pt… (including Ni-Pt, Al-Pt and Ni-Al)
- future: addition of Cr, Hf, Y,…

alloy compositions

~30 ternary alloys

~20 binary alloys



“vapor pressure technique”

comparing the sublimation behavior…

solution-phase: γ'-$(Ni,Pt)_3Al$

$$(\mathrm{Ni,Pt})_3\,\mathrm{Al_n} = (\mathrm{Ni,Pt})_3\,\mathrm{Al_{n\text{-}1}} + \mathrm{Al(g)} \qquad \Delta_{\mathrm{sub}}\overline{G}^{\gamma'}(\mathrm{Al}) = -RT\ln p(\mathrm{Al})$$

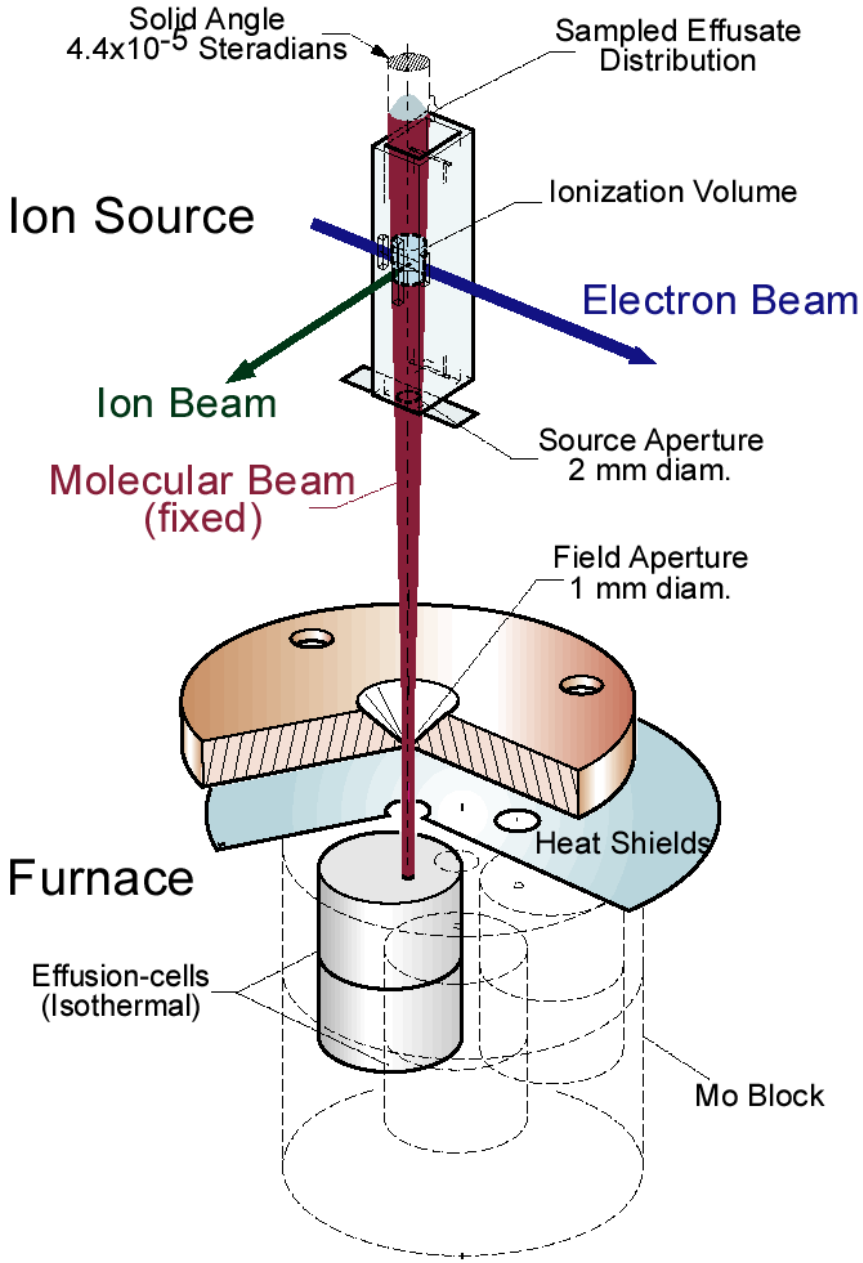
reference: Al(l)

$$\mathrm{Al}^{l} = \mathrm{Al(g)} \qquad \Delta_{\mathrm{sub}}G^{\circ} = -RT\ln p^{\circ}(\mathrm{Al})$$

$$a(\mathrm{Al}) = \frac{p(\mathrm{Al})}{p^{\circ}(\mathrm{Al})}$$

measure pressure ratio as function (*comp.*, *T*)

multi-cell *KEMS*



absolute pressures

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

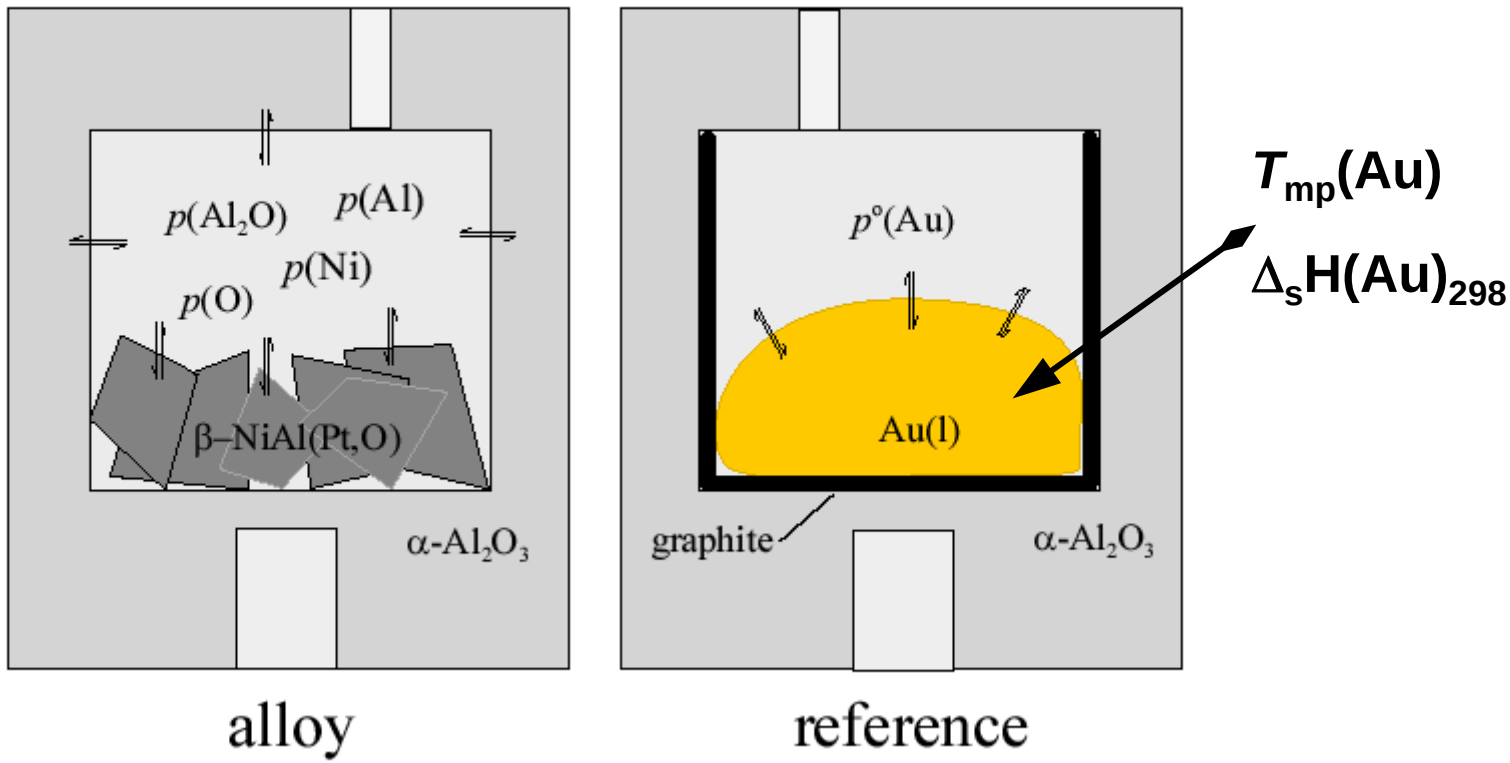
sensitivity coefficient

$$S_{ik} = g\varepsilon_k(x,y,z)\tau_k\sigma_{ik}(E)\gamma_k f_i$$

relative pressures

$$p(\mathrm{i}) \propto I_{ik}^{+} T$$

indirect measurement



$$a(\mathrm{i}) = \frac{p(\mathrm{i})}{\cancel{p^\circ(\mathrm{Au})}} \cdot \left[\frac{\cancel{p^\circ(\mathrm{Au})}}{p^\circ(\mathrm{i})}\right] = \frac{I_\mathrm{i}}{I^\circ_\mathrm{Au}} \cdot \frac{S_\mathrm{Au}}{S_\mathrm{i}} \cdot \frac{g(R)}{g(A)} \cdot \left[\frac{p^\circ(\mathrm{Au})}{p^\circ(\mathrm{i})}\right] \quad (\mathrm{i} = \mathrm{Ni, Al, Al_2O})$$

reference state calibrations…

Au(s,l) ≡ { Al(l) + Al_2O_3 }

$$\mathrm{Au(s,l)} = \mathrm{Au(g)} \qquad K_1 = p^\circ(\mathrm{Au})$$

$$\mathrm{Al(l)} = \mathrm{Al(g)} \qquad K_2 = p^\circ(\mathrm{Al})$$

$$4/3\,\mathrm{Al(l)} + 1/3\,\mathrm{Al_2O_3(s)} = \mathrm{Al_2O(g)} \qquad K_3 = p^\circ(\mathrm{Al_2O})$$

Au(s,l) ≡ { γ-Ni(s) + Al_2O_3 }

$$\mathrm{Au(s,l)} = \mathrm{Au(g)} \qquad K_1 = p^\circ(\mathrm{Au})$$

$$\mathrm{Ni(s)} = \mathrm{Ni(g)} \qquad K_4 = p^\circ(\mathrm{Ni})$$

$$\frac{p^\circ(\mathrm{i})}{p^\circ(\mathrm{Au})} = \left[\frac{p^\circ(\mathrm{i})}{p^\circ(\mathrm{Au})}\right] \qquad \frac{S_{Au}}{S_i}\left(or\ \frac{\sigma_{Au}(E)\gamma_{Au}}{\sigma_i(E)\gamma_i}\right) = \frac{I^\circ{}_{Au}}{I_i^\circ}\cdot\frac{g(i)}{g(Au)}\left[\frac{p^\circ(\mathrm{i})}{p^\circ(\mathrm{Au})}\right]$$

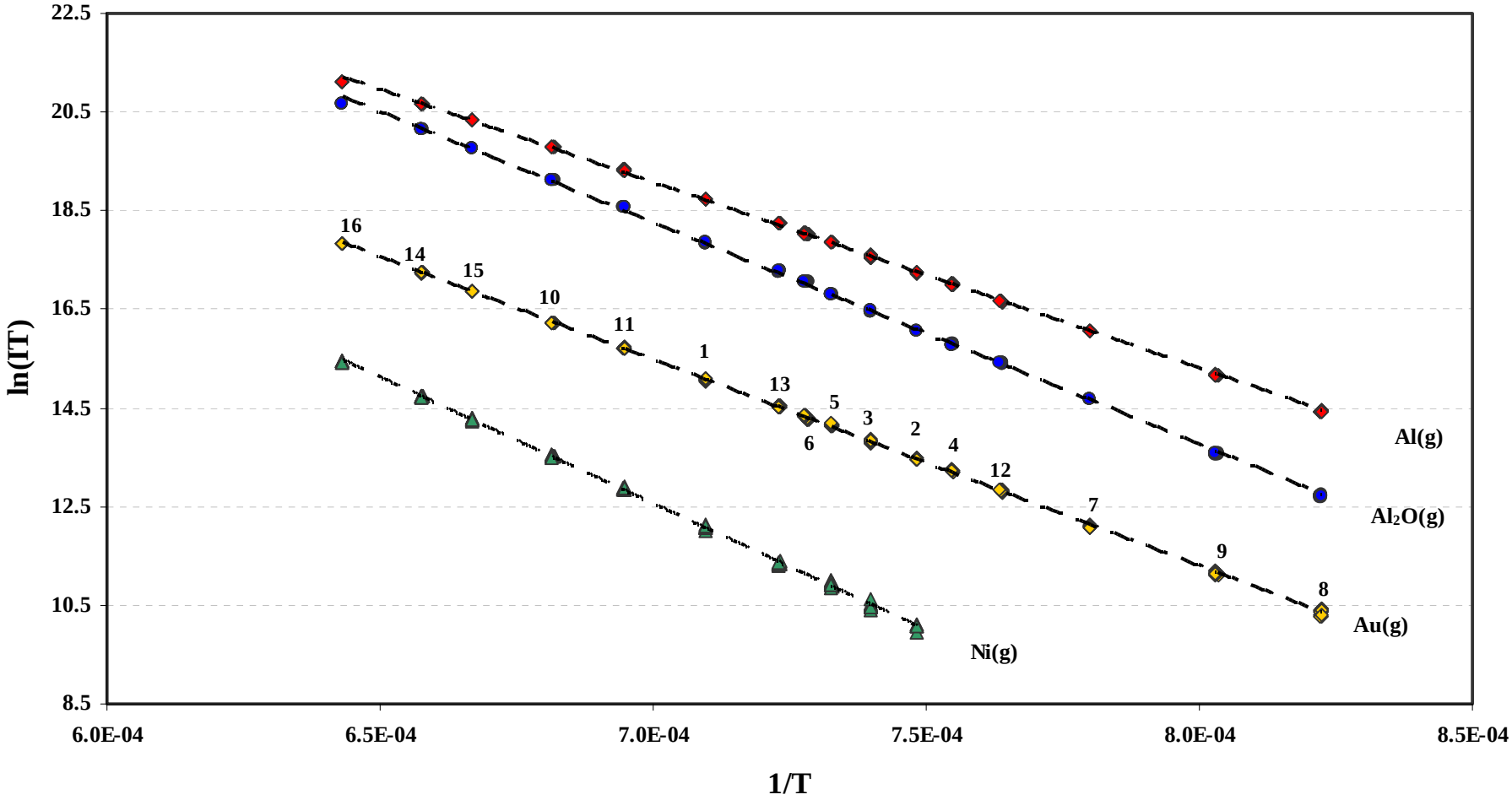
improved { Al(l) + Al_2O_3 } data

reaction (298.15K)	measured (kJmol^{-1})	IVTAN (kJmol^{-1})	JANAF (kJmol^{-1})
Au(s,l) = Au(g)	363.5±2.8 367.0±1.3*	367.0±0.9	
Ni(s) = Ni(g)	428.3±2.6	428.0±8.0	430.1±8.4
Al(s) = Al(g)	341.0±2.2	330.0±3.0	329.7±4.2
4/3Al(s) + 1/3Al_2O_3(s) = Al_2O(g)	414.2±3.6	409.9±55	413.4±50
4/3Al(g) + 1/3Al_2O_3(s) = Al_2O(g)	-41.1±3.2	-30.0±4.3	-26.2±3.0
2Al(g) + O(g) = Al_2O(g)	-1075.5±9.0	-1057.8±20.0	-1053.7 ± 150

* 3rd law measurements

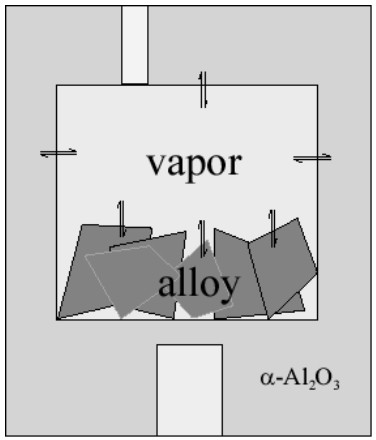
- ignore tabulated data and use measured 2nd law data…
- p^o(Al) and p^o(Al_2O) for { Al(l) + Al_2O_3 } not well known
- Au(s,l) ref. ➞ allows measurement of 2 alloys in each exp.

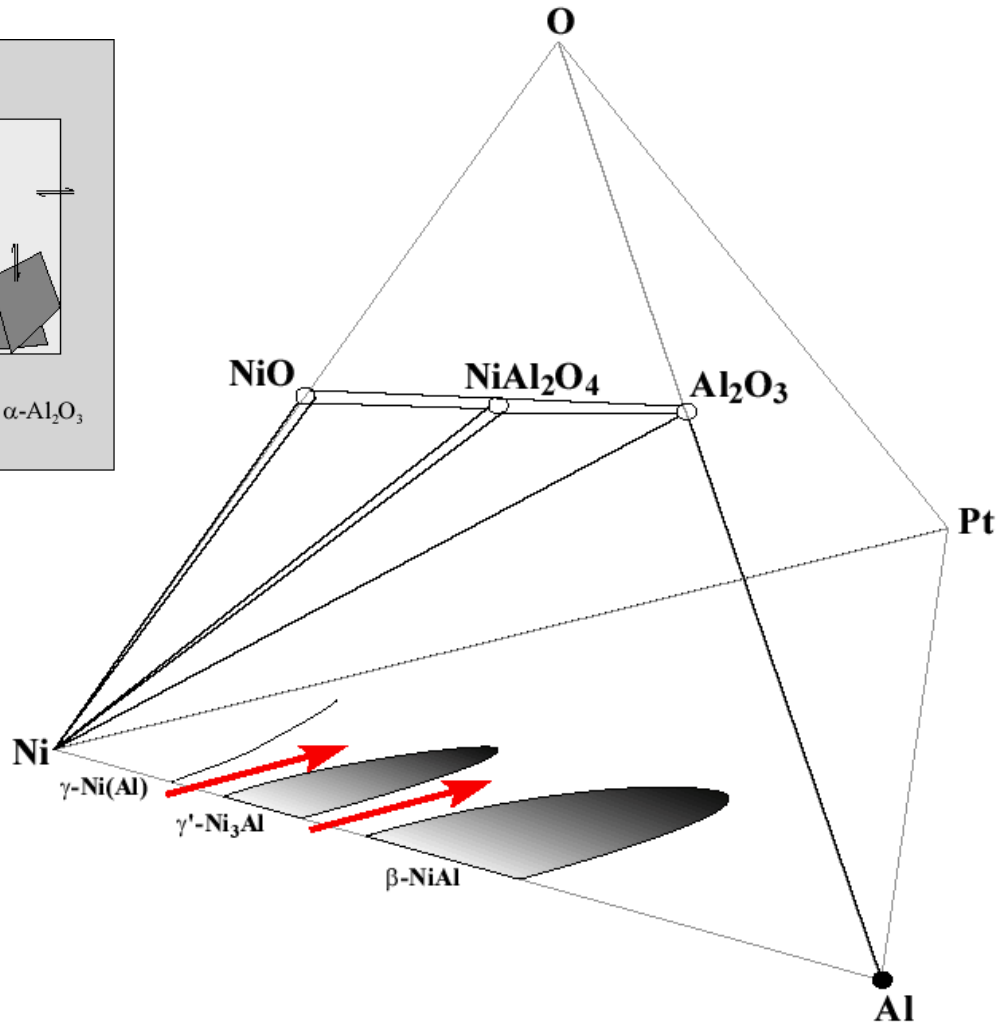
reference state calibrations…



$$\frac{S_{Au}}{S_{Al}} = 0.154 \pm 0.003 \qquad \frac{S_{Au}}{S_{Al_2O}} = 0.506 \pm 0.02 \qquad \frac{S_{Au}}{S_{Ni}} = 0.85 \pm 0.03$$

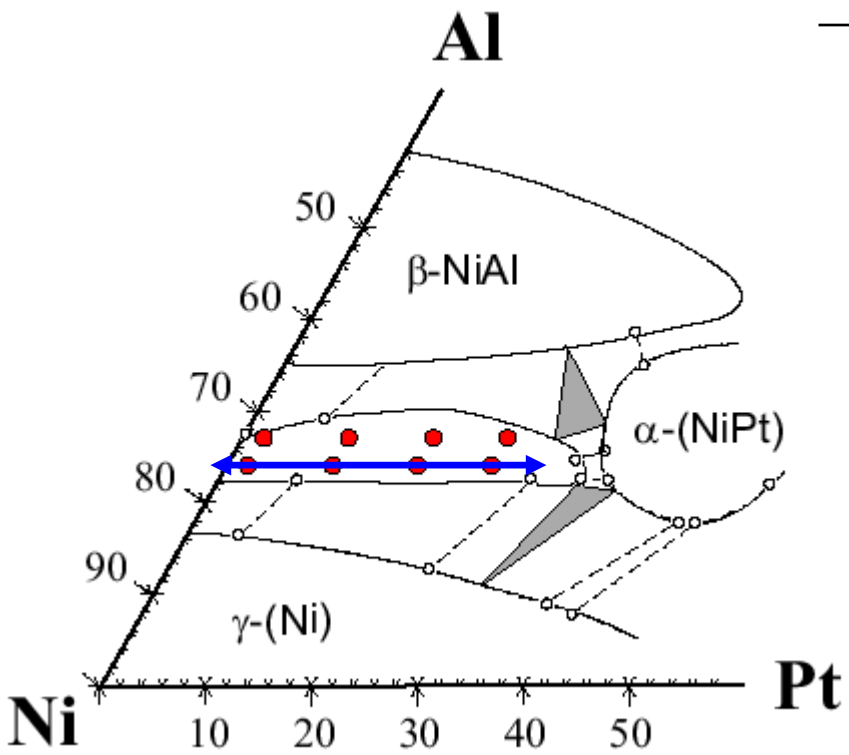
Ni-Al-Pt-O ⇔ Ni-Al-Pt





- actually studying { alloy + Al_2O_3 } equilibrium…
- limited O solubility in alloy; limited Al_2O_3 stoichiometry

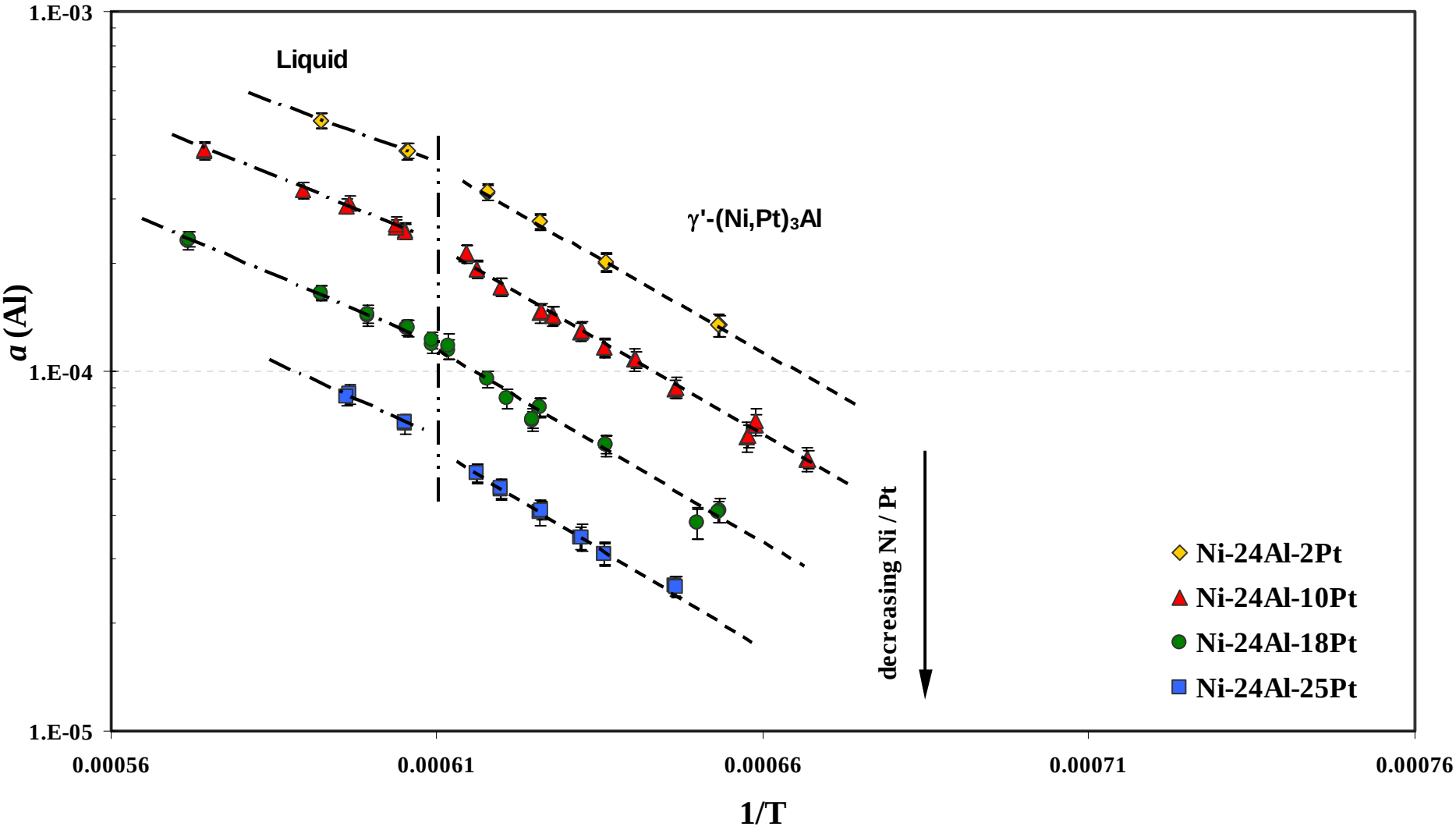
γ´-$(Ni,Pt)_3Al$, X_{Al} = 0.24



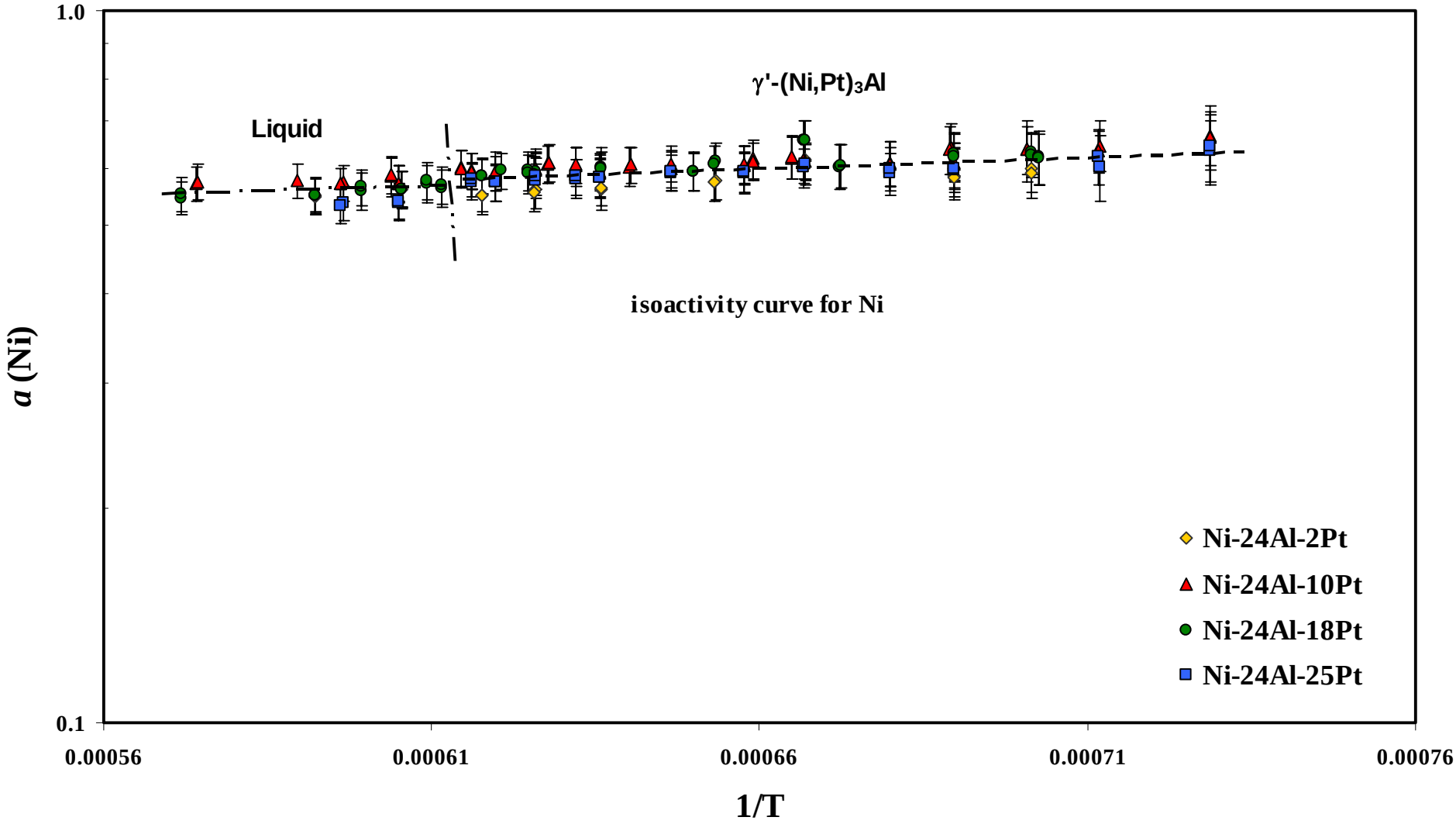
Ni	Al	Pt	Ni/Pt	Al/Pt
73.6	24.3	2.0	35.05	11.57
65.8	24.2	10.0	6.58	2.42
57.9	24.0	18.1	3.2	1.33
51.1	23.8	25.1	2.04	0.95

(at.% ± 0.5)

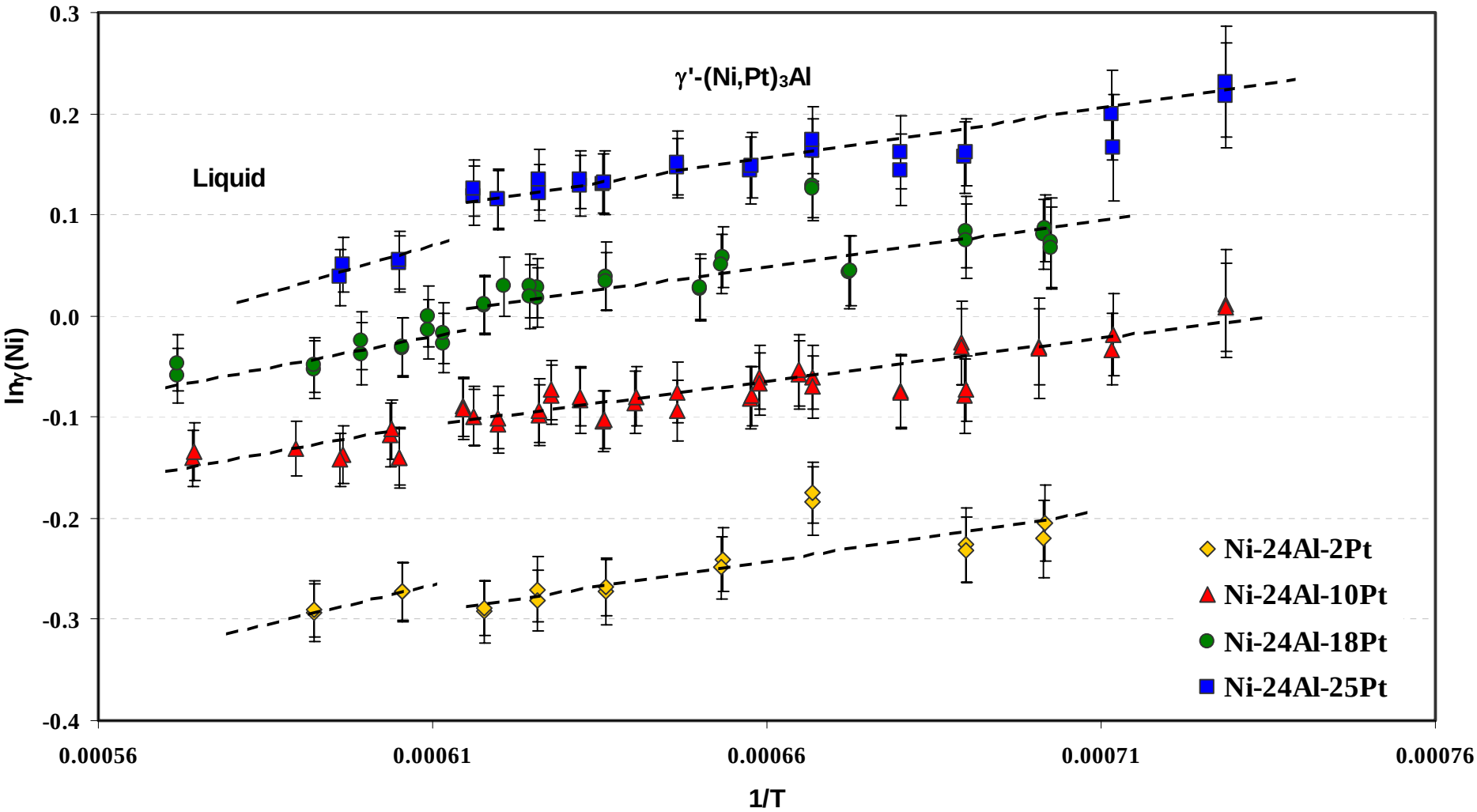
a(Al) vs 1/T (Ni-24Al-XPt)



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



lnγ(Ni) vs 1/T (Ni-24Al-XPt)



partial mixing enthalpies

$$\Delta_m \overline{H}(i) = R \frac{\partial \ln a(i)}{\partial 1/T}$$

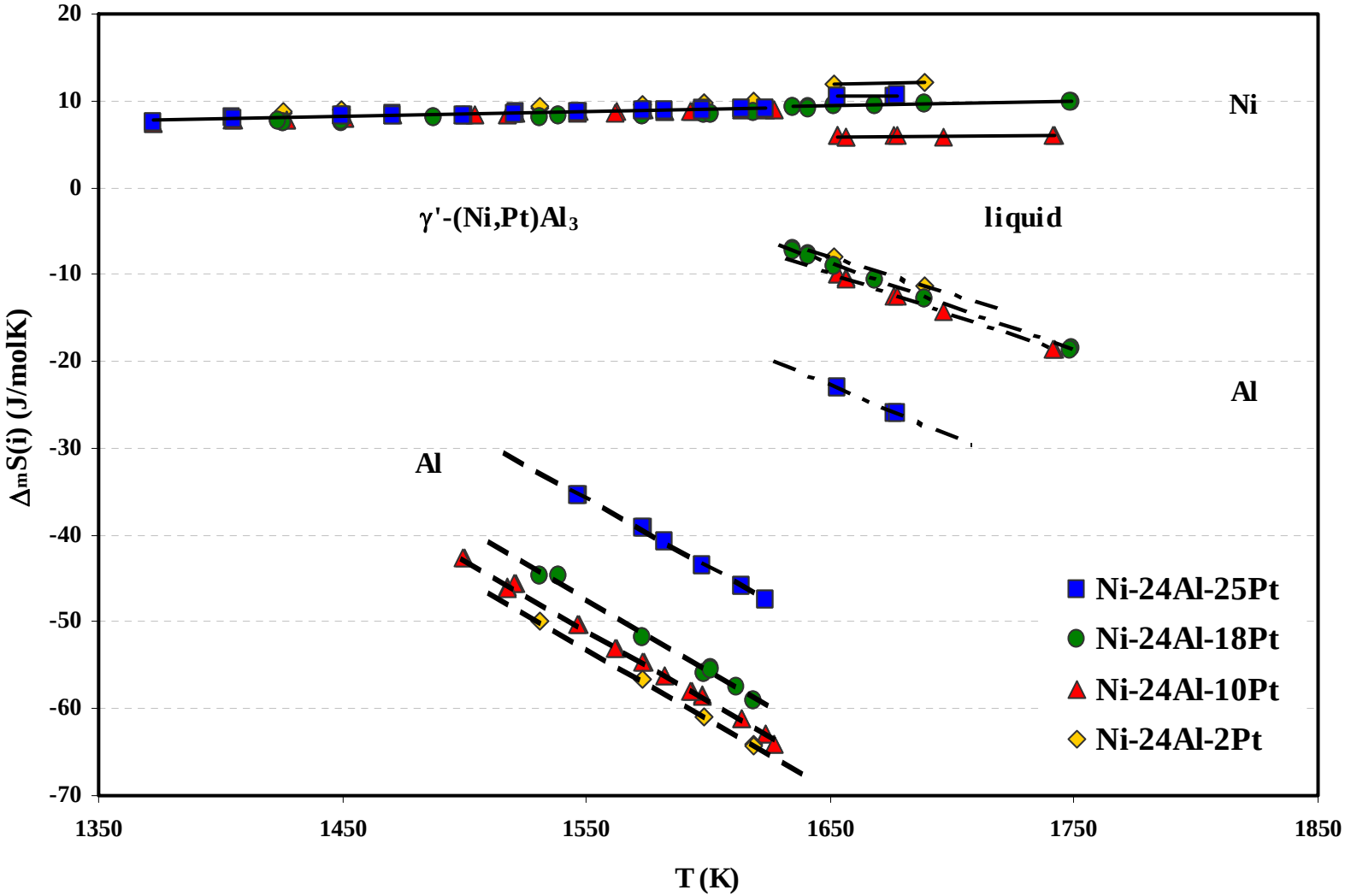
γ'-(Ni,Pt)$_3$Al	$\Delta_m \overline{H}(Ni)$ (kJ/mol)	T (K)	$\Delta_m \overline{H}(Al)$ (kJ/mol)	T (K)	T_{mp} (K)
Ni-24Al-2Pt	7.1±1.3 $_{12}$	1522	-200.5±5.8 $_{8}$	1575	1619-1651
Ni-24Al-10Pt	6.7±1.2 $_{38}$	1500	-201.9±8.0 $_{24}$	1563	1627-1651
Ni-24Al-18Pt	6.1±1.3 $_{20}$	1521	-207.8±25 $_{13}$	1575	1619-1635
Ni-24Al-25Pt	6.4±1.2 $_{24}$	1498	-200.2±11 $_{12}$	1585	1623-1653

liquid	$\Delta_m \overline{H}(Ni)$ (kJ/mol)	T (K)	$\Delta_m \overline{H}(Al)$ (kJ/mol)	T (K)
Ni-24Al-2Pt	11.9±5.0 $_{4}$	1670	-123.1±5.4 $_{4}$	1670
Ni-24Al-10Pt	2.3±6.0 $_{9}$	1697	-137.9±7.8 $_{9}$	1697
Ni-24Al-18Pt	8.3±4.0 $_{12}$	1692	-144.3±5.2 $_{12}$	1692
Ni-24Al-25Pt	8.9±20 $_{4}$	1665	-172±56 $_{4}$	1665

subscript: number of data points

partial entropy of mixing: Al, Ni

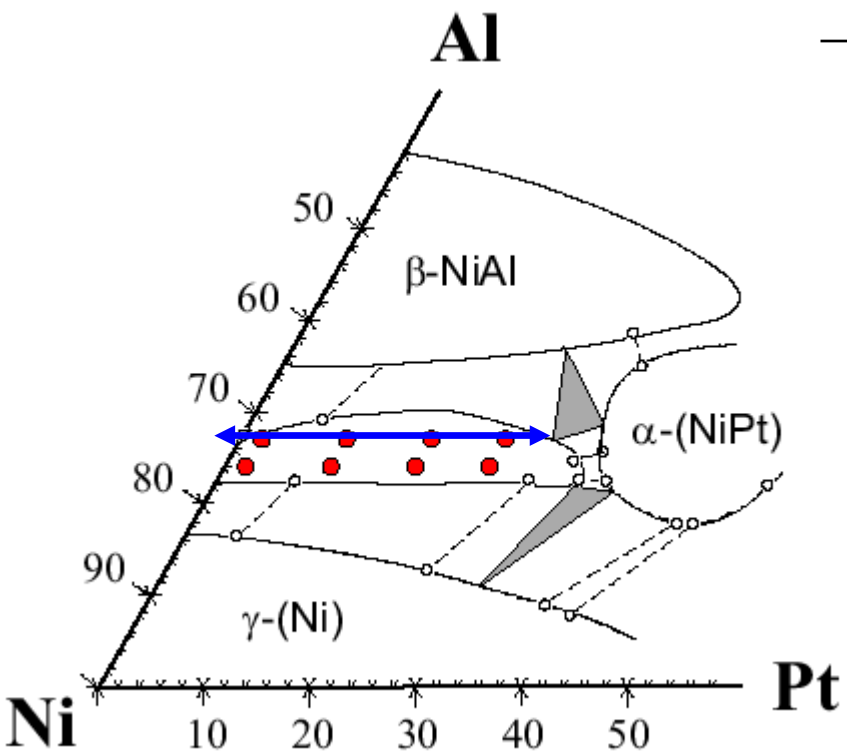
$$\Delta_m \overline{S}(i) = -R \ln a(i) - RT \frac{\partial \ln a(i)}{\partial T}$$



Ni-24Al-XPt…

- γ'-$(Ni,Pt)_3Al$: a(Al) decreases ~10 with Pt addition (Ni/Pt ↓)
- $\Delta_m H$(Al) –203±10 kJmol^{-1}, independent of Ni/Pt
  - ➥ bond strength: Al ↔ Ni identical to Al ↔ Pt (?)
  - ➥ or X_{Al} has strongest influence on Al bonding
- $\Delta_m S$(Al) –60 to –40 Jmol^{-1}K^{-1} with Pt addition (Ni/Pt ↓)
  - ➥ increase in S(Al) ➞ decreasing a(Al)
  - ➥ entropy-based interaction between Ni- and Al-lattices (?)
- liquid: a(Al) decreases with Pt addition (Ni/Pt ↓)
- $\Delta_m H$(Al) –120 to –170 kJmol^{-1}, $\Delta_m S$(Al) –10 to –25 Jmol^{-1}K^{-}
  - ➥ increasing Al ordering in liquid with Pt addition
- a(Ni) constant with Pt addition (Ni/Pt ↓): γ_{Ni} increases 0.7 to 1.2
  - ➥ $\Delta_m H$(Ni) ~7 kJmol^{-1}, $\Delta_m S$(Al) +ve
  - ➥ +ve ternary interaction between Ni ↔ (Al + Pt)

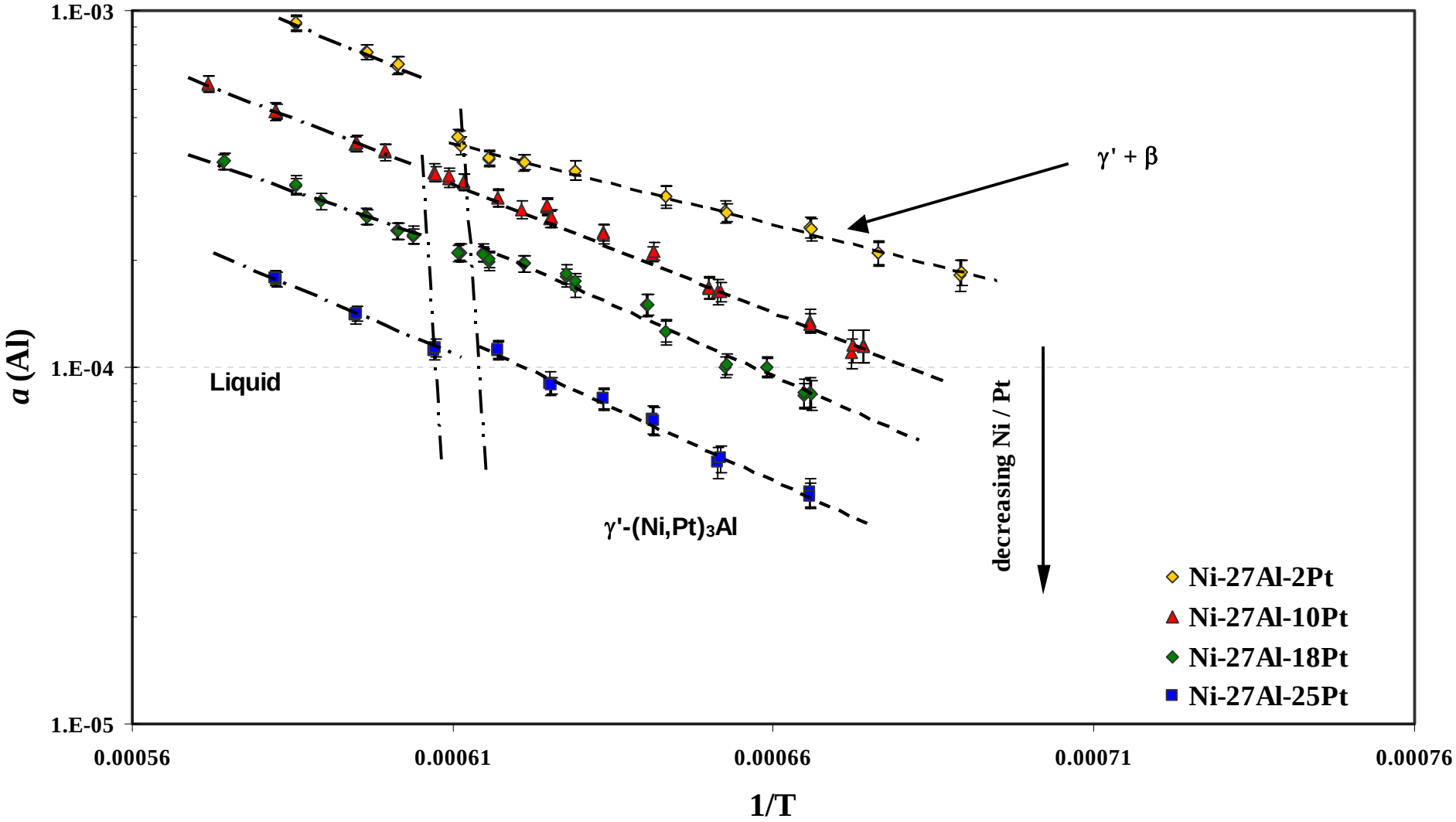
γ´-$(Ni,Pt)_3Al$, X_{Al} = 0.27



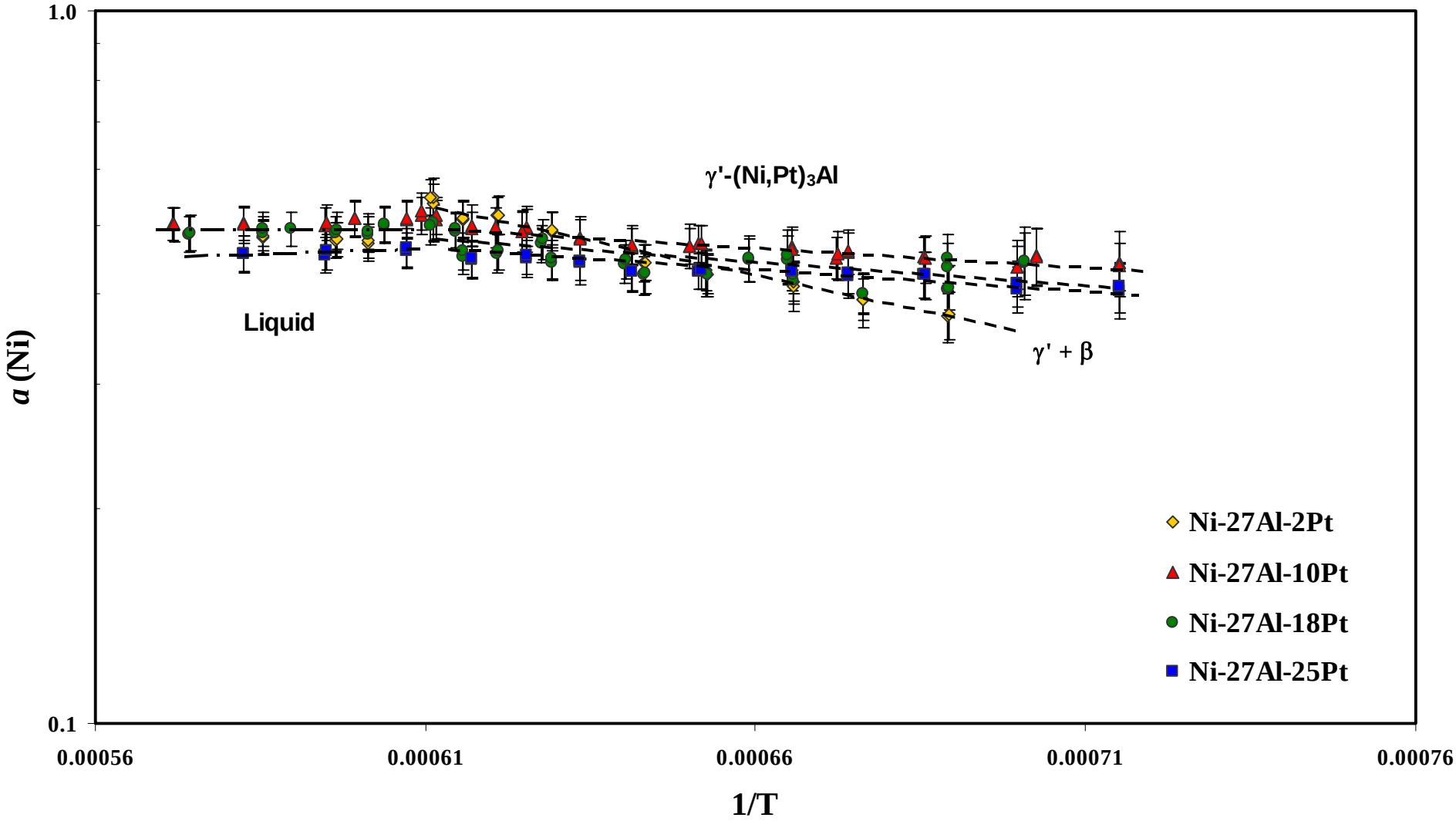
Ni	Al	Pt	Ni/Pt	Al/Pt
70.8	27.2	2.0	35.4	13.6
63.8	26.4	9.8	6.51	2.69
54.9	27.0	18.1	3.03	1.49
48.1	26.7	25.2	1.91	1.06

(at.% ± 0.5)

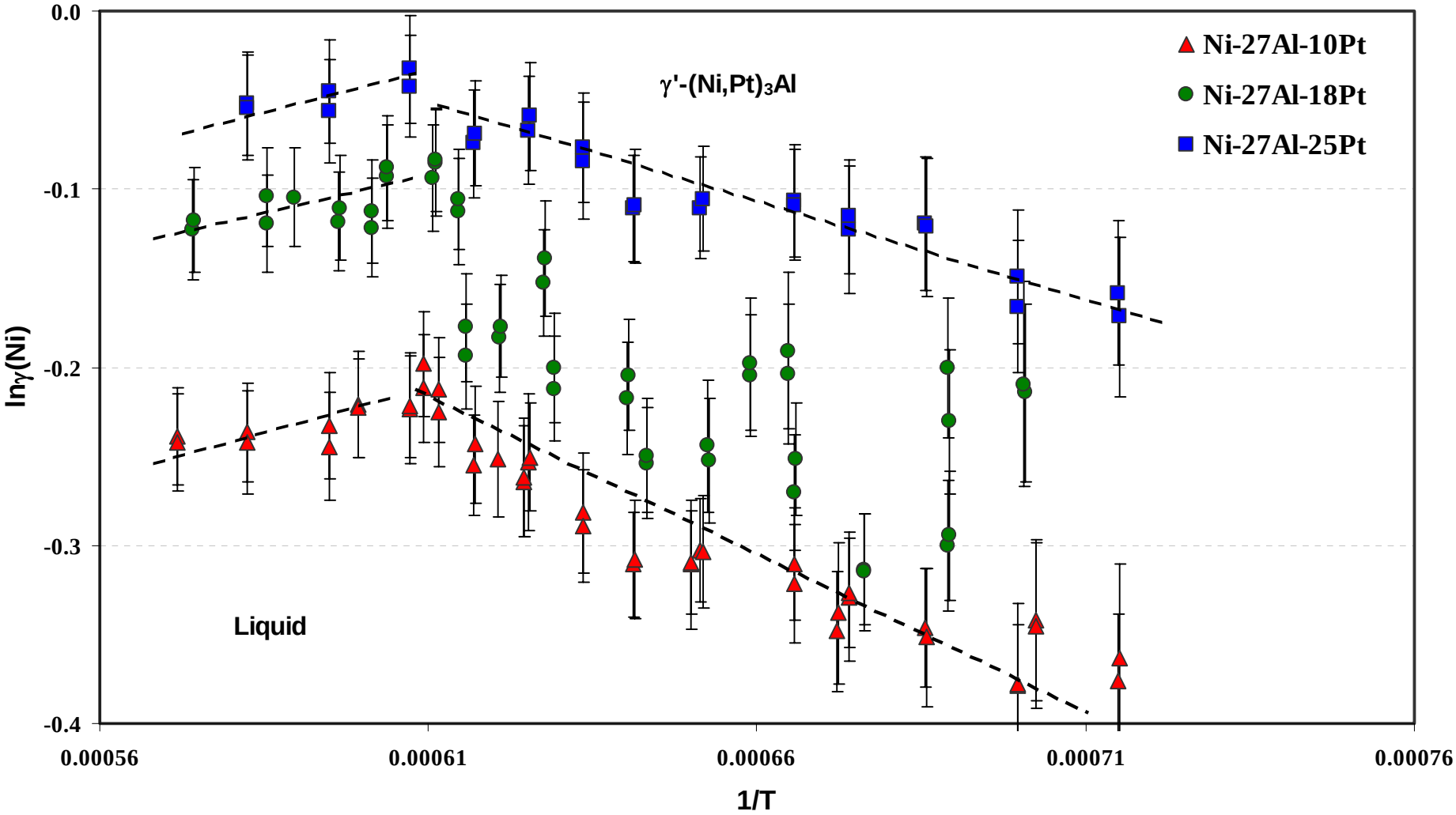
a(Al) vs 1/T (Ni-27Al-XPt)



a(Ni) vs 1/T (Ni-27Al-XPt)



lnγ(Ni) vs 1/T (Ni-27Al-XPt)



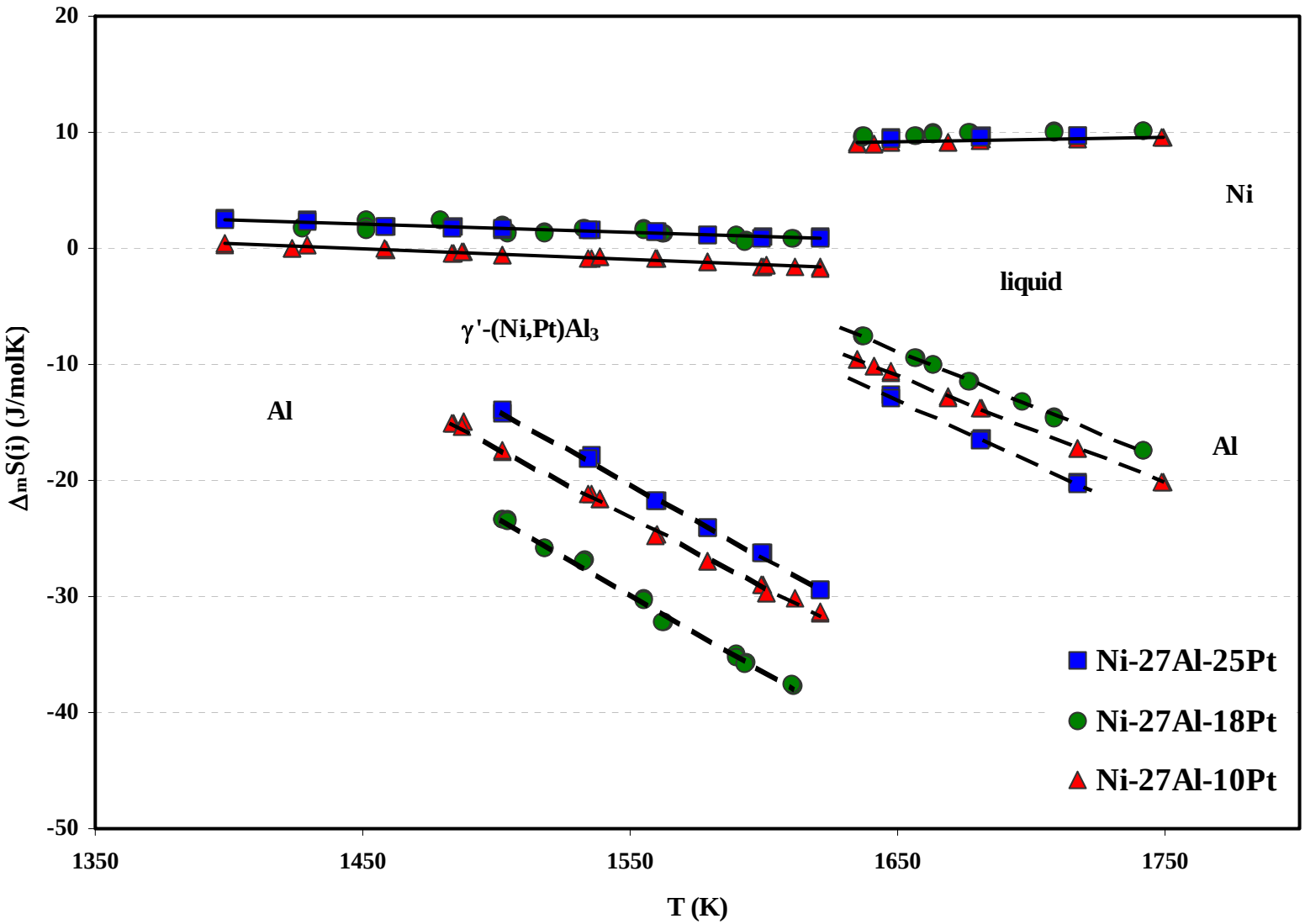
partial mixing enthalpies

γ´-(Ni,Pt)$_3$Al	$\Delta_m\overline{H}(Ni)$ (kJ/mol)	T (K)	$\Delta_m\overline{H}(Al)$ (kJ/mol)	T (K)	T_{mp} (K)
Ni-27Al-2Pt	*-39.5±2.9* $_{19}$	1544	*-88.2±3.9* $_{18}$	1544	1637
Ni-27Al-10Pt	-10.5±1.4 $_{29}$	1510	-146.5±6.8 $_{21}$	1552	1620-1634
Ni-27Al-18Pt	-7.8±5.5 $_{25}$	1519	-162.7±12.1 $_{18}$	1556	1610-1634
Ni-27Al-25Pt	-8.1±1.4 $_{20}$	1509	-157.9±11.0 $_{12}$	1562	1620-1646

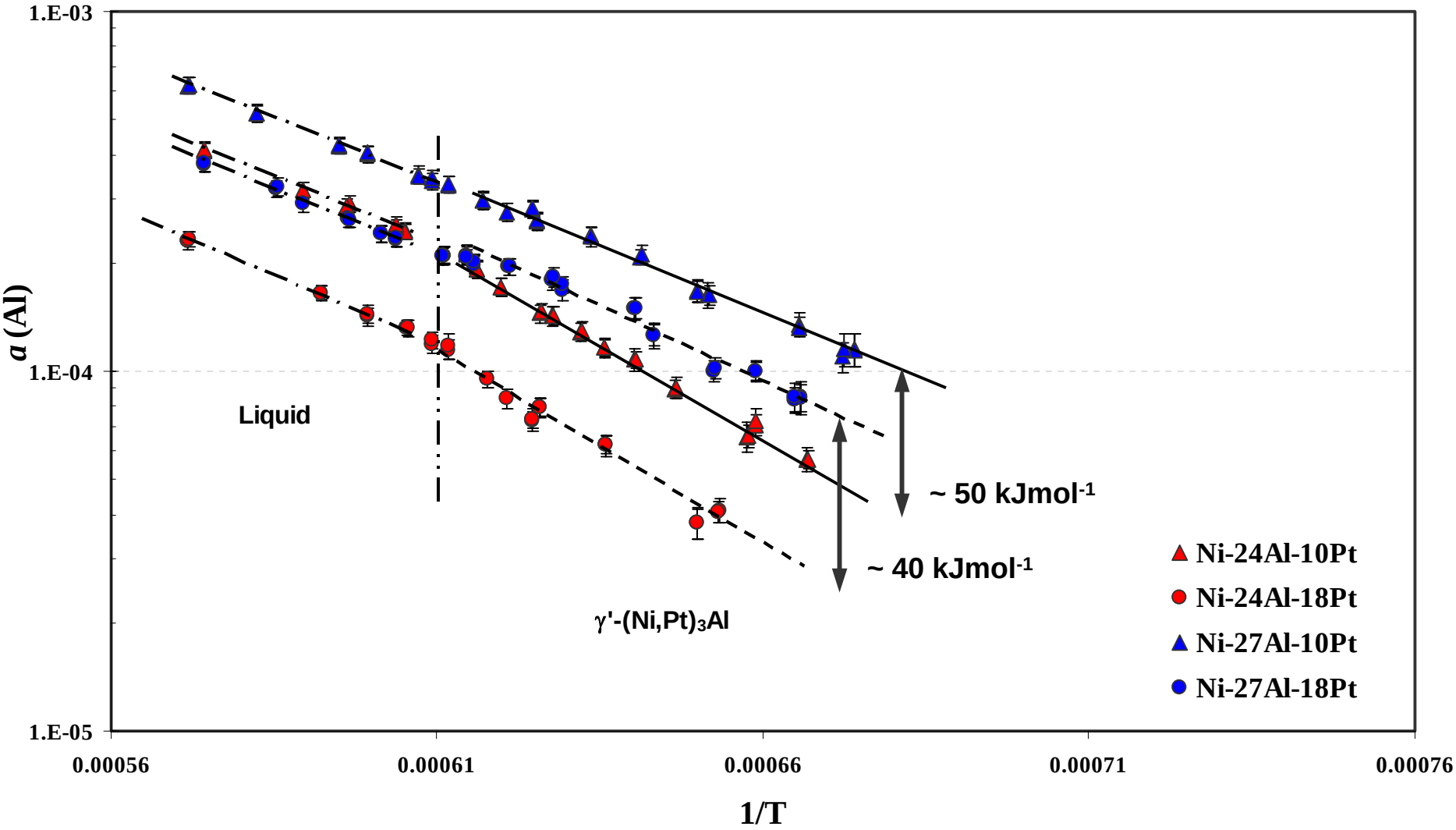
liquid	$\Delta_m\overline{H}(Ni)$ (kJ/mol)	T (K)	$\Delta_m\overline{H}(Al)$ (kJ/mol)	T (K)
Ni-27Al-2Pt	-8.4±5.1 $_{6}$	1686	-141.0±3.9 $_{6}$	1686
Ni-27Al-10Pt	6.2±3.1 $_{14}$	1692	-133.1±3.0 $_{14}$	1692
Ni-27Al-18Pt	6.9±4.3 $_{14}$	1689	-135.6±4.9 $_{14}$	1689
Ni-27Al-25Pt	5.3±5.7 $_{6}$	1682	-151.7±9.7 $_{6}$	1682

subscript: number of data points

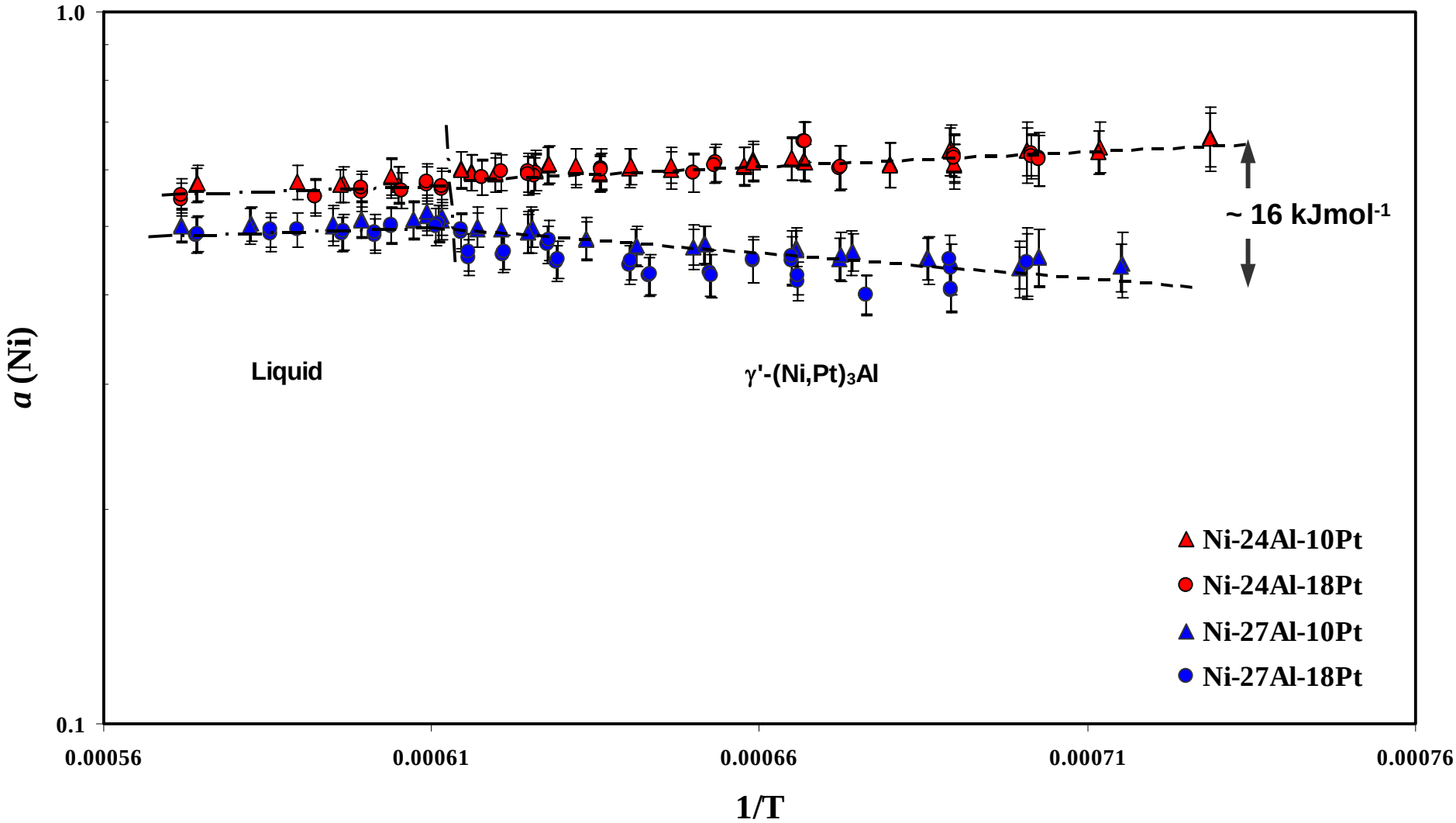
partial entropy of mixing: Al, Ni



hypo- / hyper-stoichiometric: *a*(Al)



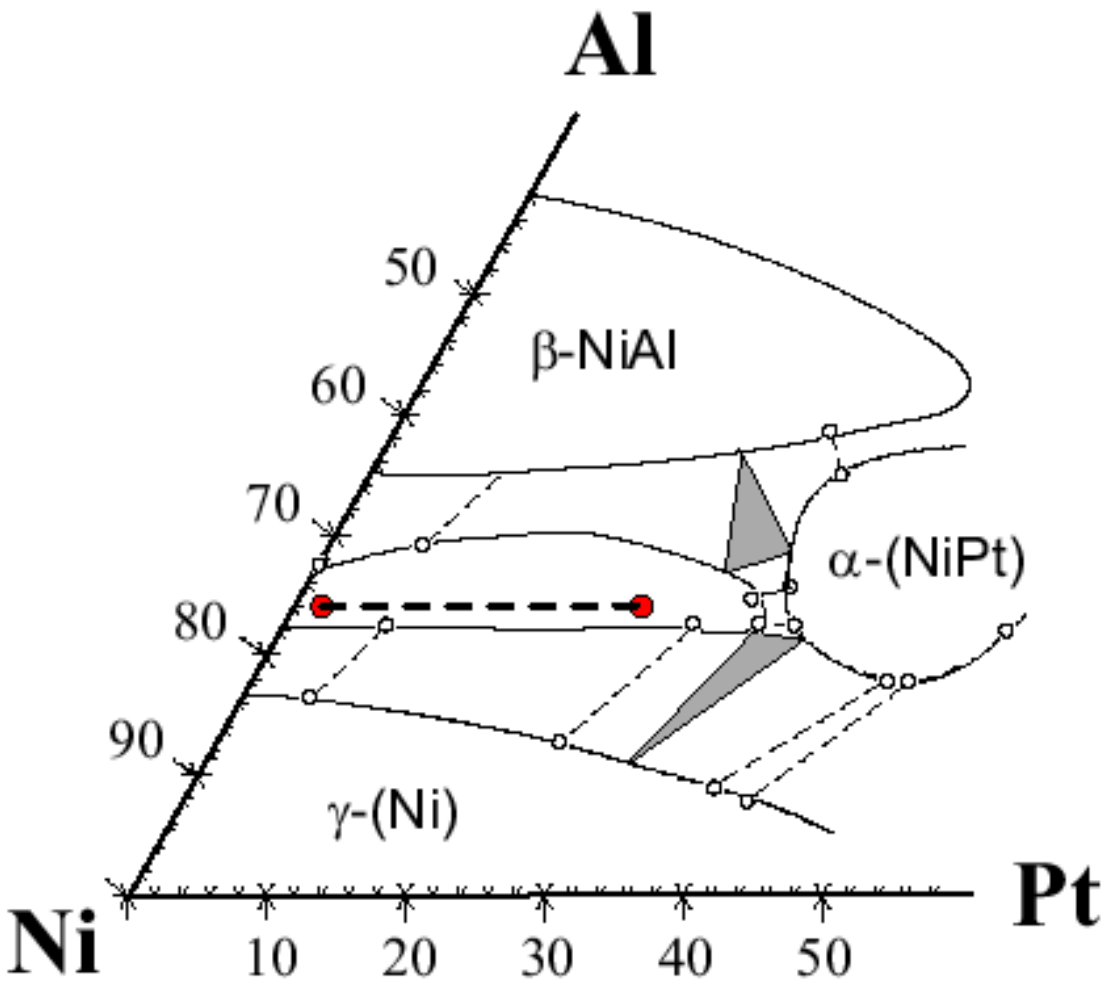
hypo- / hyper-stoichiometric: *a*(Ni)



Ni-27Al-XPt, summary

- γ'-$(Ni,Pt)_3Al$: $a(Al)$ decreases ~3 with Pt addition (Ni/Pt ↓)
- X_{Al} strongest influence on Al bonding
- $a(Al)$ relation with S(Al) not so clear
  - ➥ decrease ordering of Al-atoms
- $a(Ni)$ constant with Pt (Ni/Pt ↓): γ_{Ni} increased from 0.7 to 0.95
  - ➥ $\Delta_m H(Ni)$ –9±3.0kJmol^{-1}, $\Delta_m S(Ni)$ –ve
  - ➥ increased ordering of Ni-atoms
  - ➥ +ve ternary interaction between Ni ↔ (Al + Pt)
- liquid behavior remains similar
- dramatic change in mixing behavior for: X_{Al} = 0.24 and 0.27
  - ➥ $\Delta_m H(Al)$ ↑ 50 kJmol^{-1}, $\Delta_m H(Ni)$ ↓ 16 kJmol^{-1}
  - ➥ $\Delta_m S(Al)$ ↑ 20 Jmol^{-1}K^{-1}, $\Delta_m S(Ni)$ +ve to -ve

interesting diffusion couple…



- a(Ni) ~ constant
- Al driving force:
  S(Al) ⇔ Ni-lattice
- Pt behavior ?

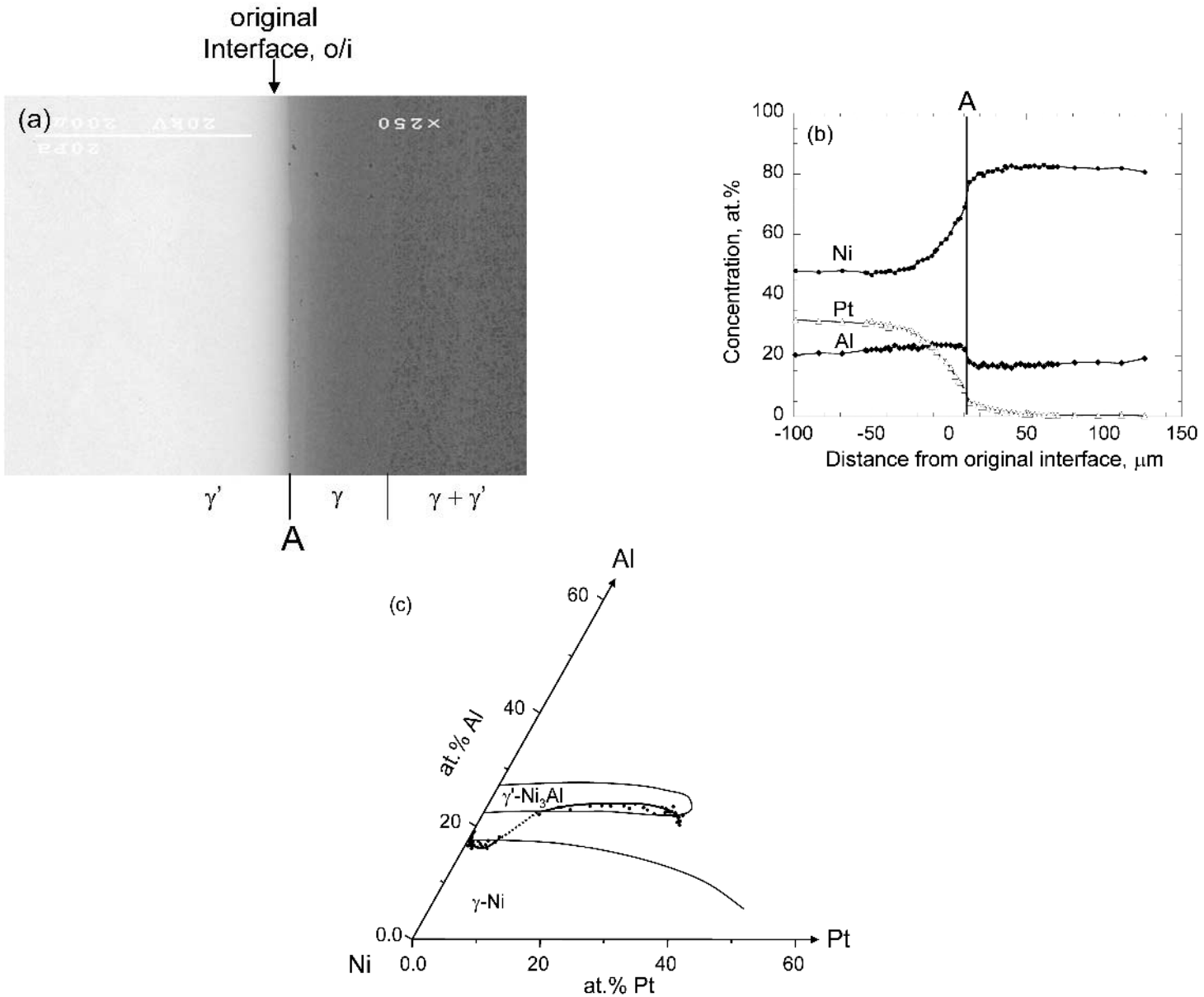


Fig. 2—Cross-sectional and concentration profiles of Ni-22Al-30Pt/Ni-19Al diffusion couple annealed for 10 h at 1150 °C: (a) cross section, (b) concentration profiles of each element, and (c) diffusion path.

S. Hayashi, W. Wang, D. Sordelet, B. Gleeson, *Metall. Mater. Trans.* 36A, (2005), 1769

co-workers / acknowledgements

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