Solidification Behaviour of γ'-Ni_3Al Containing Alloys in the Ni-Al-O System

Evan Copland

Department of Materials Science and Engineering, CWRU / NASA Glenn Research Centre, Cleveland, Ohio 44135, USA.

The chemical activities of Al and Ni in γ'-Ni_3Al-containing systems were measured using the *multi-cell* Knudsen effusion-cell mass spectrometry technique (multi-cell KEMS), over the composition range 8 – 32 at.%Al and temperature range T = 1400 – 1750 K. From these measurements a better understanding of the equilibrium solidification behaviour of γ'-Ni_3Al-containing alloys in the Ni-Al-O system was established. Specifically, these measurements revealed that (1) γ'-Ni_3Al forms via the peritectiod reaction, $\gamma + \beta$ (+ Al_2O_3) = γ' (+ Al_2O_3), at 1633 ± 1 K, (2) the $\{\gamma + \beta + Al_2O_3\}$ phase field is stable over the temperature range 1633 – 1640 K, and (3) equilibrium solidification occurs by the eutectic reaction, L (+ Al_2O_3) = γ + β (+ Al_2O_3), at 1640 ± 1 K and a liquid composition of 24.8 ± 0.2 at.%Al (at an unknown oxygen content). When projected onto the Ni-Al binary, this behaviour is inconsistent with the current Ni-Al phase diagram and a new diagram is proposed. This new Ni-Al phase diagram explains a number of unusual steady-state solidification structures reported previously and provides a much simpler reaction scheme in the vicinity of the γ'-Ni_3Al phase field.

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E. Copland

Case Western Reserve University / NASA Glenn Research Center

Cleveland, Ohio

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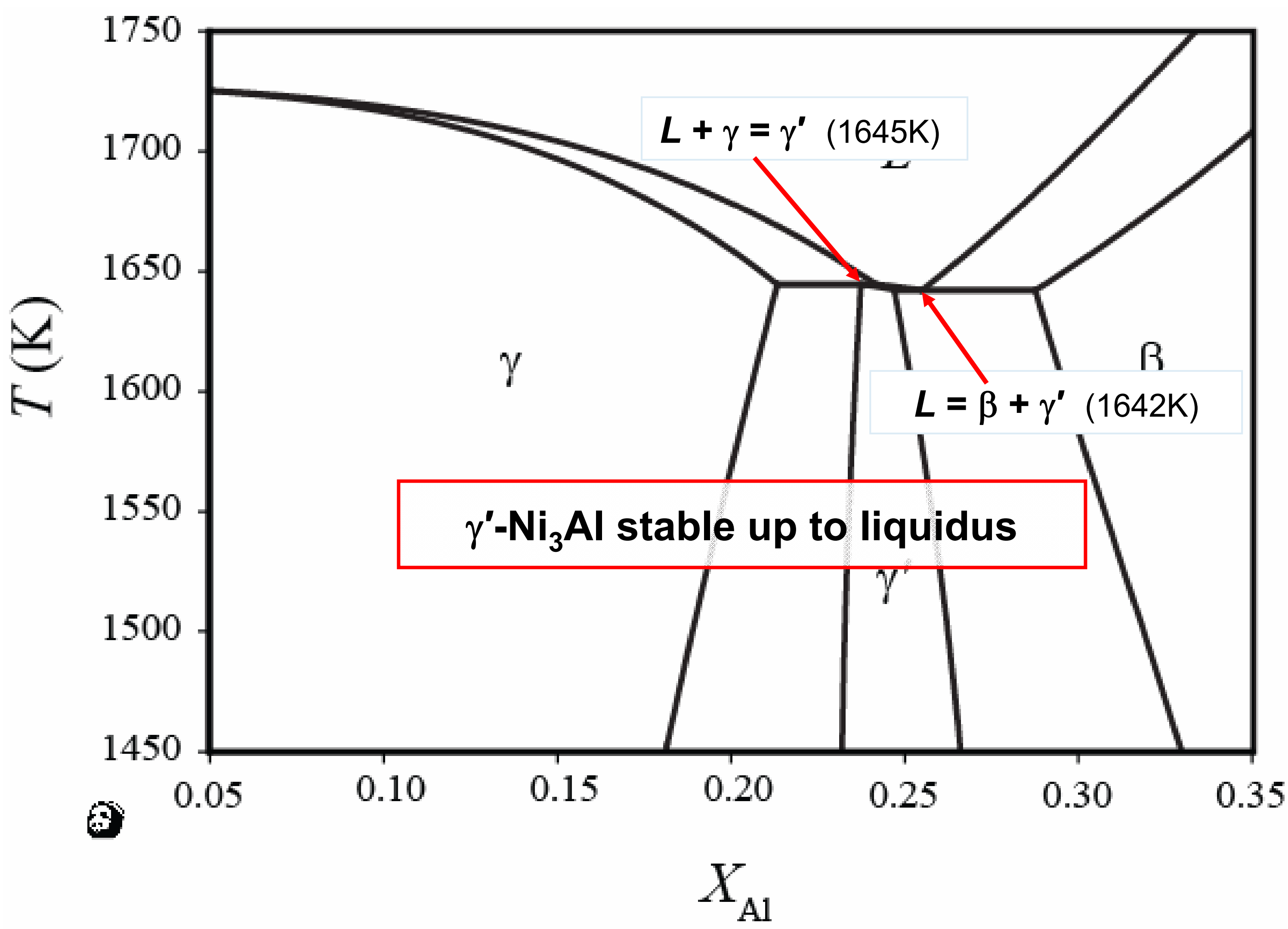
outline

- current Ni-Al phase diagram; critical experiments
- experiments; *multi-cell KEMS*, consider Ni-Al-O system
- observe different phase equilibrium, 3 independent measurements:
  - ↪ a(Al) and a(Ni): X_{Al} = 0.08 – 0.32; T = 1400 – 1750K
  - ↪ relative a(Al) and a(Ni): Ni-27Al / Ni-23Al
  - ↪ ion-intensity ratio I_{Ni} / I_{Al}: X_{Al} = 0.08 – 0.32
- propose a new "Ni-Al" phase diagram
- review "meta-stable" $\gamma + \beta$ eutectic
- compare Ni-Al diagrams and summarize

current Ni-Al phase diagram



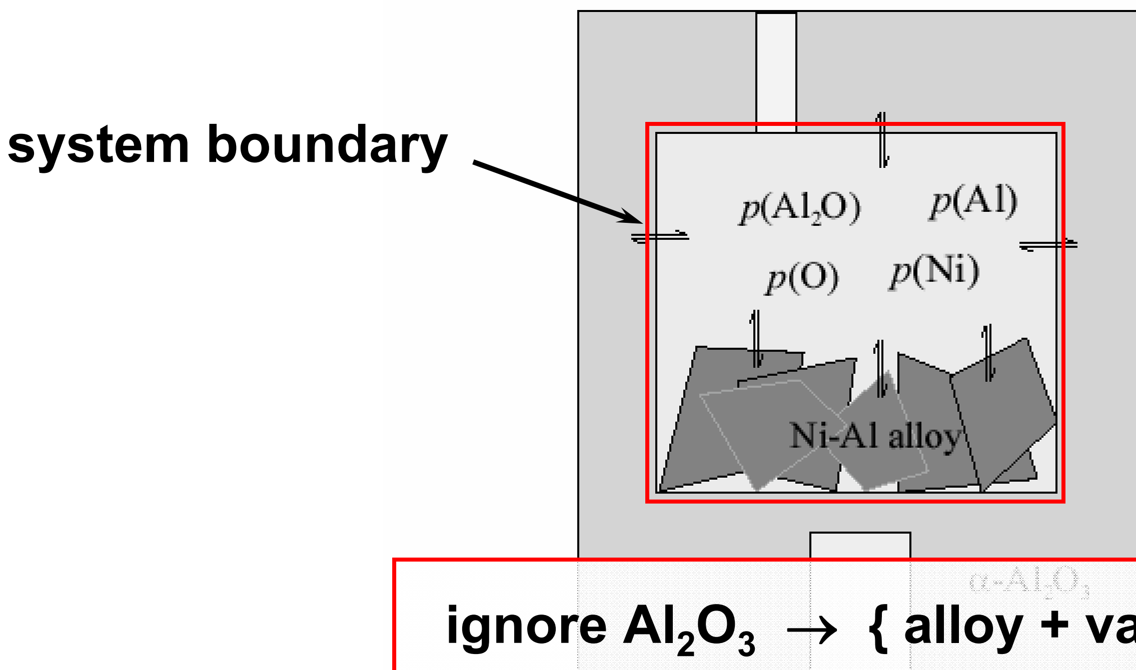
W. Huang, Y. Chang, *Intermetallics*, 1998, 6, 487.

critical studies

Reaction	T (K)	Experimental Technique	Container	Reference
$L + \beta = \gamma'$ $L = \gamma + \gamma'$	1668 1658	cooling-curves / metallography	Al_2SiO_5 / Al_2O_3 Al_2O_3	Alexander 1937 Floyd 1951, 1952
$L + \gamma = \gamma'$ $L = \beta + \gamma'$	1635 1633	cooling-curves / metallography	Al_2O_3 ?	Schramm 1941
$L + \gamma = \gamma'$ $L = \beta + \gamma'$	1639 1636	directional solidification / metallography / DTA	Al_2O_3	Bremer 1988
$L + \gamma = \gamma'$ $L = \beta + \gamma'$	[illegible] 1642 ± 1	DTA / KEMS	[illegible] Al_2O_3 (DTA)	Hilpert 1987, 1990
$L + \gamma = \gamma'$ $L = \beta + \gamma'$	1642 ± 2 1639 ± 2	[illegible]	[illegible]	Battezzati 1998
$L + \gamma = \gamma'$ $L = \beta + \gamma'$	1655 ± 1 [illegible]	directional solidification / metallography	Al_2O_3	Lee 1991-94
$L + \gamma = \gamma'$ $L = \beta + \gamma'$	1643.2 1643.0	assessment	~	Du 1996
$L + \gamma = \gamma'$ $L = \beta + \gamma'$	1643.4 1642.2	assessment	~	Ansara 1997
$L + \gamma = \gamma'$ $L = \beta + \gamma'$	1645.0 1642.0	assessment	~	Huang 1998
$L + \gamma = \gamma'$ $L = \beta + \gamma'$	1646.7 1646.0	assessment	~	Zhang 2003

- **very difficult to observe high-*T* structures:**
  - ➥ **quenching rate; γ' broadens on cooling**
- **non-isothermal techniques (apart from *KEMS*)**
- **Al_2O_3 container ignored**
- **eutectic ≈ peritectic: $\Delta T < 3K$ (to ~ 0.2K)**
- **“meta-stable” $\gamma + \beta$ eutectic (Lee, Hunziker)**

effusion-cell



ignore Al_2O_3 → { alloy + vapor }

- "closed" isothermal container: { alloy + vapor + Al_2O_3 }
- sample vapor phase by effusion
- complex vapor phase… need mass spectrometry *(KEMS)*

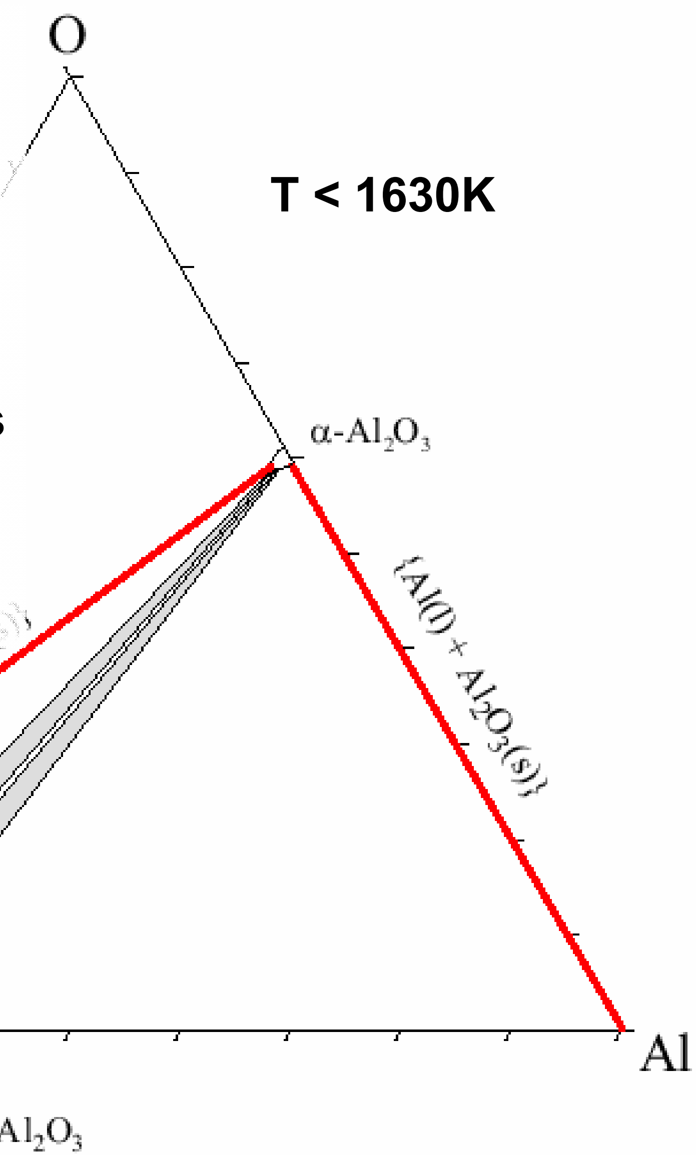
Ni-Al-O system

- phase rule (*P*, *T*): f = c - p + 2
- invariant: 5 phases
- uni-variant fields (*T*): 4 phases

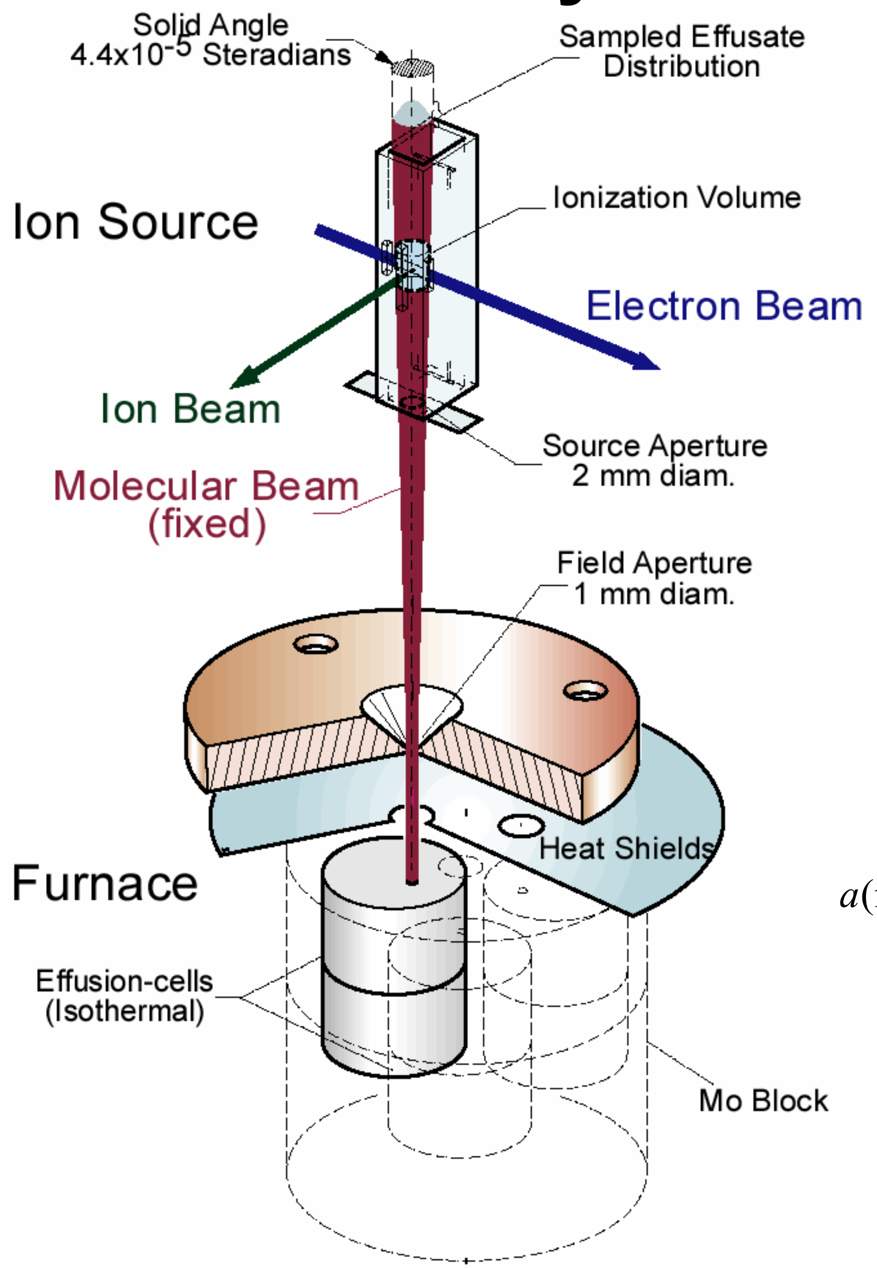
  {$\gamma + \gamma' + Al_2O_3$} or {$\gamma' + \beta + Al_2O_3$}
- bi-variant fields (X_i, *T*): 3 phases

  {$\gamma + Al_2O_3$} or {$\beta + Al_2O_3$}

… vapor always present



thermodynamic measurements



multi-cell *KEMS*

pressure measurement

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

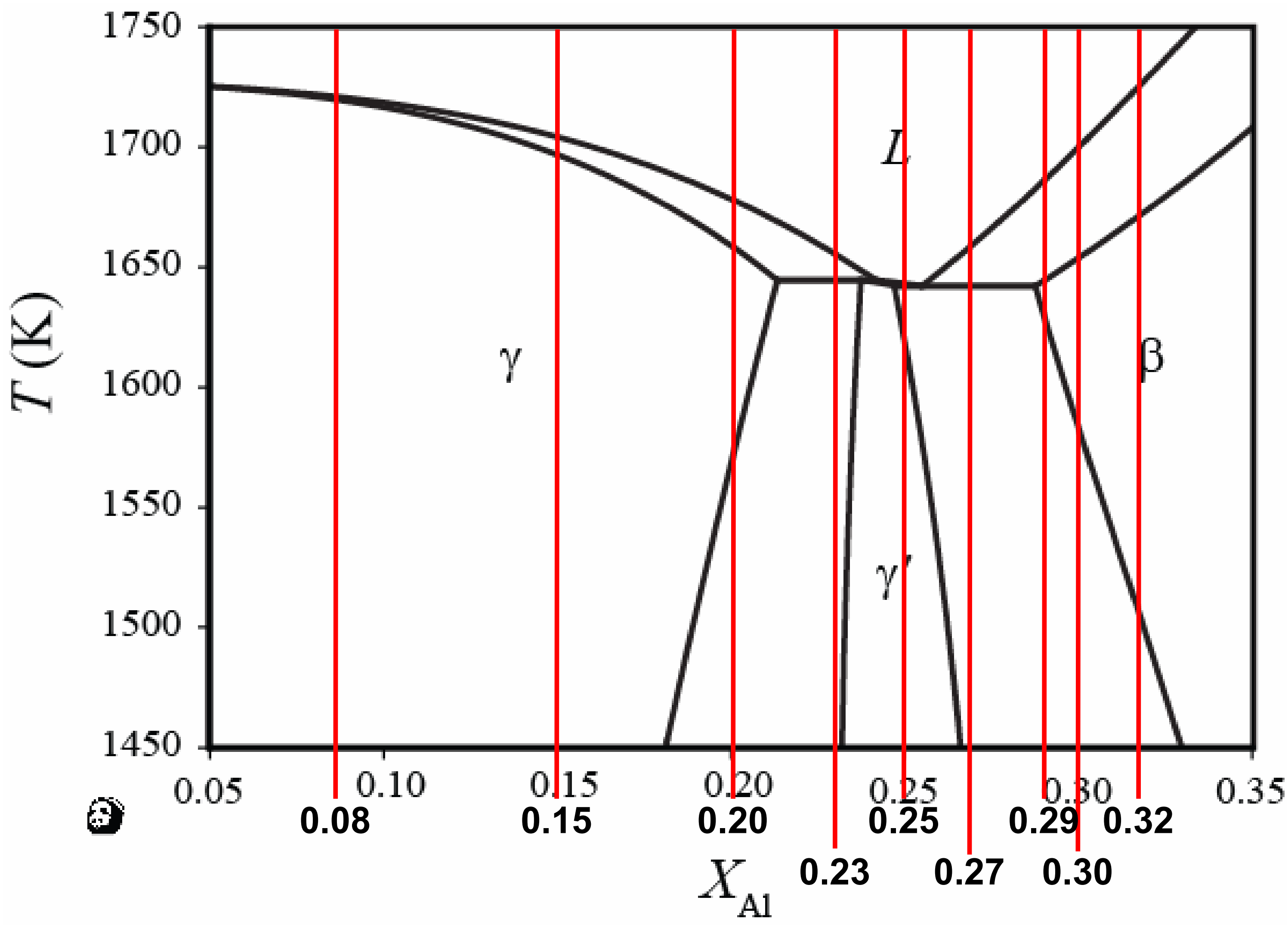
activity measurement

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

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

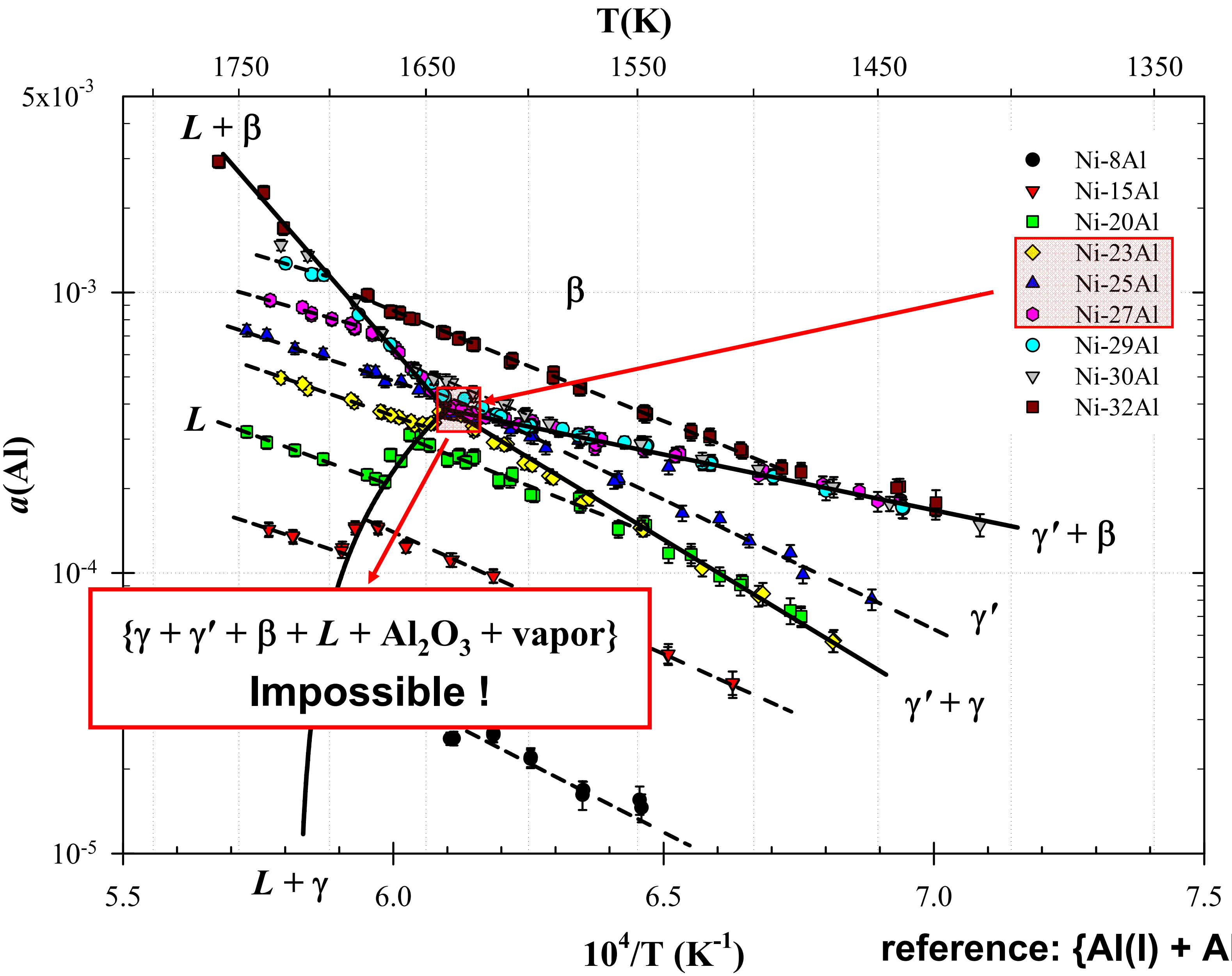
(i = Ti, Al, Al_2O)

alloys compositions



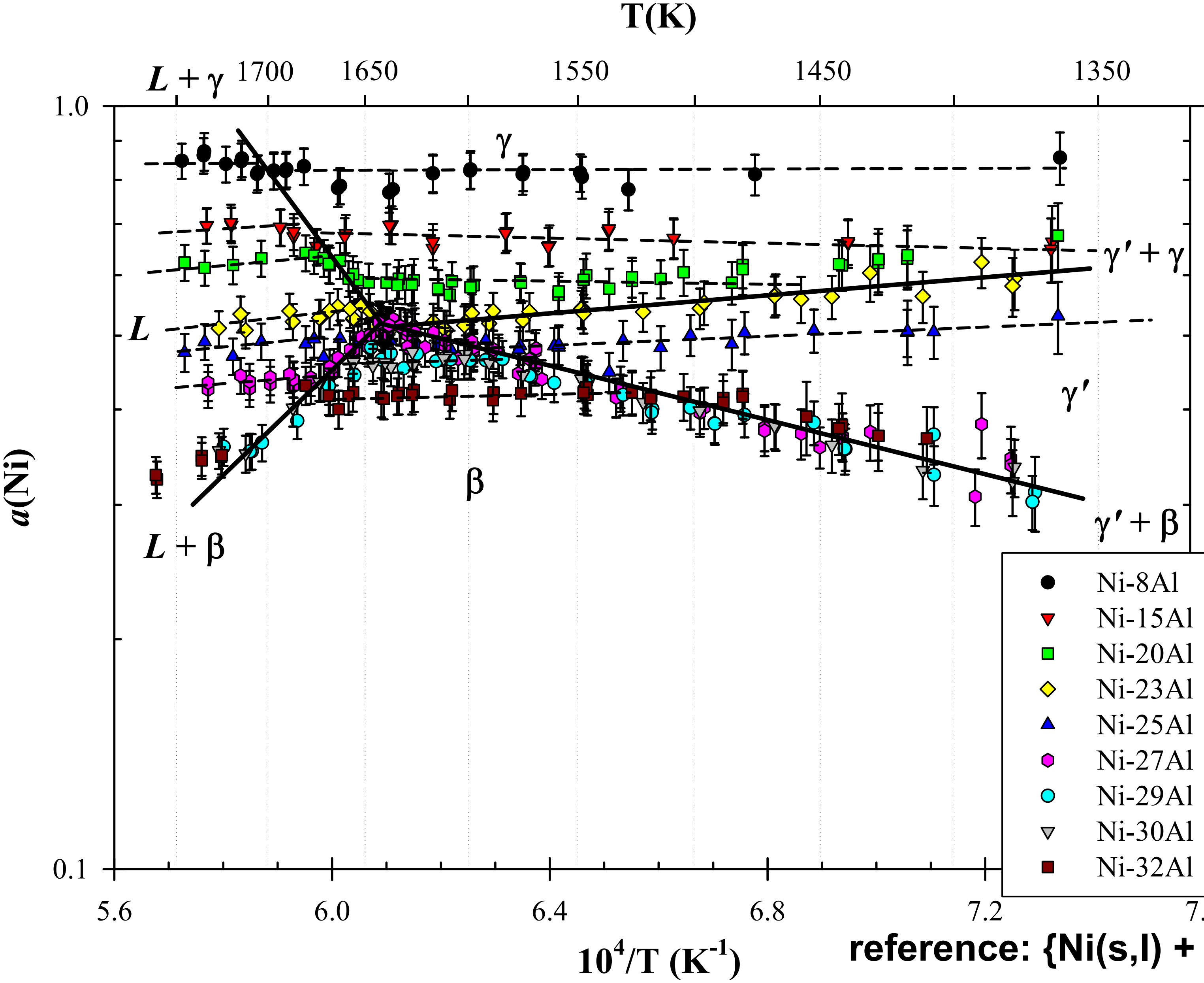
W. Huang, Y. Chang, *Intermetallics*, 1998, 6, 487.

a(Al) vs 1/T: X_{Al} = 0.08 – 0.32



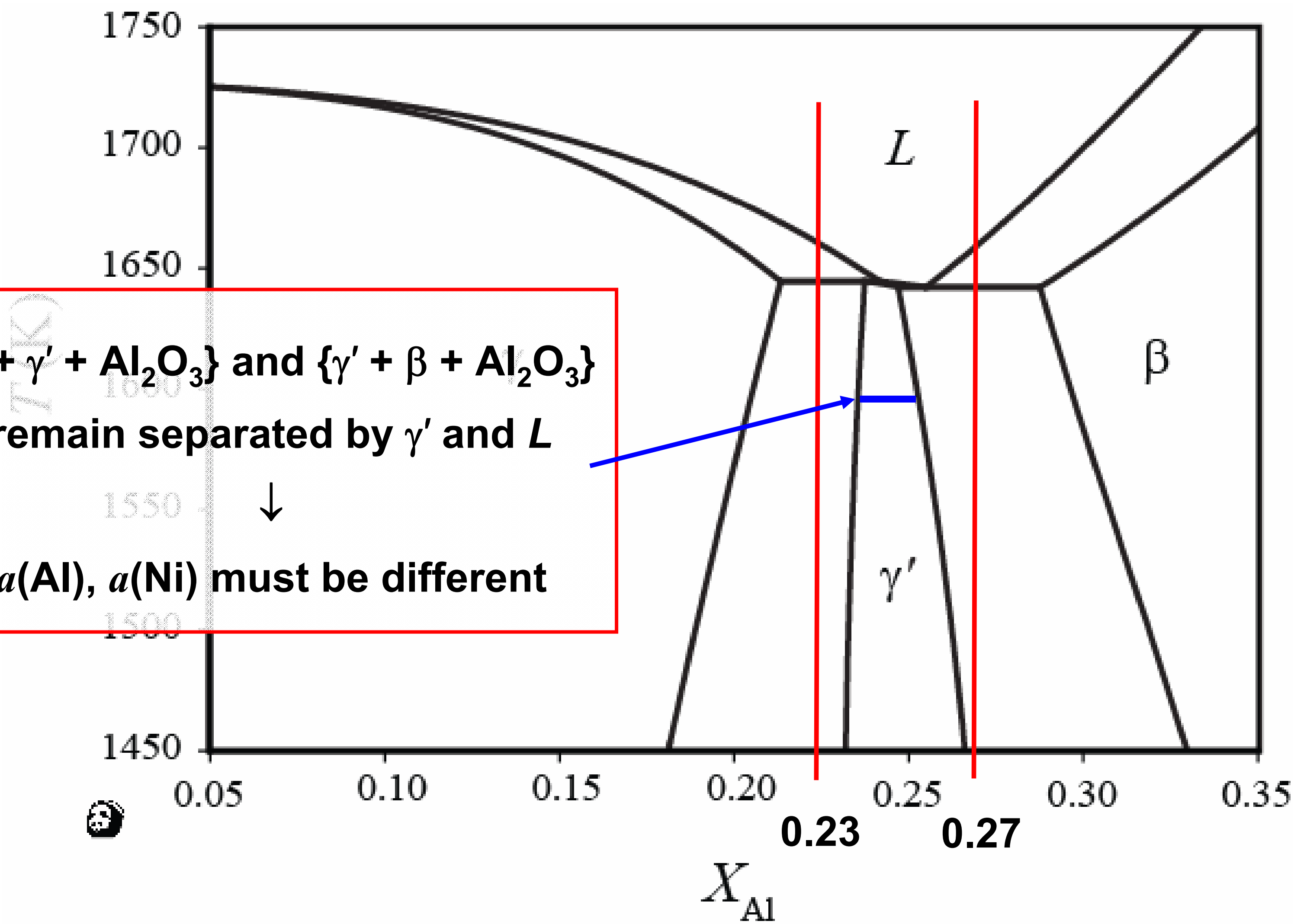
reference: {Al(l) + Al_2O_3}

a(Ni) vs 1/T: X_{Al} = 0.08 – 0.32



reference: {Ni(s,l) + Al_2O_3}

expected behavior…



{γ + γ' + Al_2O_3} and {γ' + β + Al_2O_3} remain separated by γ' and *L*

↓

a(Al), *a*(Ni) must be different

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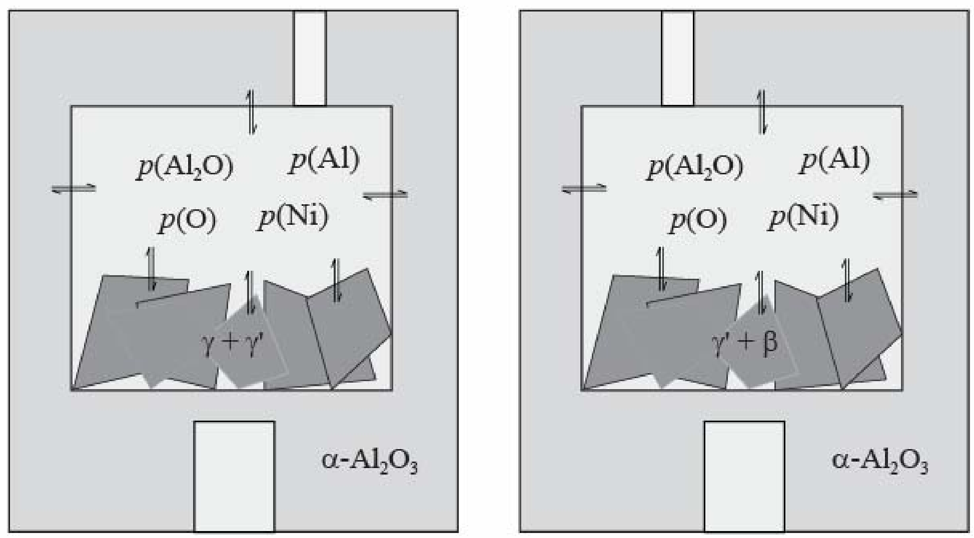
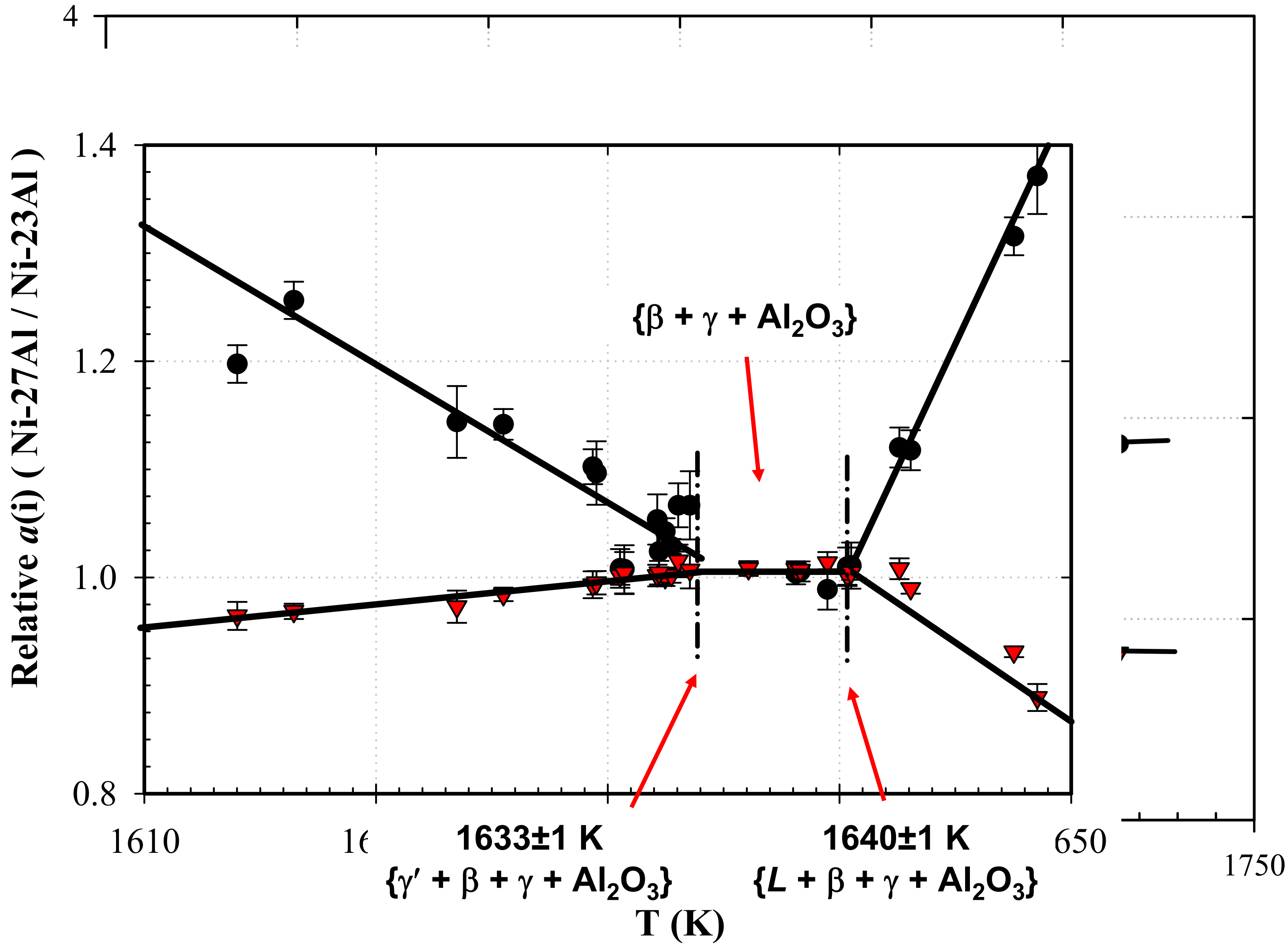
direct measurement



$$a(\mathrm{i})_{(\gamma'+\beta)-(\gamma+\gamma')} = \frac{a(\mathrm{i})^{(\gamma'+\beta)}}{a(\mathrm{i})^{(\gamma+\gamma')}} = \frac{I_i^{\gamma'+\beta}}{I_i^{\gamma+\gamma'}}$$

- **relative *a*(Al) and *a*(Ni)… Ni-27Al / Ni-23Al**
- **identify differences in phase equilibrium over range of *T***
- **isothermal condition $\rightarrow$ equilibrium at each *T***

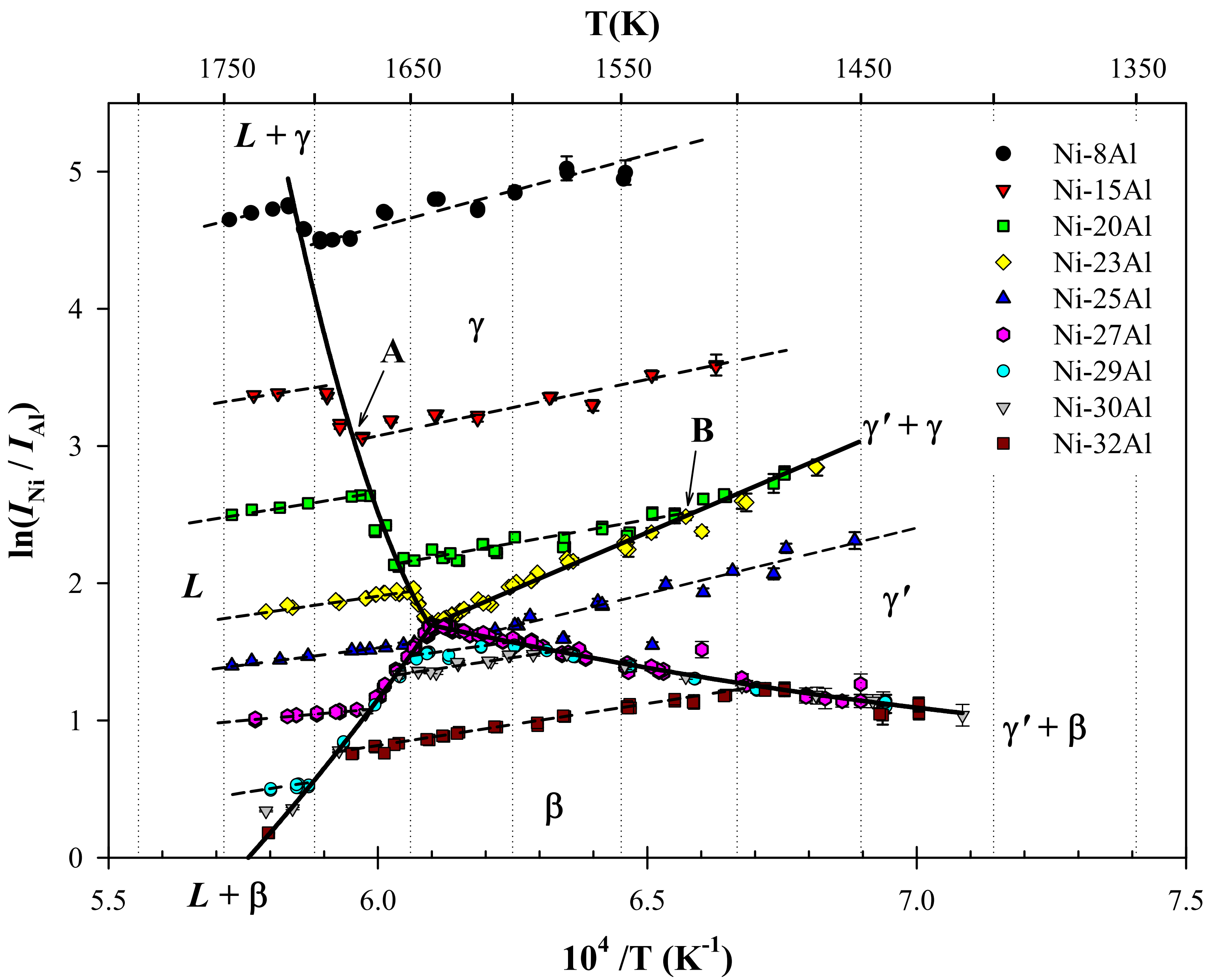
relative activities for Ni-27Al / Ni-23Al



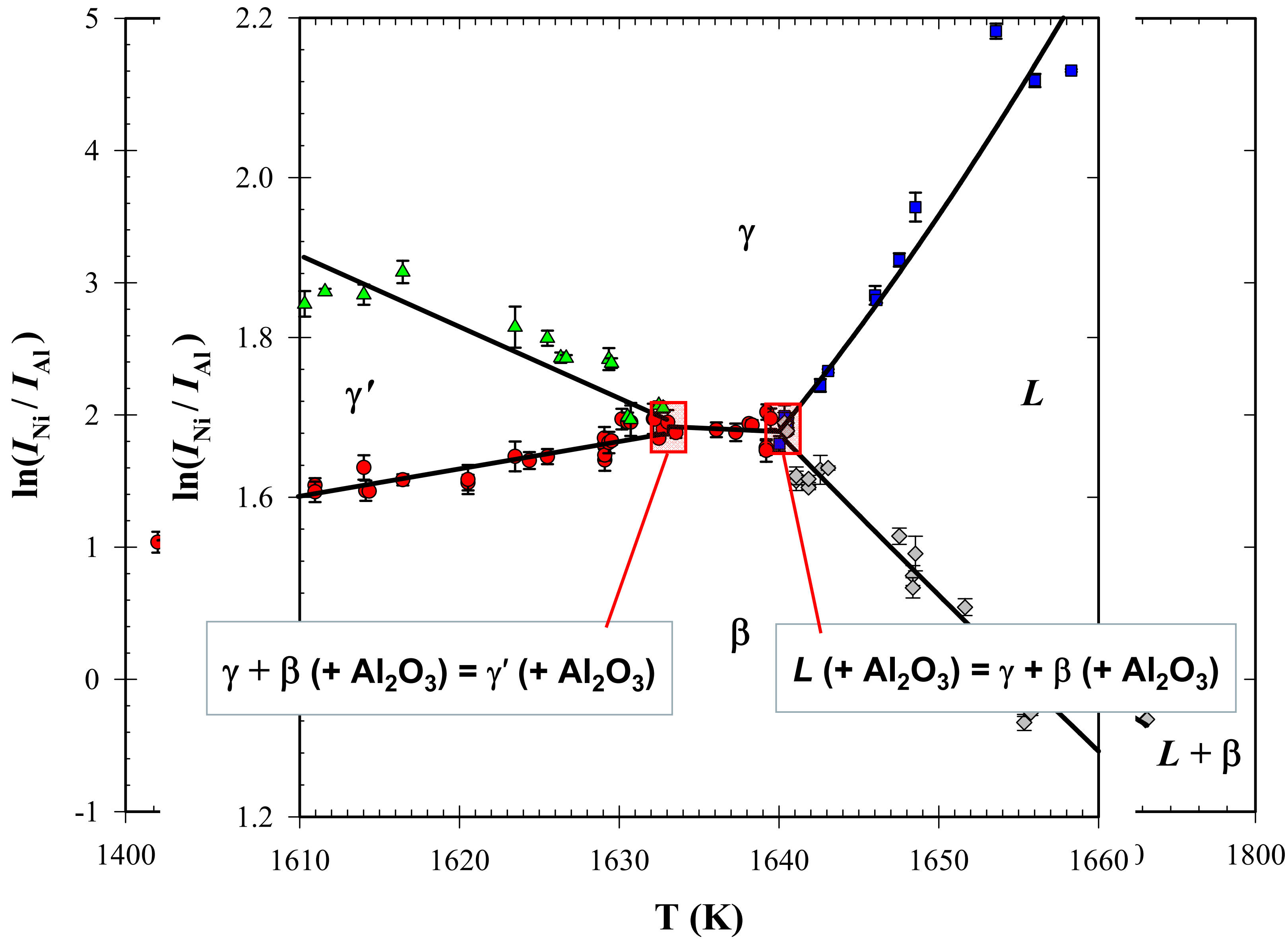
review

- same a(Al) and a(Ni) for X_{Al} = 0.23 – 0.27; T = 1633 – 1640 K
- inconsistent with current Ni-Al phase diagram…
- L unstable T < 1640±1 K; γ' unstable T > 1633±1 K
  - ↪ eutectic: L (+ Al_2O_3) = $\gamma + \beta$ (+ Al_2O_3) at T = 1640±1 K
  - ↪ peritectiod: $\gamma + \beta$ (+ Al_2O_3) = γ' (+ Al_2O_3) at T = 1633±1 K
  - ↪ $\{\gamma + \beta + Al_2O_3\}$ stable over T = 1633 – 1640 K
- need to propose new phase equilibrium…
- recheck behavior: ion-intensity ratio $I_{Ni} / I_{Al} \propto a(Ni) / a(Al)$
  - ↪ direct measurement, from a single effusion-cell
  - ↪ independent of variations in instrument sensitivity
  - ↪ more sensitive to phase transformations…

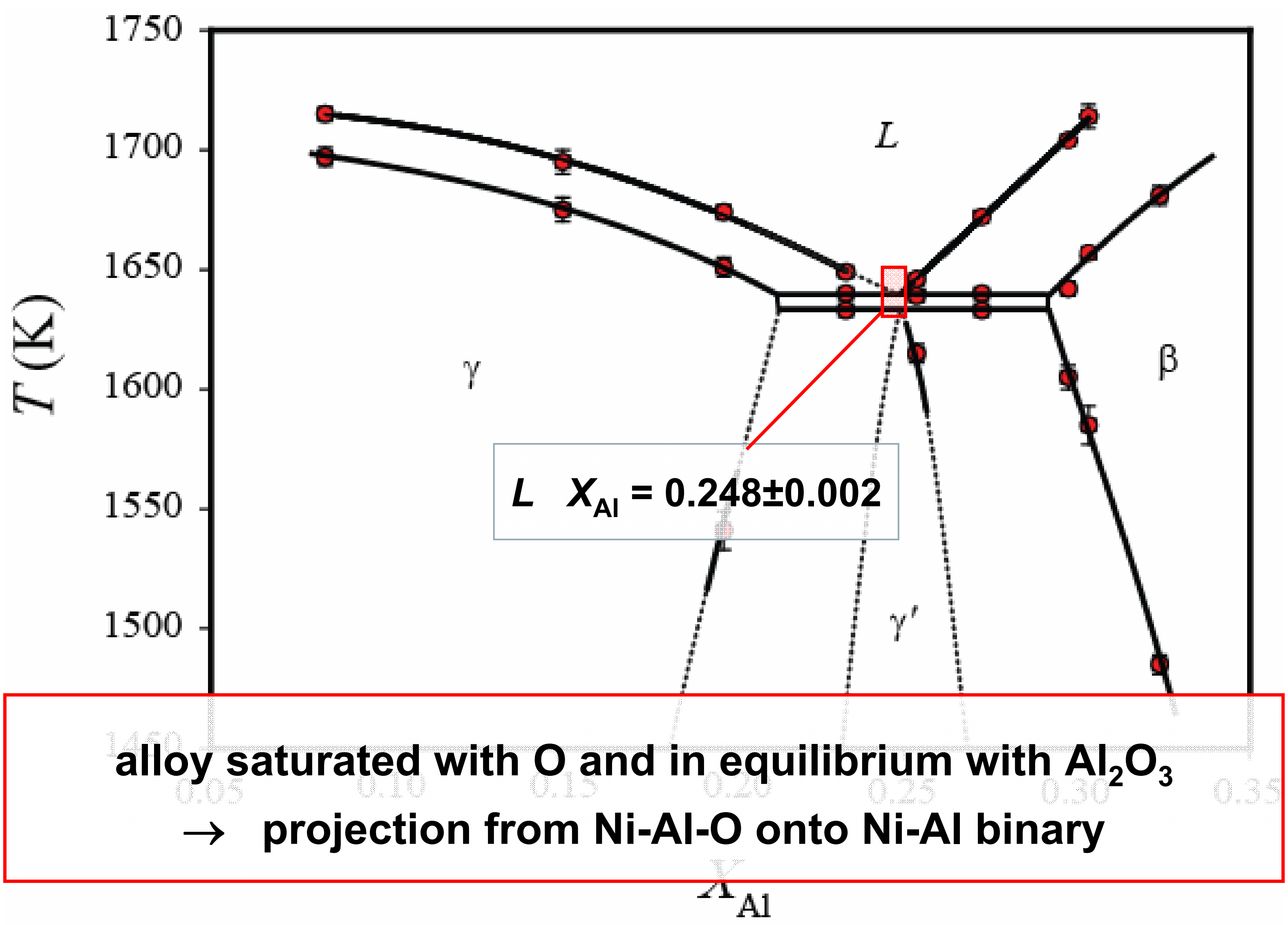
$\ln(I_{Ni} / I_{Al})$ vs. $1/T$



uni-variant phase fields



proposed “Ni-Al” diagram



alloy saturated with O and in equilibrium with Al_2O_3

→ projection from Ni-Al-O onto Ni-Al binary

"meta-stable" $\gamma + \beta$ eutectic

- **Lee: Bridgman technique**

  Hunziker: Laser surface resolid.

- **used current Ni-Al diagram**

- $\gamma + \beta \leftrightarrow \gamma' + \beta$ **independent of *DS***

  ➥ $\gamma + \beta$ **fastest cooling**

  ➥ $\gamma' + \beta$ **slower cooling**

- **unexplainable solidification**

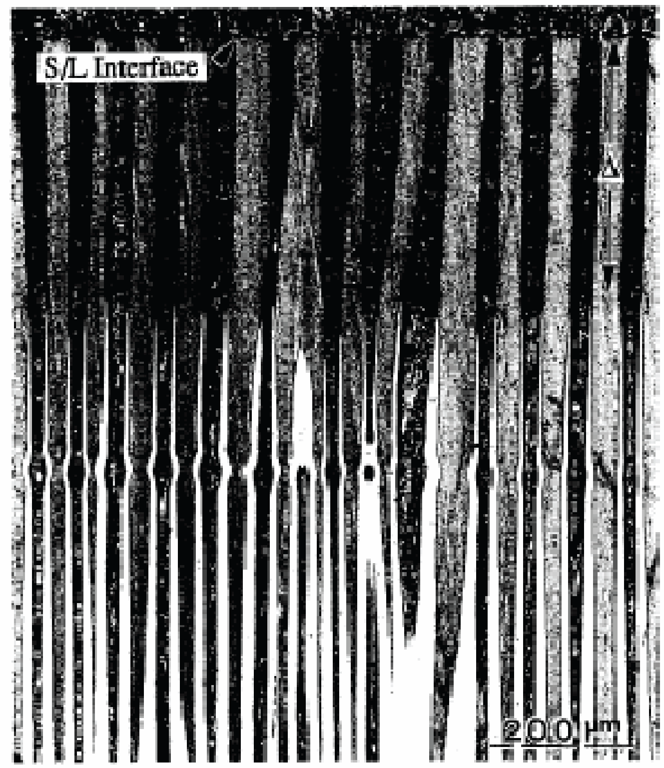


Fig. 2. The quenched solid-liquid interface in the fastest quench experiment, 3 mm tube, Ga-In quenchent. Composition of 24.5 at%Al, growth rate of 0.8 μm/s.

proposed Ni-Al phase diagram explains solidification behavior

↓

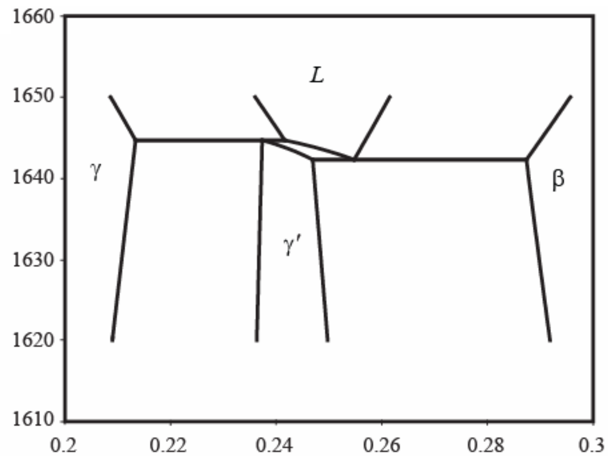
$\gamma + \beta$ **eutectic is the equilibrium structure**

J. Lee, J. Verhoeven, *J. Crystal Growth*, 1994, 143, 86.

O. Hunziker, W. Kurz, *Acta mater.*, 1997, 45(12),. 4981.

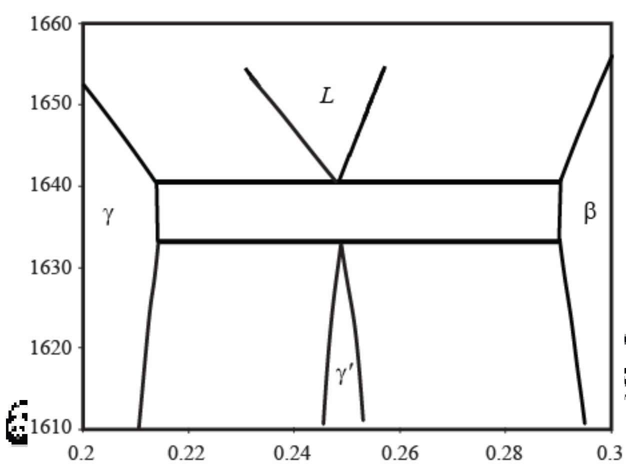
compare “Ni-Al” diagrams

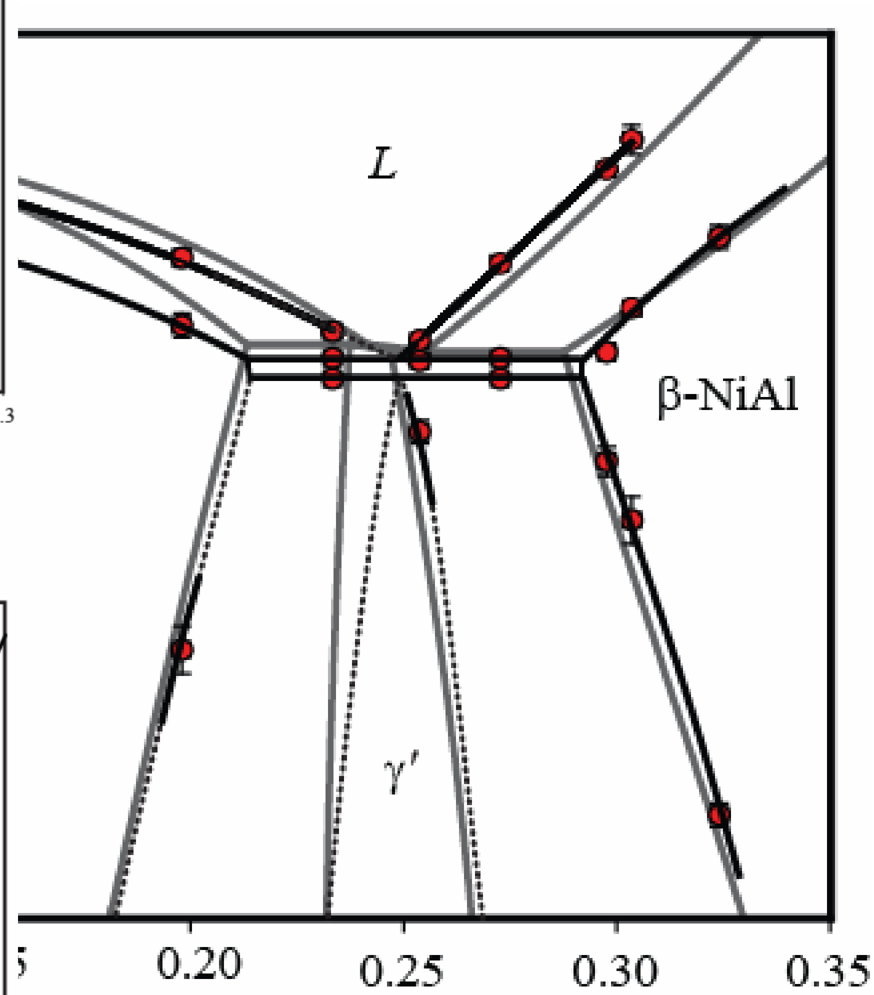
old



T (K)

new





X_{Al}

W. Huang, Y. Chang, *Intermetallics*, 1998, 6, 487.

summary

- these results show γ'-Ni_3Al is not stable up to solidus…
- equilibrium solidification:
  - ↪ eutectic: L (+ Al_2O_3) = $\gamma + \beta$ (+ Al_2O_3) at T = 1640±1 K
  - ↪ peritectiod: $\gamma + \beta$ (+ Al_2O_3) = γ' (+ Al_2O_3) at T = 1633±1 K
  - ↪ $\{\gamma + \beta + Al_2O_3\}$ stable over T = 1633 – 1640 K
- explains: "unusual" steady-state *DS* structures… consistent with all previous measurements
- need to quantify O effect… Ni-Al-O → Ni-Al
- *multi-cell* KEMS is a very powerful tool:
  - ↪ thermodynamic properties → solution behavior
  - ↪ understand complex phase transformations

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