Solidification Behaviour of $\gamma'$-Ni$_3$Al Containing Alloys in the Ni-Al-O System

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The chemical activities of Al and Ni in $\gamma'$-Ni$_3$Al-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 $\gamma'$-Ni$_3$Al-containing alloys in the Ni-Al-O system was established. Specifically, these measurements revealed that (1) $\gamma'$-Ni$_3$Al forms via the peritectoid reaction, $\gamma + \beta (+ Al_2O_3) = \gamma' (+ Al_2O_3)$, at $1633 \pm 1$ 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, $L (+ Al_2O_3) = \gamma + \beta (+ Al_2O_3)$, at 1640 $\pm 1$ K and a liquid composition of 24.8 $\pm$ 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 $\gamma'$-Ni$_3$Al phase field.
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current Ni-Al phase diagram; critical experiments
experiments; multi-cell KEMS, consider Ni-Al-O system
observe different phase equilibrium, 3 independent measurements:

\[ a(\text{Al}) \text{ and } a(\text{Ni}): X_{\text{Al}} = 0.08 - 0.32; \ T = 1400 - 1750K \]

\[ \text{relative } a(\text{Al}) \text{ and } a(\text{Ni}): \text{Ni-27Al / Ni-23Al} \]

\[ \text{ion-intensity ratio } \frac{I_{\text{Ni}}}{I_{\text{Al}}}: X_{\text{Al}} = 0.08 - 0.32 \]

propose a new “Ni-Al” phase diagram
review “meta-stable” \( \gamma + \beta \) eutectic
compare Ni-Al diagrams and summarize
current Ni-Al phase diagram

\[ L + \gamma = \gamma' \ (1645K) \]

\[ L = \beta + \gamma' \ (1642K) \]

\( \gamma'\)-Ni\(_3\)Al stable up to liquidus

<table>
<thead>
<tr>
<th>Reaction</th>
<th>T (K)</th>
<th>Experimental Technique</th>
<th>Container</th>
<th>Reference</th>
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<tbody>
<tr>
<td>$L + \beta = \gamma'$</td>
<td>1668</td>
<td>cooling-curves / metallography</td>
<td>$\text{Al}_2\text{SiO}_5 / \text{Al}_2\text{O}_3$</td>
<td>Alexander 1937</td>
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<td>$L = \gamma + \gamma'$</td>
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<td>$\text{Al}_2\text{O}_3 (\text{KEMS})$</td>
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<td>metallography / DTA</td>
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<td>directional solidification /</td>
<td>$\text{Al}_2\text{O}_3$</td>
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</tbody>
</table>

- very difficult to observe high-$T$ structures:
- quenching rate; $\gamma'$ broadens on cooling
- non-isothermal techniques (apart from KEMS)
- $\text{Al}_2\text{O}_3$ container ignored
- eutectic $\approx$ peritectic: $\Delta T < 3K$ (to $\sim 0.2K$)
- “meta-stable” $\gamma + \beta$ eutectic (Lee, Hunziker)
effusion-cell

- “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
  \{γ + γ' + Al₂O₃\} or \{γ' + β + Al₂O₃\}
- bi-variant fields ($X_i, T$): 3 phases
  \{γ + Al₂O₃\} or \{β + Al₂O₃\}
  ... vapor always present
thermodynamic measurements

multi-cell KEMS

pressure measurement

\[ p(i) = I_{ik}^+ T / S_{ik} \]

activity measurement

\[ a(i) = \frac{p(i)}{p^0(i)} = \frac{I_i}{I_i^0} \]

\[ a(i) = \frac{p(i)}{p^0(Au)} \cdot \left[ \frac{p^0(Au)}{p^0(i)} \right] = \frac{I_i}{I_{Au}^0} \cdot \frac{S_{Au}}{S_i} \cdot \frac{g(R)}{g(A)} \]

\[ p^0(Au) / p^0(i) \]

\( i = Ti, Al, Al_2O \)
alloys compositions

$a(\text{Al})$ vs $1/T$: $X_{\text{Al}} = 0.08 - 0.32$

$T \text{ (K)}$

$10^4/T \text{ (K}^{-1})$

Reference: $\{\text{Al(l) + Al}_2\text{O}_3\}$
\[ a(Ni) \text{ vs } 1/T: \quad X_{Al} = 0.08 \text{ – } 0.32 \]

\[ T(K) \]

\[ 10^4/T (K^{-1}) \]

reference: \{Ni(s,l) + Al_2O_3\}
\{\gamma + \gamma' + \text{Al}_2\text{O}_3\} \text{ and } \{\gamma' + \beta + \text{Al}_2\text{O}_3\} \text{ remain separated by } \gamma' \text{ and } L \\
\downarrow \\
a(\text{Al}), a(\text{Ni}) \text{ must be different}

W. Huang, Y. Chang, Intermetallics, 1998, 6, 487.
direct measurement

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

- 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

\[
\Delta \mu_i \text{ across } \gamma' \quad \Delta \mu_i \text{ across } \gamma + \gamma' \beta + \gamma + \Gamma + Al_2O_3
\]

\[
\ln \left( \frac{a_i}{RT} \right) = \frac{\Delta H_i}{R} - \frac{\Delta S_i}{RT}
\]

\[
T (K) \quad 1610 \quad 1620 \quad 1630 \quad 1640 \quad 1650
\]

\[
0.8 \quad 1.0 \quad 1.2 \quad 1.4
\]

\[
\{ \beta + \gamma + Al_2O_3 \}
\]

\[
\{ \gamma' + \beta + \gamma + Al_2O_3 \}
\]

\[
\{ L + \beta + \gamma + Al_2O_3 \}
\]

1633\pm1 K

1640\pm1 K
review

- same $a$(Al) and $a$(Ni) for $X_{\text{Al}} = 0.23 - 0.27$; $T = 1633 - 1640$ K
- inconsistent with current Ni-Al phase diagram...
- $L$ unstable $T < 1640\pm1$ K; $\gamma'$ unstable $T > 1633\pm1$ K
  - eutectic: $L (+ \text{Al}_2\text{O}_3) = \gamma + \beta (+ \text{Al}_2\text{O}_3)$ at $T = 1640\pm1$ K
  - peritectiod: $\gamma + \beta (+ \text{Al}_2\text{O}_3) = \gamma' (+ \text{Al}_2\text{O}_3)$ at $T = 1633\pm1$ K
  - $\{\gamma + \beta + \text{Al}_2\text{O}_3\}$ stable over $T = 1633 - 1640$ K
- need to propose new phase equilibrium...
- recheck behavior: ion-intensity ratio $I_{\text{Ni}} / I_{\text{Al}} \propto a$(Ni) / $a$(Al)
  - direct measurement, from a single effusion-cell
  - independent of variations in instrument sensitivity
  - more sensitive to phase transformations...
\[ \ln \left( \frac{I_{Ni}}{I_{Al}} \right) \text{ vs. } \frac{1}{T} \]

\[ 5.5 \quad 6.0 \quad 6.5 \quad 7.0 \quad 7.5 \]

\[ \ln \left( \frac{I_{Ni}}{I_{Al}} \right) \]

\[ 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \]

\[ \text{Ni-8Al} \quad \text{Ni-15Al} \quad \text{Ni-20Al} \quad \text{Ni-23Al} \quad \text{Ni-25Al} \quad \text{Ni-27Al} \quad \text{Ni-29Al} \quad \text{Ni-30Al} \quad \text{Ni-32Al} \]

\[ 1750 \quad 1650 \quad 1550 \quad 1450 \quad 1350 \]

\[ T(K) \]

\[ \beta \quad \gamma \quad \gamma' \quad L \quad A \quad B \]

\[ 10^4 / T(K^{-1}) \]

\[ 6.5 \quad 6.0 \quad 5.5 \]

\[ L+\gamma \quad \gamma'+\gamma \quad \gamma' \quad L \quad L+\beta \]
uni-variant phase fields

\[ \ln \left( \frac{I_{Ni}}{I_{Al}} \right) \]

\[ T (K) \]

\[ 1400 \quad 1450 \quad 1500 \quad 1550 \quad 1600 \quad 1650 \quad 1700 \quad 1750 \quad 1800 \]

\[ \gamma + \beta ( + Al_2O_3 ) = \gamma' ( + Al_2O_3 ) \]

\[ L ( + Al_2O_3 ) = \gamma + \beta ( + Al_2O_3 ) \]

\[ L + \beta \]

\[ T (K) \]

\[ 1400 \quad 1610 \quad 1620 \quad 1630 \quad 1640 \quad 1650 \quad 1660 \quad 1800 \]
proposed “Ni-Al” diagram

alloy saturated with O and in equilibrium with Al₂O₃
→ projection from Ni-Al-O onto Ni-Al binary

L  \( X_{Al} = 0.248 \pm 0.002 \)
“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

proposed Ni-Al phase diagram explains solidification behavior

$\downarrow$

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

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

Compare “Ni-Al” diagrams

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

- these results show $\gamma'$-Ni$_3$Al is not stable up to solidus...

- **equilibrium solidification:**
  - eutectic: $L (+ \text{Al}_2\text{O}_3) = \gamma + \beta (+ \text{Al}_2\text{O}_3)$ at $T = 1640\pm1$ K
  - peritectoid: $\gamma + \beta (+ \text{Al}_2\text{O}_3) = \gamma' (+ \text{Al}_2\text{O}_3)$ at $T = 1633\pm1$ K
  - $\{\gamma + \beta + \text{Al}_2\text{O}_3\}$ 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 $\rightarrow$ Ni-Al

- **multi-cell KEMS** is a very powerful tool:
  - thermodynamic properties $\rightarrow$ solution behavior
  - understand complex phase transformations
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