Measured Activities of Al and Ni in $\gamma$-(Ni) and $\gamma'$-(Ni)$_3$Al 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 $\gamma$-(Ni), $\gamma'$-(Ni)$_3$Al 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$_2$O$_3$ interface and also limits the interaction between the coating and substrate alloys in the $\gamma$-(Ni) + $\gamma'$-(Ni)$_3$Al region. This presentation will review the progress of this study.
measured $a$(Al) and $a$(Ni) in $\gamma$-(Ni) and $\gamma'$-(Ni)$_3$Al in the Ni-Al-Pt System

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motivation

$cyclic$ $oxidation$ $at$ $1150^\circ$ $C$ $in$ $air$

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

measured alloy compositions

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

→ Ni-Al-Pt-O system

<table>
<thead>
<tr>
<th>γ′</th>
<th>100%</th>
<th>50.0</th>
<th>20%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>50.0</td>
<td>~</td>
</tr>
<tr>
<td>76.8</td>
<td>23.2</td>
<td>~</td>
<td>~</td>
</tr>
<tr>
<td>75.0</td>
<td>25.0</td>
<td>~</td>
<td>~</td>
</tr>
<tr>
<td>73.7</td>
<td>27.3</td>
<td>~</td>
<td>~</td>
</tr>
<tr>
<td>73.6</td>
<td>24.3</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>65.8</td>
<td>24.2</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>57.9</td>
<td>24.0</td>
<td>18.1</td>
<td></td>
</tr>
<tr>
<td>51.1</td>
<td>23.8</td>
<td>25.1</td>
<td></td>
</tr>
<tr>
<td>70.8</td>
<td>27.2</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>63.8</td>
<td>26.4</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>54.9</td>
<td>27.0</td>
<td>18.1</td>
<td></td>
</tr>
<tr>
<td>48.1</td>
<td>26.7</td>
<td>25.2</td>
<td></td>
</tr>
</tbody>
</table>

(at.% ± 0.5)
multicell KEMS

thermodynamic measurements

pressure measurement

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

activity measurement

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

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

 routine experiment... easy

(i = Ni, Al, Al₂O)
<table>
<thead>
<tr>
<th>Reference State</th>
<th>Reaction (298K)</th>
<th>Measured (kJmol⁻¹)</th>
<th>IVTAN (kJmol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>{ Au(s,l) + C }</td>
<td>Au(s,l) = Au(g)</td>
<td>363.5±2.8</td>
<td>367.0±0.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>367.0±1.3*</td>
<td></td>
</tr>
<tr>
<td>{ Ni(s) + Al₂O₃ }</td>
<td>Ni(s) = Ni(g)</td>
<td>428.3±2.6</td>
<td>428.0±8.0</td>
</tr>
<tr>
<td></td>
<td>Al(s) = Al(g)</td>
<td>341.0±2.2</td>
<td>330.0±3.0</td>
</tr>
<tr>
<td></td>
<td>4/3Al(s) + 1/3Al₂O₃(s) = Al₂O(g)</td>
<td>414.2±3.6</td>
<td>409.9±55</td>
</tr>
<tr>
<td></td>
<td>2Al(s) + 3O(g) = Al₂O₃(s)</td>
<td>~</td>
<td>-3083.2 ±5</td>
</tr>
<tr>
<td></td>
<td>2Al(g) + O(g) = Al₂O(g)</td>
<td>-1075.5±9.0</td>
<td>-1057.8±20.0</td>
</tr>
<tr>
<td></td>
<td>4Al(g) + Al₂O₃(s) = 3Al₂O(g)</td>
<td>~</td>
<td>~</td>
</tr>
</tbody>
</table>

* 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?

\[ \Delta_{\text{sub}} H_f^\circ (\text{Au}) = \frac{d[\Delta(\text{GEF}) - R \ln I_{\text{Au}}(T)]}{d1/T} = 362.2 \pm 1.7 \text{kJmol}^{-1} \]

\[ = 6.018 \pm 0.029 \text{ eV/atom} \]

\[ \Delta_{\text{sub}} H_f^\circ (\text{Au}) = T[\Delta(\text{GEF}) - R \ln p(\text{Au})] = 366.3 \pm 0.8 \text{kJmol}^{-1} \]

\[ = 6.086 \pm 0.013 \text{ eV/atom} \]

\[ \Delta_{\text{mix}} G_f^\gamma = RT \ln a(\text{Al}) = -124.4 \pm 0.8 \text{kJmol}^{-1} \]

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

\[ \Delta_{\text{mix}} G_f^\gamma = RT \ln a(\text{Ni}) = -4.5 \pm 0.9 \text{kJmol}^{-1} \]

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

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

$\Delta_{\text{mix}} \overline{H}(\text{Al}) = -203\pm10\text{kJmol}^{-1}$

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

![Graph showing $a$(Ni) vs $1/T$ in Ni-24Al-XPt](image)
hypo- / hyper-stoichiometric $\gamma'$
$a(\text{Al})$ vs $1/T$ in $\gamma$-(Ni)

T (K)

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

1750 1650 1550 1450

Ni-15Al  Ni-15Al-2Pt  Ni-15Al-5Pt  Ni-14Al-10Pt  Ni-12Al-18Pt  Ni-10Al-25Pt

L

$\gamma$-(Ni)

$\gamma'(\text{Ni})$

incongruent melting

Ni  Al  Pt

$\beta$-NiAl  $\alpha$-(NiPt)  $\gamma$-(Ni)  $\gamma$-(Ni)$_3$Al
$a(\text{Ni})$ vs $1/T$ in $\gamma$-(Ni)
“interaction parameter formalism”

\[ a(i) = \gamma(i) X_i \bigg|_{X_j/X_k} \]

\[ \ln \gamma_{\text{solvent}} = -\frac{1}{2} \left( \varepsilon_{\text{AlAl}} X_A^2 + \varepsilon_{\text{PtPt}} X_P^2 + \varepsilon_{\text{AlPt}} X_A X_P \right) \]

\[ \ln \frac{\gamma_i}{\gamma_i^o} = \ln \gamma_{\text{solvent}} + \varepsilon_{\text{iAl}} X_A + \varepsilon_{\text{iPt}} X_P \quad i=\text{Al,Pt} \]

\[ \varepsilon_{ij} = \left( \partial \ln \gamma_i / \partial X_j \right)_{\text{solvent}} \]

- need a function to understand / observe the solution behavior...
- computational thermo \( \rightarrow GEF(X_p,T) \), 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 \( a(\text{Pt}) \)

$\gamma_{\text{Ni}}$, $a(\text{Ni})$ surfaces in $\gamma$-(Ni)

- $a(\text{Ni})$ remains high with Pt addition…
- more pronounced in $\gamma'$-(Ni)$_3$Al
- limits $\Delta G$ for $J_{\text{Ni}} \rightarrow \gamma + \gamma'(\text{Pt})$ coating
- exclusive Al$_2$O$_3$-layer not due to $\downarrow a(\text{Ni})$
\( \gamma_{\text{Al}}, \ a(\text{Al}) \) surfaces in \( \gamma-(\text{Ni}) \)

- \( a(\text{Al}) \) strong influence Al, Pt \( \varepsilon_{\text{AlAl}} \approx - \varepsilon_{\text{PtAl}} \)
- \( \downarrow a(\text{Al}) \) doesn’t destabilize \( \text{Al}_2\text{O}_3 \)
- Pt enrichment: \( \Delta G \) for \( J_{\text{Al}} \rightarrow \text{alloy/Al}_2\text{O}_3 \)
\( \gamma_{Pt}, \ a(Pt) \) surfaces in \( \gamma-(Ni) \)

- \( a(Al) \) and \( a(Ni) \), Gibbs-Duhem \( \rightarrow a(Pt) \)
- Pt behavior \( \approx \) Al behavior
- ~
summary

- $a$(Al), $a$(Ni) measured at 25 comp. in Ni-corner of Ni-Al-Pt
  - $T = 1400 – 1750$ K in $\gamma$-(Ni), $\gamma'$-(Ni)$_3$Al 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$_2$O$_3$)

- future work:
  - calculate $\gamma$-(Ni) / $L$, $\gamma$-(Ni) / $\gamma'$-(Ni)$_3$Al phase boundaries
  - show activities are as good as phase equilibria
  - introduce Al$_2$O$_3$ and O to data analysis
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