Nanoscale Study of the Phase Decomposition in Model Ni-Al-Cr Superalloys

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Part of a larger study of model Nickel-base superalloys involving experimental and simulated results for [1-5]:

- Ternary Ni-Al-Cr alloys
- Quaternary Ni-Al-Cr-Re, Ni-Al-Cr-Ru, Ni-Al-Cr-W, and Ni-Al-Cr-Ta alloys

Ni-7.5 Al-8.5 Cr at.% was designed to have relatively low equilibrium volume fraction of precipitates ($\varphi_{eq}$) of ca. 15% at 600°C. This will allow us to study the nucleation, growth and coarsening of the $\gamma'$-precipitate phase by atom-probe tomography.

Atom Probe Tomography (APT)

- APT involves ionization of atoms from the surface of a sharp microtip.
- Ions are repelled by the anode (tip) and drawn toward the cathode (electrode).

Time of flight → Chemical nature
Impact Position → Atom position on tip surface
APT Mass Spectrum

Count vs. Mass-to-Charge Ratio

Al, Cr, Ni
APT Results

APT micrograph of a model Ni-Al-Cr alloy aged at 600°C for 4 h, with Ni and Cr atoms omitted for clarity, highlighting the $\gamma'$-precipitate phase with a 11.5 at.% aluminum isoconcentration surface.

The local composition across the $\gamma/\gamma'$ interface.
Phase transformation characterized over a range of aging times from 0 to 1024 hours by APT:

1) Nanostructure
   - precipitate morphology
   - average radius, \(<R(t)\>
   - precipitate number density, \(N_v(t)\)
   - precipitate volume fraction, \(\phi\)

2) Composition
   - evolution of the \(\gamma\) and \(\gamma'\)-phases
   - equilibrium phase compositions
   - concentration profile at the \(\gamma/\gamma'\) interface
Nanometer-sized spheroidal γ’-precipitates are detected in both alloys over the full range of aging times, from 1/6 to 1024 hours.

A γ’-precipitate of radius ca. 9 nm is delineated by the dark 10.5 Al at.% isoconcentration surface, and shows {110} planes with an interplanar spacing of 0.26 nm.

The temporal evolution of the γ’-precipitate morphology in Ni-7.5 Al-8.5 Cr at.% aged at 600°C.
TEM shows the spheroidal morphology of the $\gamma'$-precipitates is maintained to an aging time of 1024 h.

A centered superlattice reflection dark–field image of spheroidal $\gamma'$-precipitates, for a Ni-7.5 Al- 8.5 Cr at.% sample aged for 1024 h at 600°C. Image recorded near the [011] zone axis, with $\mathbf{g} = [111]$ being the operating reflection.
The value of $\phi$ continues to evolve with time, transformation not complete at an aging time of 1024 h.
$\gamma'$-precipitate Number Density ($N_\nu$) and Radius $<R(t)>$

- A high maximum $N_\nu(t)$ of $(2.2\pm0.6) \times 10^{24}$ m$^{-3}$ is achieved after aging for 1 h at 600°C.
- Precipitate $<R(t)>$ values range from 1-10 nm.
Precipitate coalescence at the outset of the coarsening regime in both alloys, characterized by the formation of “necked” regions which exhibit L1$_2$-type ordering.

$\gamma'$-precipitate coagulation and coalescence is believed to result from the overlap of the diffusion fields associated with adjacent $\gamma'$-precipitates [5].

The fraction of interconnected precipitates, \( f(\%) \), achieves a maximum at 1 h, corresponding to minimum in the value of the interprecipitate spacing, \( \lambda_{e-e} \), and the peak \( N_v(t) \).
Calculated tracer D values:
Ni-5.2 Al-14.2 Cr at.% @ 600°C

<table>
<thead>
<tr>
<th></th>
<th>$m^2/s$</th>
<th>$D_i$</th>
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<tbody>
<tr>
<td>Ni</td>
<td></td>
<td>2.5 x 10^{-21}</td>
</tr>
<tr>
<td>Al</td>
<td></td>
<td>9.7 x 10^{-21}</td>
</tr>
<tr>
<td>Cr</td>
<td></td>
<td>3.0 x 10^{-21}</td>
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</tbody>
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Thermodynamics: Ni-Data (N. Saunders)
Diffusion Mobilities: Ni-Mob database (NIST C. E. Campbell)
Compositional Evolution

\[ C(t=\infty) = 76.34 \pm 0.2 \text{ at.\%} \]
\[ C(t=\infty) = 17.79 \pm 0.3 \text{ at.\%} \]
\[ C(t=\infty) = 5.87 \pm 0.4 \text{ at.\%} \]

\[ C(t=\infty) = 85.19 \pm 0.02 \text{ at.\%} \]
\[ C(t=\infty) = 5.42 \pm 0.03 \text{ at.\%} \]
\[ C(t=\infty) = 9.39 \pm 0.04 \text{ at.\%} \]
The trajectories of the compositional evolution of the $\gamma$-matrix and $\gamma'$-precipitate phases of Ni-7.5 Al-8.5 Cr at.% on a partial Ni-Al-Cr ternary phase diagram at 600°C.

- \(\gamma\)-matrix and \(\gamma'\)-precipitate compositions continue to evolve with time.
- A transient enrichment of chromium and a depletion of aluminum are observed on the \(\gamma\)-matrix side of \(\gamma/\gamma'\)-interfaces.
- This transient behavior is believed to be a result of flux coupling.
Basic Conclusions from APT

- A spheroidal $\gamma'$-precipitate morphology is maintained over the full range of aging times, with some $\gamma'$-precipitate coalescence around the peak in number density.

- APT allows for the quantification of the nanostructural and compositional evolution during phase decomposition.
Where does diffusion fit into this?

- In order to understand phase decomposition, it is essential to understand:
  1) Thermodynamics (driving force for phase decomposition)
     - ThermoCalc
     - APT chemical characterization
  2) Kinetics (nucleation and coarsening rates, coalescence)
     - Dictra
     - Comparison of APT experimental data and KMC data (Zugang)
Questions?