Harder, Cheaper, Greener:
Design and Deployment of Nanostructured Alloys

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The structure of metal

Polycrystal
(“many crystals”)
The Hall-Petch effect: smaller is stronger...
The thermodynamic challenge

\[ dG = \gamma dA \]
Severe deformation methods

Angular Extrusion

Repetitive Corrugation and Straightening

High Pressure Torsion

Twist Extrusion

Equal channel angular extrusion

Dalla Torre et al., *Acta Mat.*, 2004
How far can this get us?

Hardness [GPa] vs. Grain size [nm]

- Pure Ni

Graph shows a downward trend indicating a relationship between hardness and grain size.
Deposition techniques

Pulsed Laser Deposition
(Knapp et al., J. Appl. Phys. 79, 1996)

Electrodeposition
(Erb et al., 1993)
Deposition methods work well…

![Graph showing hardness vs. grain size for conventional microcrystalline nickel](image)

- Conventional microcrystalline nickel
- Pure Ni

- Hardness [GPa]
- Grain size [nm]
Is this successful nano-engineering?

- Typical hardness range for engineering steels.
- Conventional microcrystalline nickel.

Graph showing the relationship between hardness [GPa] and grain size [nm] for Pure Ni.
No! There is a serious problem here…

\[ dG = \gamma dA \]
Grain growth

Gibbs ‘n me

How can we fight against surface energy?

Kinetics?
Thermodynamics?

\[ dG = \gamma dA \]

Gibbs
Surfactant for grain boundaries?

\[ dG = \gamma dA \]

\[ dG = \left[ \gamma \left( \frac{N_\beta}{A} \Delta H_{seg} \right) \right] dA \]

The thermodynamically preferred grain size
Surfactant for grain boundaries?

\[ dG = \gamma dA \]

\[ dG = \left[ \gamma - \frac{N_\beta}{A} \Delta H_{\text{seg}} \right] dA \]

\[ \gamma_A = \frac{zt X_{ig}}{\Omega} \left[ \omega_b - \omega_{ig} \left( 1 - \frac{v}{1 - f_{ig}} \right) - \frac{\Omega}{zt} (\gamma_B - \gamma_A) \left( 1 - \frac{v}{1 - f_{ig}} \right) \right] - \frac{zt}{\Omega} \left[ (X_b^2 - 2 X_b X_{ig}) \omega_b + X_{ig}^2 \omega_{ig} \left( 1 - \frac{v}{1 - f_{ig}} \right) \right] \]

\[ + \frac{zt v}{\Omega (1 - f_{ig})} \left[ \{X_{ig} (X_{ig} - X_b) + X_b (1 - X_{ig})\} \omega_{ig} + X_b \frac{\Omega}{zt} (\gamma_B - \gamma_A) \right] + \frac{tkT}{\Omega} \left[ X_{ig} \ln \left( \frac{X_{ig}}{X_b} \right) + (1 - X_{ig}) \ln \left( \frac{1 - X_{ig}}{1 - X_b} \right) \right] \]
Calibrate with simulations

Start with pure Ni structure

Add an alloying element

Monte Carlo (with conjugate gradient relaxation)

Measure solute distribution and grain boundary energy

Finnis-Sinclair multi-body potentials, Periodic boundary conditions
Control of grain size?

Graph showing the relationship between grain size and global solute content for Ni-W.
Electrodeposited Ni-W alloys
3-D atom probe tomography
Are they stable?

Hibbard et al., Scripta Mater (2002): \(420^\circ \text{C}\)

Ni-W

Present work: \(500^\circ \text{C}\)
Nano is not exciting…

Control is exciting
Optimizing combinations of properties

Composition (at% W)

Position (µm)

(a)

300 nm
Optimizing combinations of properties

Optimizing combinations of properties
<table>
<thead>
<tr>
<th>Feature</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness</td>
<td>8x</td>
</tr>
<tr>
<td>Wear</td>
<td>100x</td>
</tr>
<tr>
<td>Corrosion Protection</td>
<td>&gt;500x</td>
</tr>
<tr>
<td>Luster/ Antitarnish</td>
<td>100x</td>
</tr>
</tbody>
</table>

Xtalic Corp.
Marlborough, MA
www.xtalic.com
Application example: wear components

Lifetime, chrome: 19 miles

Lifetime, XPROTECT™: >200 miles

Xtalic Corp.
Marlborough, MA
www.xtalic.com
On the road…

**Lifetime, chrome:**
1 yr, 100,000 miles

**Xtalic XBRIGHT™:**
2 yrs, 200,000 miles
Saving precious resources...

Gold: 2
Ni-Sulfamate: 1.75+ μm
Brass/Bronze

Gold: 0.6
XTRONIC BL: 0.75 μm
Brass/Bronze
How general is this?
Electroformed nanostructured Al
What will happen when things get 2/3 lighter?
Special thanks!

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Designing nanocrystalline alloys

Simulations and theory:
Lower grain boundary energy and stabilize nanocrystalline metals by alloying.

Experiments:
Synthesize new materials and characterize their structure and stability.

Properties:
Tune properties by control of grain size in nanocrystalline Ni-W.

Applications:
“Designer” nanocrystalline materials can reduce economic and societal costs.