Physical Metallurgy of High-Entropy Alloys (HEAs) that I know

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Docent Lecture

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Outline

- High-Entropy Alloys: what are they and why people are interested?

- Physical Metallurgy of High-Entropy Alloys
  - Phase Selection Rules
  - Meta-Stability of SS
  - Mechanical Behavior
  - Solidification Behavior
Alloy & Solid Solution

- an alloy is a mixture of metals, or a mixture of metals and other elements (C, Si, etc.).

- an alloy may be a solid solution of alloying elements (a single phase), or a mixture of multiple phases.

- a solid solution is a solid-state solution of one or more solutes in a solvent. Such a mixture is considered a solution, rather than a compound, when the crystal structure of the solvent remains unchanged by addition of the solutes, and when the mixture remains in a single homogeneous phase.

- (substitutional) solid solutions, in accordance with the Hume-Rothery rules, may form if the solute and solvent have:
  - similar atomic radii (< 15%)
  - same crystal structure
  - similar electronegativities (< 0.4)
  - similar valancy

William Hume-Rothery
breaking of H-R limit?

XRD patterns of Ce3Al at high pressure

Intermetallic compounds $\rightarrow$ solid solution

Atomic structure models of Ce-Al alloy

Intermetallic compounds $\rightarrow$ solid solution
“opposite” side of H-R rules

(1990) Inoue’s three empirical rules to prepare BMGs (>1 mm):
• at least 3 alloying elements;
• large mismatching atomic sizes of constituent elements
• large negative heat of mixing among major alloying elements

(Pd$_{42.5}$Cu$_{30}$Ni$_{7.5}$P$_{20}$ BMG
Φ80*85 mm
3.4 Kg!)

(Miedema, William Hume-Rothery Award, 1981)
(Nishiyama, Intermetallics, 2012)
Conventional alloys

- Conventional alloys normally have only 1 principal element (e.g., Fe in steels)

<table>
<thead>
<tr>
<th>Amounts in Weight %</th>
<th>316L SS</th>
<th>316 SS</th>
<th>304L SS</th>
<th>304 SS</th>
<th>302 SS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>16 - 18</td>
<td>16 - 18</td>
<td>18 - 20</td>
<td>18 - 20</td>
<td>17 - 19</td>
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<tr>
<td>Nickel</td>
<td>10 - 14</td>
<td>10 - 14</td>
<td>8 - 12</td>
<td>8 - 10.5</td>
<td>8 - 10</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>2 - 3</td>
<td>2 - 3</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Manganese</td>
<td>≤ 2</td>
<td>≤ 2</td>
<td>≤ 2</td>
<td>≤ 2</td>
<td>≤ 2</td>
</tr>
<tr>
<td>Silicon</td>
<td>≤ 0.75</td>
<td>≤ 0.75</td>
<td>≤ 0.75</td>
<td>≤ 0.75</td>
<td>≤ 1</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>≤ 0.045</td>
<td>≤ 0.045</td>
<td>≤ 0.045</td>
<td>≤ 0.045</td>
<td>≤ 0.045</td>
</tr>
<tr>
<td>Sulfur</td>
<td>≤ 0.03</td>
<td>≤ 0.03</td>
<td>≤ 0.03</td>
<td>≤ 0.03</td>
<td>≤ 0.03</td>
</tr>
<tr>
<td>Carbon</td>
<td>≤ 0.03</td>
<td>≤ 0.08</td>
<td>≤ 0.03</td>
<td>≤ 0.08</td>
<td>≤ 0.15</td>
</tr>
<tr>
<td>Iron</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Typical compositions of stainless steels
High entropy alloys
(multi-principal-element alloys/compositionally complex alloys)

- High-entropy alloys have at least 5 (4?) principal metallic elements, and have equal or close-to-equal compositions

Example, 6-element Al-Co-Cr-Cu-Fe-Ni system
Equimole: AlCoCrCuFeNi
Non-equimole: AlCo$_{0.5}$CrCuFe$_{1.5}$Ni$_{1.2}$
Minor element addition: AlCo$_{0.5}$CrCuFe$_{1.5}$Ni$_{1.2}$B$_{0.1}$C$_{0.15}$

So why “high-entropy”? And what’s the big deal?
Entropy & Entropy of mixing

- **Entropy**: In thermodynamics, entropy \( (S) \) is a measure of the number of microstates that may realize a thermodynamic system in a defined state specified by macroscopic variables; a measure of molecular disorder within a macroscopic system.

- **Boltzmann's equation**: \( S = k_B \ln \Omega \), where \( \Omega \) is the number of microstates.

- **Entropy of mixing (\( \Delta S_{\text{mix}} \))**: increase in the total entropy when several initially separate systems of different composition are mixed.

\[
\Delta S_{\text{mix}} = -k_B \sum_{i=1}^{n} N_i \ln \left( \frac{N_i}{N} \right) = -N k_B \sum_{i=1}^{n} x_i \ln x_i = -nR \sum_{i=1}^{n} x_i \ln x_i
\]

The mixing entropy reaches the maximum, when elements are mixed **equiatomically**.
Do high-entropy alloys really possess high entropy? How high is high anyway?

It is more convenient to define HEAs by the magnitude of configuration entropy in the high temperature (ideal or regular solution) state: $\Delta S_{\text{mix}} > 1.5R$
High-entropy stabilizes the formation of solid solution phases

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}$$

- **Single phase solid solution**
- **Co-existence of two solid solution phases**
High-entropy stabilizes the formation of solid solution phases

(Murty, Yeh and Ranganathan, *High Entropy Alloys*, Elsevier, 2014)

There's plenty of room at the middle.

—— Richard P. Feynman ——
Era of High-Entropy Alloys?

Nanostructured High-Entropy Alloys with Multiple Principal Elements: Novel Alloy Design Concepts and Outcomes**

(Yeh, et al., Mater Chem Phys, 2007)
Mechanical Properties of HEAs

Very high hardness can be achieved

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Hardness, HV as-cast</th>
<th>Hardness, HV annealed (after 1000 °c/12h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuTiVFeNiZr</td>
<td>590</td>
<td>600</td>
</tr>
<tr>
<td>AlTiVFeNiZr</td>
<td>800</td>
<td>790</td>
</tr>
<tr>
<td>MoTiVFeNiZr</td>
<td>740</td>
<td>760</td>
</tr>
<tr>
<td>CuTiVFeNiZrCo</td>
<td>630</td>
<td>620</td>
</tr>
<tr>
<td>AlTiVFeNiZrCo</td>
<td>790</td>
<td>800</td>
</tr>
<tr>
<td>MoTiVFeNiZrCo</td>
<td>790</td>
<td>790</td>
</tr>
<tr>
<td>CuTiVFeNiZrCoCr</td>
<td>680</td>
<td>680</td>
</tr>
<tr>
<td>AlTiVFeNiZrCoCr</td>
<td>780</td>
<td>890</td>
</tr>
<tr>
<td>MoTiVFeNiZrCoCr</td>
<td>850</td>
<td>850</td>
</tr>
<tr>
<td>316 Stainless Steel</td>
<td>189</td>
<td>155</td>
</tr>
<tr>
<td>17-4 PH Stainless Steel</td>
<td>410</td>
<td>362</td>
</tr>
<tr>
<td>Hastelloy C[9]</td>
<td>236</td>
<td>280</td>
</tr>
<tr>
<td>Stellite 6[8]</td>
<td>413</td>
<td>494</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>412</td>
<td>341</td>
</tr>
</tbody>
</table>

460 MPa@1600 °C better than superalloys

Disordered bcc solid solution was reserved after annealing at 1400 °c for 19h

Refractory high entropy alloys (Senkov, et al., Intermetallics, 2011)
A fracture-resistant high-entropy alloy for cryogenic applications

CoCrFeMnNi

(Ritchie, Acta Gold Medal, 2014)
Q1: Solid solution or amorphous phase?

Confusion by design

A. Lindsay Greer (Nature, 1993)

It seems to have been widely accepted by those working on metallic glass formation that a ‘confusion principle’ should apply: the more elements involved, the lower the chance that the alloy can select viable crystal structures, and the greater the chance of glass formation. So why have there been so few attempts to exploit the idea? The answer, it seems, is that ‘two’s company, three’s a crowd’ to those wishing to analyse fully the thermodynamics and kinetics of alloy transformations — the more elements, the more difficult the analysis.

\[ \Delta S_{\text{mix}} = -R \sum_{i=1}^{N} c_i \ln c_i \]

when \( N \) elements are mixing in equiatomic ratio \( (c_1=c_2=\ldots=c_N) \), the mixing entropy reaches the maximum:

\[ \Delta S_{\text{mix}} = R \ln N \]

Based on the confusion principle and high entropy points of view, we can easily understand that random solid solutions tend to be stable in HEAs.

but, why not form a glassy (amorphous) phase then?
High-entropy bulk metallic glasses

(Ma et al., Mater Trans, 2002)

(1.5mm)

(Takeuchi et al., Intermetallics, 2011)

(Sr,Ca,Yb,Li,Mg,Zn)$_{20}$

(Sr,Ca,Yb,Mg,Zn,Cu)$_{20}$

(Pd,Pt,Cu,Ni,P)$_{20}$ Alloy

(12 mm$^3$

(10 mm$^3$

(Gao et al., J Non-Crys. Solids, 2011)
Intermetallic compounds can certainly form in equiatomic multi-component alloys

For example:

\[
\begin{align*}
\text{CoCrFe}_{0.6}\text{NiAlMo}_{0.5} & \quad \text{BCC +} \sigma \text{ phase} \\
\text{CoCrFeNiAlMo}_{0.5} & \quad \text{BCC +} \sigma \text{ phase} \\
\text{CoCrFe}_{1.5}\text{NiAlMo}_{0.5} & \quad \text{BCC +} \sigma \text{ phase} \\
\text{CoCrFe}_{2}\text{NiAlMo}_{0.5} & \quad \text{BCC +} \sigma \text{ phase} \\
\text{Co}_{0.5}\text{CrFeNiAlMo}_{0.5} & \quad \text{BCC +} \sigma \text{ phase} \\
\text{Co}_{1.5}\text{CrFeNiAlMo}_{0.5} & \quad \text{BCC +} \sigma \text{ phase} \\
\text{Co}_{2}\text{CrFeNiAlMo}_{0.5} & \quad \text{BCC +} \sigma \text{ phase} \\
\text{TiCoCrNiCuAl} & \quad \text{BCC + Cu + Cr} \\
\text{CoCrNiCuAlAu} & \quad \text{FCC + AuCu} \\
\text{CoCrFeNiCuAlMo}_{0.4} & \quad \text{BCC +} \alpha \text{ phase} \\
\text{CoCrFeNiCuAlMo}_{0.6} & \quad \text{BCC +} \alpha \text{ phase} \\
\text{CoCrFeNiCuAlMo}_{0.8} & \quad \text{BCC +} \alpha \text{ phase} \\
\text{CoCrFeNiCuAlMo} & \quad \text{BCC +} \alpha \text{ phase} \\
\text{ZrHfTiCuFe} & \quad \text{Compounds} \\
\text{ZrHfTiCuCo} & \quad \text{Compounds} \\
\text{AlCrMoSiTi} & \quad \text{Ordered BCC + Mo}_3\text{Si}_3 \\
\text{Ti}_2\text{CoCrFeNiCu} & \quad \text{Compounds} \\
\text{AlTiVYZr} & \quad \text{Compounds} \\
\text{ZrTiVCuNiBe} & \quad \text{Compounds} \\
\text{TiCoCrNiCuAlY}_{0.5} & \quad \text{Cu}_2\text{Y + AlNi}_2\text{Ti + Cu + Cr} \\
\text{TiCoCrNiCuAlY}_{0.8} & \quad \text{Cu}_2\text{Y + AlNi}_2\text{Ti + Cu + Cr}
\end{align*}
\]

XRD patterns of the \textbf{CoCrCuFeNiTi}_x samples (x = 0, 0.5, 0.8, and 1)

So, can we predict the phase selection (\textit{solid solution, amorphous phase and intermetallic compound}) in equiatomic multi-component alloys?
Reminder of Darken-Gurry map

(Cahn and Haasen, Physical Metallurgy, 1996)
- **Cahn**: Acta Gold Medal, 2002
- **Haasen**: Acta Gold Medal, 1994
- **Massalski**: Acta Gold Medal, 1995 & William Hume-Rothery Award, 1980
- **Darken**: William Hume-Rothery Award, 1979

*Forming Ta-X solid solution*
### Periodic Table

#### Atomic Properties of the Elements

**Frequently used fundamental physical constants**

- Speed of light in vacuum: $c = 299,792,458 \text{ m s}^{-1}$ (exact)
- Phonon constant: $a = 0.8205 \times 10^{-12} \text{ cm}$
- Elementary charge: $e = 1.6022 \times 10^{-19} \text{ C}$
- Electron mass: $m_e = 9.1094 \times 10^{-31} \text{ kg}$
- Proton mass: $m_p = 1.6726 \times 10^{-27} \text{ kg}$
- Fine-structure constant: $\alpha = 1/137.036$
- Rydberg constant: $R_H = 10.97374 \times 10^9 \text{ m}^{-1}$
- Boltzmann constant: $k_B = 1.304 \times 10^{-20} \text{ J K}^{-1}$

#### Structure Types

- **fcc prototype**
- **bcc prototype**

**Section Heading:**

- Periodic Table of the Elements

**Additional Information:**

- For a description of the data, visit physics.nist.gov/data
- NIST SP 966 (September 2010)
A1: 2-parameter map for phase selection in HEAs

Solid solution phases form when $\delta$ is small, and $\Delta H_{\text{mix}}$ is either slightly positive or insignificantly negative;

Amorphous phases form when $\delta$ is large, and $\Delta H_{\text{mix}}$ is noticeably negative;

In the intermediate conditions (in terms of $\delta$ and $\Delta H_{\text{mix}}$), intermetallic compounds compete with both amorphous phases & solid solution phases.

atomic size difference

$$\delta = \sqrt{\sum_{i=1}^{n} c_i (1 - r_i / \bar{r})^2}, \bar{r} = \sum_{i=1}^{n} c_i r_i$$

mixing enthalpy

$$\Delta H_{\text{mix}} = \sum_{i=j}^{n} \Omega_{ij} c_i c_j$$

$$\Omega_{ij} = 4 \Delta H_{\text{mix}}^{AB}$$

(Guo et al., Intermetallics, 2013)
Improvement of $\delta - \Delta H_{mix}$ map using the concept of $Md$, d-orbital energy level

(Sheikh et al., J Appl Phys, 2015)
Q2: fcc or bcc solid solution?

(Yeh, et al., Mater Chem Phys, 2007)

(Tong et al., Metall Mater A, 2005)
Q2: fcc or bcc solid solution?


FCC AND BCC EQUIVALENTS IN AS-CAST SOLID SOLUTIONS OF Al₆Co₅Cr₂Cu₀.₅Fe₄Ni₄ HIGH-ENTROPY ALLOYS
Guan-Yu KEᵃ, Swe-Kai CHENᵇ, Tung HSUᵇ, Jien-Wei YEHᵇ

maintaining the other elements and Cu at 1 and 0.5, respectively. It was shown by X-ray diffraction (XRD) that Ni and Co are FCC stabilizers, Al and Cr are BCC stabilizers and Fe is neutral in the solid-solution phases that form. From energy dispersive spectroscopy chemical analysis and XRD, it was determined that 1.11 Co_{FCC} is equivalent to Ni_{FCC} for the FCC stabilizers, and that 2.23 Cr_{BCC} is equivalent to Al_{BCC} for the BCC stabilizers. A 45-55 % rule is found for judging whether a phase will be FCC or BCC, wherein a phase has an FCC structure if the % Co_{FCC} is greater than 45 at. % and a BCC structure if the % Cr_{BCC} is greater than 55 at. %.
Reminder of Hume-Rothery electron concentration rule

(Mizutani, Hume-Rothery Rules for Structurally Complex Alloy Phases, 2011)  
(Mizutani, William Hume-Rothery Award, 2005)
A higher VEC favors the formation of fcc solid solutions, while a smaller VEC tends to stabilize the bcc solid solutions.

A mixture of fcc and bcc solid solutions forms at intermediate VEC.

(Guo et al., JAP, 2011)
Mechanical behavior
Case I: Ductile Refractory High Entropy Alloys: single bcc solid solution

Nanostructured high-strength molybdenum alloys with unprecedented tensile ductility

G. Liu¹, G. J. Zhang¹, F. Jiang¹, X. D. Ding¹, Y. J. Sun¹, J. Sun³,⁴ and E. Ma³,⁴,⁎

The high-temperature stability and mechanical properties of refractory molybdenum alloys are highly desirable for a wide range of critical applications. However, a long-standing problem for these alloys is that they suffer from low ductility and limited formability. Here we report a nanostructuring strategy that achieves Mo alloys with yield strength over 800 MPa and tensile elongation as large as ~40% at room temperature. The processing route involves a molecular-level liquid-liquid mixing/doping technique that leads to an optimal microstructure of submicrometre grains with nanometric oxide particles uniformly distributed in the grain interior. Our approach can be readily adapted to large-scale industrial production of ductile Mo alloys that can be extensively processed and shaped at low temperatures. The architecture engineered into such multicomponent alloys offers a general pathway for manufacturing dispersion-strengthened materials with both high strength and ductility.
Mechanical behavior
Case II: Eutectic High-Entropy Alloys: dual-phase (soft/hard) solid solutions

(Wani et al., Mater Res Lett, 2016)
Summary

- **High-entropy** alloys are highly concentrated, multi-component alloys (the name is a bit controversial, but a name is just a name)
- Empirical science, like **Hume-Rothery rules**, are very useful even for this type of new and compositionally complicated materials (old wisdom is classical)
- **Electron theory** helps a lot (phase selection/mechanical behavior)
- New materials → new properties (high-temperature/cryogenic temperature, etc.) & new applications (???)
- **Structural** or **functional** properties? (always a dilemma)