Metastable High Entropy Alloys

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Short version
Max-Planck High Entropy Alloy Team

Interdepartmental research: High & Medium Entropy Alloys – from ab initio thermodynamics to properties
• Global metal market: 3000 billion € / year
• Green energy supply
• e\(^-\) and H in transport and industry
• Sustainable production and CO\(_2\) reduction
Alloy thermodynamics

Metastability high entropy alloy design

Mechanistic alloy design

Mechanism selection
- Twinning
- Martensite
- Precipitates
...

Mechanical Metastability

Chemical Metastability

Mechanistic high-entropy alloy design

Effects
- TWIP
- TRIP
- Multiphase
- Ultra fine grained
- Dislocation patterning
- Nano precipitates
- Phase metastability
- Metallic glass
- Interstitials
- Spinodal
- Maraging
...

TWIP HEA
TRIP HEA
Spinodal HEA
Maraging HEA
Metallic glass HEA
Interstitial HEA
Dual-phase HEA
Microalloyed HEA
...

High-entropy alloy design

Compositional tuning
- Stacking faults
- Spinodal
- Misfit
...

Effects
- Cottrell clouds
- Stability by entropy
- Massive solid solution
- Dislocation decoration
- Gibbs segregation
- Intermetallics
- Suzuki effect
- Precipitation
...

Dislocations and strain hardening

Raabe et al. Metastability alloy design, MRS Bull. 44 (2019) 266-272
Dislocations and strain hardening

\[
\frac{d\sigma}{d\varepsilon}
\]

martensite / twinning

\( \varepsilon \) true strain

\( \sigma \) stress

\( \varepsilon \) true strain
Dislocations and strain hardening

\[ \frac{d\sigma}{d\varepsilon} \]

\( \sigma \)  true strain

\( \varepsilon \)  stress
Metastability Alloy Design

Mechanical Metastability

Chemical Metastability

ΔG

metastable

stable

c, p

ΔG

metastable

stable

c, p
Athermal transformations not affine, not commensurate - high misfit deformation

Multiple strain hardening effects
Mechanical Metastability

Confined at lattice defects

Chemical and structural size effects

Size effects in the bulk
- All for free and self-organized
- Thermodynamically tuned
Role of the stacking fault energy

lower SFE

**high-Mn (15-30%), HEA**

\[ \gamma \text{ (fcc) cells } \rightarrow \gamma \text{ (fcc) planar } \rightarrow \gamma \text{ (fcc+order) planar } \rightarrow \gamma \text{ (fcc+twins) } \rightarrow \epsilon \text{ (hcp) } \rightarrow \alpha' \text{ (bcc/bct) } \]

**medium-Mn (5-12%)**

**high-Mn+Al**

\[ \Delta G^{\gamma \rightarrow \epsilon} \gg 0 \]

Critical stress for twin growth:

\[ \tau_c = \frac{\gamma_{sf}}{3b_s} + \frac{3Gb_s}{L_0} \]

Critical stress for \( \epsilon \)-martensite growth:

\[ \tau_c = \frac{\gamma_{sf}}{3b_s} + \frac{3Gb_s}{L_0} + \frac{h\Delta G^{\gamma \rightarrow \epsilon}}{3b_s} \]

\[ \Delta G^{\gamma \rightarrow \epsilon} \ll 0 \]

\[ \Delta G^{\gamma \rightarrow \epsilon} = 0 \]

Fe-Mn-Al-C solid solution

Fe-30.5Mn-2.1Al-1.2C (wt. %)

Fe-30.4Mn-8Al-1.2C (wt%) quenched

Electron Channeling Contrast Imaging (ECCI)

Fe-30Mn-8Al-1.2C, annealing at 600°C

30 min at 600°C: saturation in yield strength

Strain rate 800/s: TWIP steel & DP800

\[ W_V = \int_0^{\varepsilon_f} \sigma \, d\varepsilon \approx \sigma_f \varepsilon_f \]

Bambach et al., DFG SFB 761 ‘Steel ab-initio’
Role of the stacking fault energy

50 mJ/m²  Stacking fault energy  ≈ 0 mJ/m²

Dislocation slip

Stacking faults

Dislocation cell structures

Partial dislocations, reduced cross slip, planar slip

Chemical short range ordering and decomposition effects possible

Slip band formation

Dynamic slip band refinement

Mechanical twinning

Coexistence of fcc (γ), hcp (ε), bcc (α) / bct (α’)

Less  More

Unidirectional TRIP effect

Bidirectional TRIP effect

Raabe et al. Metastability alloy design, MRS Bull. 44 (2019) 266-272
Dual phase high entropy alloy

Dual phase high entropy alloy

Fe$_{80-x}$Mn$_x$Co$_{10}$Cr$_{10}$

2 homogeneous solid solution HEA phases
Dual phase high entropy alloy

Interface between \( \varepsilon \) and \( \gamma \) (quenched)

- Fe50Mn30Co10Cr10
- STEM-EDS / APT / z-contrast: both phases chemically homogeneous
- SAED: \(<11\overline{2}0>\ \varepsilon \ // <110>\ \gamma ;\ \{0001\} \ \varepsilon \ // \{111\} \ \gamma \)
Nano-γ lamellae in ε under load

Transformation inside $\varepsilon$ block ($\varepsilon \rightarrow \gamma$)

Process 1 (perfect FCC)

$\text{HCP} \rightarrow \text{Nano-FCC}$:

1. BCBCBCBCBCBCBC
2. BCBCABABABABAB
3. BCBCABCAACACACA

Process 2 (nano-twin)

$\text{HCP} \rightarrow \text{Nano-FCC}$:

1. BCBCBCBCBCBCBC
2. BCBACACACACACACA
3. BCBACBABABABABAB

Deformed sample (twin relation)


Transformation inside $\gamma$ block ($\gamma \rightarrow \varepsilon$)

Shockley partial dislocations

$\frac{1}{2}[110] \rightarrow \frac{1}{6}[211] + \frac{1}{6}[12\overline{1}]$

Leading  Trailing

SF

Leading  Trailing

$\gamma \rightarrow \varepsilon$:

1. ABCABCABCABC
2. ABCBCABCABCA
3. ABCBABCBCBCABC

6 layers  20 layers  36 layers

Nano-lamellae in $\varepsilon$ and $\gamma$ (quenched)

- Linear features in both the $\varepsilon$ and $\gamma$ blocks (DF-TEM)
- SFs ($\gamma$ nano-lamellas): $87.6 \pm 5.4$ nm
- Thermodynamic stable at RT

In-situ LAADF-STEM reverse transformation ($\epsilon \rightarrow \gamma$)

Effect of Hydrogen: equim.-FeNiCrMnCo

HEA

56Ni-18Fe-18Cr-5Nb-3Mo

Superalloy

Stainless steel

55Fe-25Cr-20Ni

Metastability Alloy Design

Mechanical Metastability

Chemical Metastability

\[ \Delta G_{c, p} \]

\[ \Delta G_{c, p} \]

\[ c, p \]

\[ \text{metastable} \]

\[ \text{stable} \]
Interface co-segregation in FeMnCrNiCo

**Analysis perpendicular to grain boundary**

- **450°C, 6h**
  - Composition analysis showing Co, Fe, Ni, Mn, and Cr distributions.
  - peaks indicating segregation at the grain boundary.

- **450°C, 48h**
  - Similar analysis with extended time showing more pronounced segregation patterns.

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GB co-segregation in Cantor HEA

Interface co-segregation in FeMnCrNiCo

450°C, 6h

Analysis inside grain boundary plane

25at. % Ni, 21.5at. % Mn

25.5at. % Ni, 19.5at. % Mn

450°C, 18h

Interface co-segregation in FeMnCrNiCo

Ni in GB plane, 450°C, 6h

Mn in GB plane, 450°C, 6h

Defect decoration & thermodynamics

1. GB is NOT part of equilibrium, it is frozen in
2. BUT local composition / segregation is in equilibrium (Gibbs isotherm)
3. YET, segregants can interact (Fowler & Guggenheim, Hart, Guttmann isotherms)

‘Heterogeneous‘ nucleation:
- Different compositional equilibrium working point
- Different driving force
- Different interface energy (isotherm)
- GP-like precursor states or other…
Defect decoration & thermodynamics

\[ \Delta G \]

\[ \mu_{Mn}^\gamma = \mu_{Mn}^\alpha = \mu_{Mn}^{\alpha,GB} \]

Bulk spinodal: tuning for ferromagnetism

$\text{Fe}_{15}\text{Co}_{15}\text{Ni}_{20}\text{Mn}_{20}\text{Cu}_{30}$

- Cast
- Homogenization (1000 °C 24h)
- Anealing (600 °C 2h, 6h, 24h)
Temperature, in-situ heating

200 °C  2 min  600 °C  2 min  700 °C  2 min  800 °C  6 min

Bulk spinodal: tuning for ferromagnetism
FeCoNiMnCu annealed at 600°C for 6 h

Cu rich phase

Fe-Co-Ni-Mn rich phase
FeCoNiMnCu annealed at 600°C for 6 h
FeCoNiMnCu annealed at 600°C

Annealing time

0 h  2 h  6 h  24 h  240 h

Iso-surface: 50 at% Cu

Cu

20 nm
FeCoNiMnCu annealed at 600°C

Experimental results
Message & Conclusions

• Metastability alloy design (displacive, spinodal)
• Multicomponent thermodynamics, also at confined scales

• Combine mechanical properties with magnetism, corrosion, H-resistance, …
Thank you for the attention

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