Short-range order and microhardness of the compositionally complex alloy Al$_8$Co$_{17}$Cr$_{17}$Cu$_8$Fe$_{17}$Ni$_{33}$

Andrea Fantin$^1$, Anna Manzoni$^2$, Tobias Scherb$^2$, Yao Liu$^3$, Gerhard Schumacher$^{1,2}$, John Banhart$^{1,2}$

$^1$Technische Universität Berlin, Germany
$^2$Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Germany
$^3$Shandong University at Jinan, China
Introduction

Experimental

Results
• Soft X-ray absorption spectroscopy
• Extended X-ray absorption spectroscopy
• Hardness
• Molecular dynamic simulations

Conclusions and outlook
Short-range order in superalloys

by neutron scattering

- Diffuse scattering hints of Short-Range Order
  - superstructure peak at [1 ½ 0]
  - diffuse background at [2 1 0]
- ~ 1.5 nm ordered domains at room temperature (MC-2)
- Short-Range Order dissolves above $T = 600 \, ^\circ C$ (MCW)

Short-Range Order in Compositionally Complex Alloys?
Short-range order in compositionally complex alloys

FeCoNiCrMn
*Entropy 2016, 18, 321*

- Small element-resolved mean lattice distortions (~0.1%)
- High local fluctuations of lattice distortions (~2-3%)

Al1.3CoCrCuFeNi
*Nat. Comm. 2015, 6, 5964*

- Structure <10 Å not well modelled by cubic fcc
- AIMD simulations show preferred nearest neighbors
Experimental

**BESSYII: beamlines KMC-2 and KMC-3**
- Mode: fluorescence
- Temperatures: 20 K – 300 K

**BESSYII: Russian-German beamline**
- Mode: total electron yield (<10nm information depth) in ultra-high vacuum

**Hardness measurements**
- Vickers indentation
- Nanoindentation

**Ab-initio molecular dynamics simulations**

**Al₈Co₁₇Cr₁₇Cu₈Fe₁₇Ni₃₃ specimens**
- 2-to-4 components precursors

**Dr. Yao Liu (Shandong University)**
- Vienna ab initio simulation package

**Bulk (Single crystal, polycrystal)**
- Splat
Results: Soft X-ray absorption spectroscopy

Spin-orbit splitting visible in all spectra ($\Delta E(\text{Co})$: $\approx 15$ eV), $\Delta E(\text{Fe})$: $\approx 13$ eV, $\Delta E(\text{Ni})$: $\approx 17$ eV)

- Absorption spectrum of Co/Fe in CCA similar to absorption spectra of Co/Fe pure metals
  $\Rightarrow$ Electronic structure of Co/Fe in CCA similar to that of Co/Fe metals

- Absorption spectrum of Ni in CCA shifted to higher energy compared with Ni in Ni metal
  $\Rightarrow$ Electronic structure of Ni in Ni dissimilar to Ni in CCA
  (i) higher binding energy of Ni 2p levels in CCA
  (ii) shift in density of empty Ni d-states

Senkovskiy et al., J. Alloys and Compounds 537 (2012)
Al missing. Al-K edge logistically difficult to measure (few beamlines available)

1\textsuperscript{st} shell bond lengths depend on the element (Short-range order!)

- Lowest for Co (2.510(2) Å, extrapolation for T < 50K)
- Highest for Cu (2.536(3) Å, extrapolation for T < 50K)

$\sigma^2$ for Ni-1\textsuperscript{st} shell is half the value compared to that of Cr, Fe and Co

- 1\textsuperscript{st} shell around Ni more ordered (highest at.% of Ni in CCA a possible reason)
- Noisy spectra at Cu-K edge do not allow reliable $\sigma^2$ refinement
Results: hardness

- Hardness of splats higher than hardness of bulk specimens
- Data scattering on splats higher than on bulk specimens
- Decrease in hardness at 850 °C with increasing annealing time

Two-hardening mechanisms:

- $T > 900^\circ C$: short-range order in single phase region
- $T < 900^\circ C$: precipitation mechanism in $\gamma/\gamma'$ phase region
Results: ab initio molecular dynamics

- Crystalline state not reached at 1000°C (still liquid state)
- Liquid state reveals pronounced Short-Range Order
- Al prefers Ni/Co/Cu as nearest neighbors

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Cr</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>R(Å)</td>
<td>1.43</td>
<td>1.25</td>
<td>1.24</td>
<td>1.25</td>
<td>1.25</td>
<td>1.28</td>
</tr>
</tbody>
</table>
**Conclusions and outlook**

**Soft X-ray absorption spectroscopy:**
Ni electronic structure seems to be different than the corresponding Ni pure metal.

Further studies and measurements (e.g. at Al and Cr L-edges) needed.

**Extended X-ray absorption fine structure:**
- 1st shell around Co and Cu atoms are the smaller and the bigger, respectively.
- 1st shell around Ni is the most ordered.

Al-K edge spectrum still missing.

Any relation to Ni-electronic structure?

**Hardness**
- Depends on temperature and annealing time.
- Depends on specimen nature (bulk vs splat).

Two hardening mechanisms:
- SRO increase (single phase).
- Precipitation (\(\gamma/\gamma'\) region).

Splat vs bulk CCAs in XAS?

**Ab initio molecular dynamics**
Preferred nearest neighbors for Al (Ni, Co, Cu).

To be proved experimentally (e.g. XAS on Al-K edge).
Acknowledgements

• Prof. Dr. John Banhart, as principal investigator of the project

• Prof. Dr. Gerhard Schumacher and Dr. A. Manzoni as additional and helpful project investigators

• Dr. A. Manzoni, Dr. T. Scherb, Dr. D. Zhou, D. Ning, L. Zhang, C. Касатиков for performing/helping the X-ray absorption spectroscopy measurements and analysis

• A. Öner, C. T. Cakir, for the hardness measurements

• Dr. Y. Liu, for molecular dynamics simulations

Thank you for your attention!
Results: K-edge X-ray absorption near edge structure (XANES)

XANES spectra for Cr, Fe, Co, Ni and Cu K-edges at 20 K in the CCA. Black lines represent reference foils.

Pure metals and CCA:

K-edge split into two transitions

1s → mixed state (4s-4p-3d)
1s → 4p state

• Fe, Cr metals have bcc structure, Co metal hcp structure. Metals spectra not easily comparable with CCA spectra

Study of e.g. 2-component (FeNi) and 3-component (CoFeNi) alloys with fcc structure is necessary.