Microstructural properties of Al-containing refractory high entropy alloys for high temperature applications

Peculiarities of ordering in Ta-Nb-Mo-Cr-Ti-Al

H. Chen¹, A. Kauffmann¹, S. Seils¹, T. Boll¹, D. V. Szabó¹, F. Müller², B. Gorr², H.-J. Christ², K. S. Kumar³, M. Heilmaier¹

¹Institute for Applied Materials (IAM-WK), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany
²Institut für Werkstofftechnik, University of Siegen, Siegen, Germany
³School of Engineering, Brown University, Providence (RI), USA

HE 1872/34-1

Institute for Applied Materials IAM–WK

SPP project meeting in Hannover, 14.02.2018
Introduction

- Alloy development → for high temperature applications

- Lack of ductility on macroscopic scale between room temperature and 400 °C\(^1,2\) → characterization of mechanical properties difficult

- Microstructural characterization to understand intrinsic brittleness

---


Microstructure

- Arc melting → Homogenization

- Suppression of competing phases

MoCrTiAl 1200 °C / 20 h

Mo L

250 µm

Cr K

Al K

OK

TaMoCrTiAl 1500 °C / 20 h

Mo L

Cr K

Ti K

Al K

Ta L

OK

hex. Laves phase Cr₂Ta

Cr₂Ta

Cr₂Nb

Al(Mo,Nb)₃

Ti(Al,Cr)₃
Atom probe tomography (APT)

MoCrTiAl

Atoms homogeneously distributed within APT tip

Homogeneous microstructure down to nm scale
Indications of ordering

- bcc
- possible B2

- XRD: gentle indications of B2 superstructure in Nb-Mo-Cr-Ti-Al

- TaMoCrTiAl exhibits significant superlattice peaks

- Morphology of B2 ordered phase? → TEM
Peculiarities of ordering

- TEM-SAD: Superlattice spots observable in all investigated alloys
- TEM-BF: Antiphase domain boundaries (APBs) reveal disorder-order phase transformation during cooling

Homogeneously ordered B2 crystal structure in all alloys
Properties of ordering

- Lattice shift at APB → chemical inhomogeneity
- APBs reveals site occupation
  Cr: site 1  Ti: site 2  Mo, Al: evenly distributed
- MoCrTiAl

(100) ½ [111] APB

- APBs enriched in Cr (occupies lattice site 1) and depleted in Ti (site 2)
Summary

- Ta-Nb-Mo-Cr-Ti-Al: Uniform element distribution after homogenization treatment
- B2 type ordered crystal structure forms during cooling
- Approach to reveal site occupation by APT on APBs
- Contribution of ordering to lack of ductility \(\rightarrow\) project outlook

\[
\text{Ta-Nb-Mo-Re-Cr-Ti-Al}
\]

- High melting point
- Suppress Laves phase
- Low density
- Decrease DBTT
- Passivating
Thank you for your kind attention.

Many thanks to:

Deutsche Forschungsgemeinschaft (DFG), HE 1872/31-1 and HE 1872/34-1
Karlsruhe Nano Micro Facility (KNMF)
Carl Zeiss Stiftung
Thermal stability of ordering

MoCrTiAl, as homogenized

- At which temperature does bcc-B2-transformation occur?
  - TEM heating experiment
- TEM-SAD: Super lattice spots completely vanish at 1000 °C
Disorder-order phase transformation

- λ-shaped peaks reveal second order phase transformation at $T_{\text{peak}}$
- Observable in all alloys
- DSC at varying heating rates $\rightarrow T_{\text{onset}}$ does not seem to be related to disorder-order phase transformation
Solid solution strengthening of HEAs

- Atomic size difference $\delta \leftrightarrow$ mechanical properties

$$
\delta = \sqrt{\sum_i x_i \left(1 - \frac{r_i}{\bar{r}}\right)^2}
$$

$x_i$: Concentration of element $i$
$r_i$: Atomic radius of element $i$
$\bar{r}$: Mean atomic radius

- Bcc alloys: T dependent mechanical properties

- Influence of thermally activated processes on strengthening of bcc high entropy alloys
Suppression of 
$\text{Cr}_2\text{Nb}$ and $\text{Al}(\text{Mo},\text{Nb})_3$

Cr reduction

 NbMoCr$_{0.75}$TiAl
 NbMoCr$_{0.5}$TiAl
 NbMoCr$_{0.25}$TiAl

Nb reduction

 Nb$_{0.75}$MoCrTiAl
 Nb$_{0.5}$MoCrTiAl
 Nb$_{0.25}$MoCrTiAl

MoCrTiAl

$\delta \leftrightarrow$ alloy composition

NbMoTiAl

NbMoCr$_{0.25}$TiAl

NbMoCr$_{0.5}$TiAl

NbMoCr$_{0.75}$TiAl

H. Chen - Microstructural properties of Al-containing refractory high entropy alloys for high temperature applications
Asymmetric trend of $\delta$

Microhardness at RT $\mu H^{RT}$

$\mu H^{RT}$ in good accordance with $\delta$

Contribution of T dependency of mechanical properties in bcc alloys not considered, so far
Section II: Lattice – dislocation interactions are revealed

- Responsible mechanism regarding solid solution strengthening

- Determining T-range of athermal plateau properties $\sigma_{f}^{\text{plateau}}$
T dependency of mechanical properties

- Alloys: NbMoCrTiAl, MoCrTiAl, NbMoTiAl
- 400 °C – 1200 °C
  - Compression tests → T dependent flow stress $\sigma_f$
- RT - 400 °C
  - Lack of ductility on macroscopic scale

- Nanoindentation → T dependent nanohardness $nH$

Determination of $nH_{\text{plateau}} / \sigma_{f\text{plateau}}$
T dependency of mechanical properties

- RT – 400 °C: Varying increase of mechanical properties of respective alloys
- 400 °C – 600 °C: $nH_{\text{plateau}} / \sigma_{f_{\text{plateau}}}$
δ $\leftrightarrow$ nH$_{\text{plateau}}$ $\sigma_{\text{plateau}}$

Scattering: varying contributions of...
- Short range ordering
- Work hardening
- Shear modulus

...to respective alloys

$\delta$ tends to correlate with athermal properties nH$_{\text{plateau}}$ / $\sigma_{\text{plateau}}$
Deformation mechanism by EBSD

- EBSD maps show orientation of the grains

- Undeformed: Random distribution of grain orientations

- Deformed: Amount of orientation with [001] and [111] crystallographic axes parallel to the compression direction increased
Deformation behavior

- EBSD: Inverse pole figures

- Increase of orientation density at [001] and [111] crystallographic axes parallel to compression direction

- Deformation by dislocation slip with <111> slip direction is observed

**EBSD: Dislocation mediated plasticity within solid solution**
Deformation behavior

**NbMoCrTiAl**

Compression @ $10^{-3}$ s$^{-1}$

- No plastic deformation on macroscopic scale below 400 °C
- Temperature-dependent strength

**Macroscopic plasticity between 400 °C and 1200 °C**