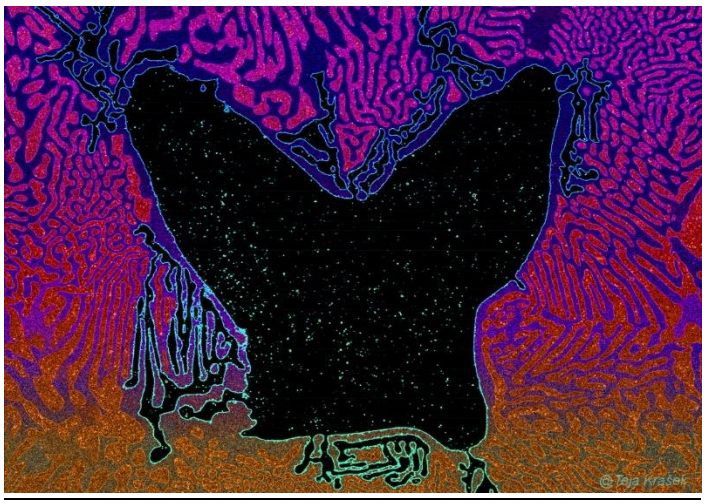
ECMetAC on-line dedicated workshop on

„High-Entropy Alloys: from basic studies to industrial applications”

March 18th, 2021

Chairperson: Dr. Magdalena Wencka

ABSTRACTS



Slovenian artist's Teja Krašek art
based on SEM image of $CrCuFeNiZr_x$ eutectic alloy microstructure,
material delivered by prof. Sheng Guo
(Chalmers University of Technology, Göteborg, Sweden)

Schedule:
/presenting authors only/

OPENING:
9:00 – 9:30 *Janez Dolinšek, Juri Grin, Julian Ledieu, Magdalena Wencka, Boštjan Zalar*

Session 1: FORMATION AND STABILITY
Chairing person: Julian Ledieu

9:30 – 10:10 *Sheng Guo*: Phase selection rules in high-entropy alloys
10:10 – 10:50 *Fevzi Kafexhiu:* On the precipitation of micro-phase in the $AlCoCrFeNi_{2.1}$ EHEA and its effect on mechanical properties

Break: 10:50 – 11:00

Session 2: SURFACES
Chairing person: Janez Dolinšek

11:00 – 11:40 *Frédéric Danoix:* Contribution of atom probe tomography to the investigation of high entropy alloys
11:40 – 12:05 *Julian Ledieu:* The (110) and (320) surfaces of a Cantor alloy
12:05 – 12:30 *Andreja Jelen:* Polymorphism and nanostructure of Y-Gd-Tb-Dy-Ho and other rare-earth-based HEAs

Break: 12:30 – 13:30

Session 3: PHYSICAL PROPERTIES
Chairing person: Sheng Guo

13:30 – 14:10 *Darja Gačnik:* Superconductivity in Sn-containing High-Entropy Alloys
14:10 – 14:35 *Stanislav Vrtnik:* Magnetism of single-crystalline nanocomposite AlFeCoMnCr

Chairing person: Frédéric Danoix
14:35 – 15:00 *Mitja Krnel:* Physical properties of Sc-based high-entropy alloys
15:00 – 15:25 *Primož Koželj:* The CoCrFeMnNi HEA – a concentrated, randomly disordered and frustrated multielement magnetic system

Break: 15:25 – 15:40

Chairing persons: Darja Gačnik, Fevzi Kafexhiu, Magdalena Wencka

15:40 – 16:10 Round-table discussion: Trends in development of high-entropy alloys

CLOSING:
16:10 – 16:25 *Janez Dolinšek, Juri Grin, Julian Ledieu, Magdalena Wencka*

Phase selection rules in high-entropy alloys

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Since about 17 years ago, there has been a new trend in designing alloys in the physical metallurgy community, which differs significantly to previous practices. In the new category of alloys, high-entropy alloys (HEAs), there is no longer a clear distinction of dominant alloying element and other elements, and basically all alloying elements are mixed equiatomically or close to equiatomically. This novel alloy design strategy opens up a vast unexplored compositional space, and potentially new opportunities to numerous new materials and new applications, but also brings new challenges on how to design these alloys properly. In this talk, I will give an overview of HEAs from the physical metallurgy perspective, starting from the definition, moving to the alloy design strategies that are currently adopted to HEAs, and then some typical properties of this relatively new class of metallic materials. The focus of this talk will be on phase selection rules in HEAs, specifically, 1) forming solid solutions or intermetallic compounds, or even the amorphous phase, and 2) forming fcc or bcc typed solid solutions, if solid solutions would form.

On the precipitation of micro-phase in the $AlCoCrFeNi_{2.1}$ EHEA and its effect on mechanical properties

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In the present study, the precipitation of micro-phase by ageing the $AlCoCrFeNi_{2.1}$ eutectic high-entropy alloy (EHEA) at 800 °C and its effect on mechanical behavior of the alloy was elaborated. The alloy at the as-cast state consists of B2 (BCC) and $L1_2$ (FCC) lamellar phases at a volume ratio of 0.3/0.7. From the supersaturated $L1_2$ phase, by ageing at a constant temperature of 800 °C up to 500 hours, a micro-phase with a B2-like structure precipitates and grows to an equivalent circle diameter of 0.42 ± 0.1 μm; by further ageing (in our case up to 1000 h) the precipitates coarsen according to the Ostwald ripening mechanism [1]. Nanoindentation measurements were performed in order to evaluate the local mechanical behavior of two different phases with different chemistry, structure, and lattice orientations. It was found that after 20 h of ageing at 800 °C, where the B2-like microphase already precipitated, the microstructure is still in a metastable condition with high scatter of hardness values and lattice distortion. After 100 h of ageing, the number and size of precipitates in the $L1_2$ phase increase and the microstructure reaches a fairly stable condition, where there is almost no scatter of lattice misorientation and chemical composition, but still a fairly high scatter in hardness levels, due to the presence of precipitates. In general, the B2 phase has a higher hardness when compared to the $L1_2$ phase.

1. Kafexhiu, F.; Podgornik, B.; Feizpour, D. Tribological Behavior of As-Cast and Aged $AlCoCrFeNi_{2.1}$ CCA. *Metals* **2020**, *10*, 208, doi:10.3390/met10020208.

Contribution of atom probe tomography to the investigation of high entropy alloys

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Atom Probe Tomography (APT) is a unique analytical microscopy technique for exploring materials in three dimensions down to atomic scale. As an analytical microscope, it has the possibility of characterizing quantitatively nanometer scale composition fluctuations, which is often of paramount importance to understand properties of metallic alloys.

In this presentation, after a brief introduction to the techique itself, some of its recent application in the field of HEA will be reviewed, from solid solution to precipitated phases characterization, and from interfacial segregation quantificationof chemical long range ordering.

High Entropy Alloy Surfaces: an Introduction with a Cantor Alloy

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High entropy alloys (HEA) [1] are alloys containing at least five elements in equiatomic or near-equiatomic concentration. They adopt simple crystallographic structures such as bcc, fcc and hcp structure solid solution phases. Identified rapidly for their outstanding mechanical properties, HEA have also been considered as potential coatings for thermal and diffusion barriers, and for oxidation resistance [2]. Synthesized as nanoparticles, HEA exhibit interesting catalytic properties towards ammonia oxidation for instance, adding to the long list of their attractive physical and chemical properties [3].
As explained above, several HEA potential applications make use of their surface properties. However, fundamental questions remain open on the structural and chemical stabilities of HEA surfaces under operating conditions.
Here, we will report our first investigation of two HEA model surfaces namely the FeCrMnNiCo(110) and (320), system also referred as Cantor alloy [4]. The structural and compositional evolutions of surfaces will be presented for various preparation conditions under ultra high vacuum using a multi-technique approach. While the (320) surface presents an ordered structure, the (110) surface reveals an important degree of structural disorder and local reconstructions. These works will also highlight important surface chemical segregation, demonstrate the influence of the sample annealing history on the surface composition and set an annealing upper limit above which elemental desorption occurs. Finally, the impact of the thermal history on this random solid-solution will be discussed based on transition electron microscopy experiments performed on HEA lamellae.

[1] J.W. Yeh, S.K. Chen, S.J. Lin *et al*., Adv. Eng. Mater. 6, (2004) 299.
[2] Y. Zhang, T.T. Zuo, Z. Tang, M.C. Gao, *et al.*, Prog. Mater. Sci. 61, (2014) 1-93.
[3] Y. Yao, Z. Huang, P. Xie, S.D. Lacey *et al.*, Science 359, 1489–1494 (2018).
[4] B. Cantor, I.T.H. Chang, P. Knight and A.J.B. Vincent, Mater. Sci. Eng. A 375-377, (2004) 213-218.

Polymorphism and nanostructure of Y-Gd-Tb-Dy-Ho and other rare-earth-based HEAs

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Rare-earths (RE)-based hexagonal HEAs composed of the elements from the heavy half of the lanthanide series are much closer to an ideal solid solution than HEAs composed of any other elements in the periodic table.
In order to see how "ideal" RE-based HEA samples can be synthesized in laboratories, we have undertaken a structural and compositional study of three candidates for a physical realization of an ideal HEA, an Y-Gd-Tb-Dy-Ho, a Gd-Tb-Dy-Ho-Lu and a Tb-Dy-Ho-Er-Tm. We found that all three HEAs exhibit a nanostructure of a hexagonal close-packed (hcp) matrix and rod-like cubic close-packed (ccp) precipitates. HAADF image of their interface is presented in Fig. 1.

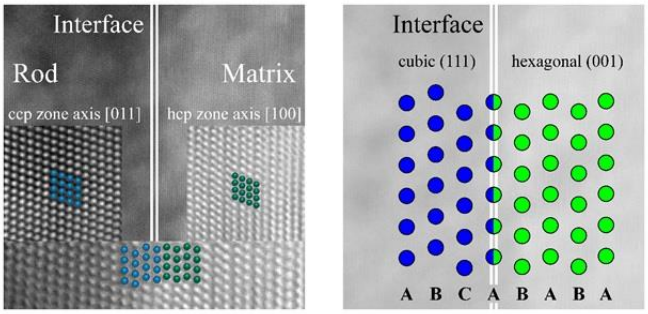

Fig. 1: HAADF image of the interface region in the direct space (left panel) and schematic representation in the right panel, showing the polymorphism.

A physical realization of an ideal HEA (a single-phase solid solution with no enthalpy of mixing, $\Delta H_{mix} = 0$, and randomly distributed elements on an undistorted lattice) is not met even in the most promising theoretical candidates [1].

[1] A. Jelen, Jae Hyuck Jang, Junhyup Oh, Hae Jin Kim, A. Meden, S. Vrtnik, M. Feuerbacher, J. Dolinšek: Mater. Char. **172**, 110837 (2021).

Superconductivity in Sn-containing High-Entropy Alloys

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[1]M. van Midden, [1]E. Zupanič, [3]A. Meden, [4]Q. Hu, [1,2]J. Dolinšek

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HEA superconductors might constitute a new class of superconducting materials while still exhibiting type-II superconductivity. Their superconducting behavior differs from the conventional, metals-based superconductors, copper-oxide (high-T_C) superconductors, and Fe-based superconductors (iron pnictides). However, their transition temperatures are limited to the range below 10 K and are, like in the conventional metals-based superconducting alloys, greatly impacted by the concentrations of the elements with higher SC-N transition temperatures. Under externally applied pressure HEA superconductors are robust against volume shrinkage and retain a constant T_C until a certain value of a critical pressure [1].

Our research has focused on Sn-containing superconducting alloys from the system TiZrHfSn(Fe,Ni,Cu,Nb), where superconductivity was studied experimentally via the electrical resistivity, the specific heat, and the scanning tunnelling spectroscopy. Additionally, magnetic measurements were conducted at both atmospheric pressure and applied pressure to 1.2 GPa. Experimentally evaluated superconducting properties are comparable with metals-based superconducting alloys involving 3*d*, 4*d*, and 5*d* transition metals. The superconductivity in investigated Sn-containing alloys is extremely robust concerning all kinds of structural and chemical disorder, making them typical BCS type “dirty” superconductors.

[1] L. Sun, R.J. Cava. High-entropy alloy superconductors: Status, opportunities and challenges. Phys. Rev. Mater. **3** (2019) 090301.

Magnetism of single-crystalline nanocomposite AlFeCoMnCr

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We have investigated the nature of the magnetic state of a single-crystalline AlFeCoMnCr nanocomposite high-entropy alloy (HEA), composed of crystallographically oriented magnetic nanoplatelets embedded in a magnetic matrix of different magnetic order [1]. The two-phase nanocomposite was formed by a bcc-B2 spinodal decomposition. Due to the single-crystalline nature of the material, there is no symmetry breaking of the surface atomic monolayer at the borders between the two phases and there are no interface regions between the nanoplatelets and the matrix [2]. The material also does not exhibit grain structure, allowing for the observation of the true intrinsic magnetism of a nanocomposite HEA. Upon cooling, the predominantly Fe–Cr–Mn chemically disordered bcc matrix orders first at $T_{C1} \approx 425$ K in an asperomagnetic-type magnetic state. Below $T_{C2} \approx 370$ K, the B2 nanoplatelets that are predominantly an $Al_{30}(Co,Mn)_{70}$ pseudo-binary intermetallic compound, start to order in a ferromagnetic (FM)-type manner. We have focused to the question whether the magnetic state of the nanocomposite below T_{C2} is a collective state of the interacting nanoplatelets and the matrix or their coupling is weak enough that the magnetic ordering of each of them can be treated independently. Experimental results support the development of a single collective, disordered FM-type magnetic state upon cooling due to the exchange coupling between the nanoplatelets and the matrix. The nanocomposite is magnetically soft and the strong variation of the magnetization with the temperature in a large interval $\Delta T \approx 125$ K just above room temperature due to two successive magnetic phase transitions make this material promising for the application in magnetocaloric refrigeration.

[1] A. Jelen *et al.*, *J. Alloys Compd.* **In Press**, 158115 (2020).
[2] M. Feuerbacher *et al.*, *Mater. Res. Lett.* **5**, 128–134 (2017).

Physical properties of Sc-based high-entropy alloys

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I will present physical properties of four high-entropy alloy polycrystalline samples from Ti-Zr-Hf-Nb-Ta-Sc system and compare them with samples from the system Sc-Zr-Nb-Ta-Rh-Pd measured by others[1].

All of the samples from Ti-Zr-Hf-Nb-Ta-Sc system were found to be type II superconductors despite Sc is not superconducting at ambient pressure. The superconducting transition temperatures T_c of the samples determined from electrical resistivity measurements vary between 6.6 K and 8 K. The T_c were found to be quite insensitive to the degree of structural and chemical disorder. XRD characterization revealed each sample has a bcc and hcp phase. However SEM measurements showed complex microstructure including dendrites. Broad peaks in specific heat $C(T)$ measurements further confirmed that each phase is inhomogeneous and $C/T(T^2)$ plots that only one phase is superconducting. The temperature dependence of the $C(T)$ peaks resulting from the formation of Cooper pairs allowed us to estimate the zero-temperature values of upper critical field, ranging from $\mu_0 H_{c2}(0) \approx 7{,}7$ T to 14,3 T. From magnetization vs field measurements we estimated the lower critical fields $\mu_0 H_{c1}(0)$, which go from 250 mT to 700 mT.

On the other hand samples from Sc-Zr-Nb-Ta-Rh-Pd system contain only one CsCl-type phase. They are not all superconducting, their transition temperatures depends strongly on the chemical composition and reach the highest value of $T_c = 9.3$ K for $(ScZrNb)_{0.65}[RhPd]_{0.35}$. The upper critical field values are lower, with maximum value $\mu_0 H_{c2}(0) \approx 10{,}7$ T.

[1] K. Stolze *et al.*: Chem. Mater **30**, 906 (2018).

The CoCrFeMnNi HEA – a concentrated, randomly disordered and frustrated multielement magnetic system

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[3]M. Wencka, [4,5]Z. Jagličić, [6]A. Meden, [7]F. Danoix, [8]J. Ledieu,
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Previous experimental investigations into the CoCrFeMnNi high-entropy alloy [1,2], have given contradicting indications for its low-temperature magnetic state. This contribution [3] will present experiments on a high-quality non-equiatomic Czochralski-grown material which was homogenous on the microscale (SEM elemental mapping) and had only negligible chemical inhomogeneities on the nanoscale without observable short-range ordering (APT, HAADF STEM and EELS spectroscopy).

The above means that our non-equiatomic CoCrFeMnNi HEA was an example of an interestingly complicated magnetic system as it is: a) magnetically concentrated with all sites magnetic, b) severely multicomponent with 5 elements, c) a completely random solid solution and d) frustrated due to competing FM and AFM interactions. We observed no long-range ordering but a kinetic freezing transition to a spin glass state at $T_f \approx 20$ K. The broken ergodicity below T_f was illustrated through the splitting of zero-field- and field-cooled magnetization, a shift of the cusp in the AC measurements with frequency, ultra-slow decay of the thermoremanent magnetization and via the thermal memory effect (the state made in isothermal aging is retrieved on a reverse temperature cycle).

[1] O. Schneeweiss, *et al.*, Phys. Rev. B **96**, 014437 (2017).
[2] K. Jin, *et al.*, Sci. Rep. **6**, 20159 (2016).
[3] P. Koželj, *et al.*, J. Magn. Magn. Mater. **523**, 167579 (2021).