Final Project Report
OTKA No. 109570, (2013-2018)

Abstract

The aim of the project is the design, development and optimization of a new high-strength, high-temperature and ductile multicomponent metallic alloy for structural applications in harsh environmental conditions. The investigated multicomponent high entropy alloys (HEAs) represent a solution for an age-old problem: combination of high strength and high ductility of metallic alloys. Started in 2004, this new class of alloys seems to promise a low-cost solution for many applications where the high strength at moderately high temperatures and good ductility are sufficient for several industrial applications like high-temperature drilling head, neutron-irradiation resistant nuclear reactor vessel, etc. During the four-year project, we prepared and studied several such HEAs experimentally and by computational quantum mechanics and we proposed alloy solutions for further investigations for scaling up.

Introduction

High temperature and high strength metallic alloys are highly desirable for a wide range of engineering applications. In this respect, at present two competing materials are in the frontier of material research:

- **Nanoscale particle strengthened steels** like the old oxide dispersion strengthened (ODS) alloys and the newly developed co-precipitation strengthened steels (Iron as a major component and doped with precipitating elements like Cu, and precipitating metallic compound like Ni3Ti, NiAl, NiMn) [Z.B. Jiao, et al., Mater. Today (2016), http://dx.doi.org/10.1016/j.mattod.2016.07.002] and

- **Multicomponent High entropy alloys** (HEAs) based on solid solution strengthening.

Both materials have received increasing attention in the recent years and have become bases for the development of advanced structural materials with superior combination of mechanical, chemical, welding, and irradiation properties.

In this project, we focus on multicomponent high entropy alloys, highlighting the recent advances in computation-aided alloy design, structural characterization, and unique properties of newly developed HEAs. In particular, our emphasis is on elucidating alloy design strategies, the cooperative evolution of multiple types of phases, and the correlation between microstructures and bulk properties.

High Entropy Alloys (HEAs) are crystalline solid solutions containing at least 5 elements in equal (or nearly equal) atomic fractions. They form an exciting new class of engineering materials showing great promise for various applications. Compared to other extended solid solutions, the HEAs show excellent mechanical properties, corrosion resistance and thermal stability. The first HEAs, synthesized more than ten years ago by J.-W. Yeh [Jien-Wei Yeh, US patent, 2002/0159914A1; J. W. Yeh, et al., Adv. Eng. Mater. 6, 299 (2004).], were based on 3d transition metals. A few years after the initial discovery, O. N. Senkov [O.N. Senkov, et al., Intermetallics 18, 1758 (2010).] and coworkers designed HEAs based on refractory transition metals, as potential candidates for high-temperature applications. Motivated by

these pioneering works, the number of scientific publications on the subject matter increased nearly exponentially during the last decade.

Today the search for new HEAs is based on a substantial amount of accumulated knowledge on composition-processing-property correlations. So far these correlations were established mostly by trial-and-error methods. Despite these efforts, the knowledge of the microstructure and the main deformation mechanisms in HEA alloys is still far from satisfactory, which limits the reliability of the modeling of their properties. In order to turn the composition-processing-property correlations more 'intelligent' one should look inside the HEAs, to the networks of atoms and reveal the various interactions between them. In recent years, it has become clear that in the search for advanced alloys, multi-scale modelling built on first-principles quantum theory is going to play an increasingly important role.

In this project, we have followed an integrated computational–prediction and experimental-validation approach. The computational-aided alloy design was based on first-principles calculations. The samples were prepared by us using pure elements and induction melting method under protecting Argon and home-made water-cooled copper molding. XRD, SEM, ADSM and AFM methods have been used for structural characterization using the facilities of Wigner RCP and ELTE. The bulk mechanical properties were determined by tensile-stress-strain ultrasonic velocity, nanointendation and hardness measurements. In this way new features of composition-processing-microstructure-property relationship of HEAs have been revealed and published in a number of publications.

In connection with the present project, two masters diploma works (Vida Ádám and Molnár Dávid), four PhD dissertations (Vida Ádám, Fuyang Tian, Xiaoqing Li, and Liyun Tian) and one Licentiate dissertation (Shuo Huang) have been prepared. The research by the four foreign students were supported from other financial resources but they greatly contributed to success of the present project especially in the theoretical modeling of the HEAs.

Below we quote our original work plan and then present the major scientific results during the project period. For more details, the reader is kindly requested to study the relevant publications listed at the end of the report.

Work Plan as described in the application

2013-2014:
The project will be started by a state-of-the-art report on high-entropy alloys (HEA) with special emphasis on the forming ability of single-phase solid solutions and a review of the efficient quantum-physical theories with sophisticated numerical techniques. Our primary goal is to assess the performance of standard alloy theory based on ab initio density functional theory for the case of HEAs. To this end, we employ the exact muffin-tin orbitals (EMTO) method in combination with the coherent potential approximation (CPA) and investigate the basic bulk properties of a few selected HEAs based on 3d transition metals (abbreviated by 3d-HEAs).

Preparation by induction melting and vacuum casting of novel HEA alloys based on a combination of 3d, 4d and 5d elements for the following purposes:
- to check the validity of the conjecture about strength (hardness) versus e/a correlation,

- to assess the corresponding values for one- and two-phase HEA alloys in ΔH (or ΔG) versus atomic mismatch diagram,

- to select radiation-immune HEA alloys, which can replace the presently favorite ODS steels and experimental investigation after irradiation in reactor zone.
A method will be developed for quantitative phase analysis based on XRD, neutron diffraction and density measurements.

2014-2015:
The first results of ab initio calculations will be published and some of the predictions will be tested experimentally like the validity of the conjecture about the temperature stability versus average elastic module.

The dislocations will be studied by XRD line profile analysis on compressed (torsionated) cylinder samples.

The plastic behavior will be studied by the compression of micro-pillars.
The electrical transport properties will be measured as a function of temperature.
The thermal stability of the HEA microstructures is monitored as a function of time by in-situ high-temperature XRD and neutron diffraction measurements. The structural changes as a function of applied heat treatment will be studied at room temperature as well by hardness measurements, optical and electron microscopy. DTA will be applied to monitor the thermal transformations up to the melting point.

The resistance against irradiation will be studied by monitoring the swelling by high-precision density measurements and by small-angle neutron scattering.

The microstructure and the mechanical and corrosion behavior will be studied immediately after casting and after different heat treatments.

2015-2016:
In situ neutron diffraction study of the solidification and subsequent crystalline transformations of the HEA alloys during slow cooling.

Preparation of the HEA alloys and investigation of their resistance against oxidation.
The creep behavior at and above the expected working temperature of the reactor vessel will be investigated for radiation-immune HEA alloys.

Welding of the cast HEA alloy will be studied and the properties of the heat-affected zone will be compared with the initial HEA structure.

2016-2018:
Based on the experimental and theoretical results obtained on HEA samples, we plan to develop a model for single-phase forming ability of HEA alloys.
This new model will be used for tailoring the properties of the HEA alloys.
The results obtained during the project will be evaluated, summarized and several compositions will be indicated for large-scale production in different industrial applications, like irradiation-resistant HEA alloy and wear-resistant tools.

Major research achievements

Below we list the major research achievements within the present project both for experimental and theoretical sides. A more detailed list of the results is provided in the following two sections including the list of publications.

Experimental research

- Three different experimental techniques have been developed to prepare HEA samples from elemental metals: (i) casting in water cooled copper mould, (ii) centrifugal casting and (iii) mechanical alloying. Varying the composition HEA ingots of about 4-6 mm diameter and 60-80 mm long could be obtained (corresponding to a critical cooling rate of about 10^2-10^3 K/s).
- The thermal stability was checked after different heat treatments with and without prior plastic deformation.

- The study of welding possibilities of the cast HEA alloys is in course.

- Preparation and investigation of hard metal composites using HEA alloys as binding materials. Five new alloys have been prepared from high purity (99.99%) elements by induction melting under inert atmosphere: $Ni_{24}Co_{24}Fe_{24}Cr_{8.7}Al_{18}Zr_1B_{0.3}$ and $Ni_{34.43}Co_{16.39}Fe_{16.39}Cr_{16.39}Al_{16.39}$; $Ni_{55}Fe_5Cr_{22}Mo_5Nb_5Al_8$ and $Ni_{24}Co_{24}Fe_{24}Al_{18}Cr_{10}$ and $Ni_{25}Fe_{25}Mn_{15}Cr_{10}Nb_5Ti_5Al_{15}$. The aim of the selection is to replace the toxic Co powder, and find HEAs with similar properties. The as cast HEA samples were ball milled and a composite was prepared from 20 wt% HEA + 80 wt% NbC. mixed by further ball milling. The "green" cylindrical sample (Φ = 8 mm, H = 5 mm) was prepared by compaction under 10 T. The sintering temperature was near the melting point of the HEA (binder) 1400 ^oC for 120 min. The obtained 1000 HV (at 0.3 kg) is promising and further investigations of the structure and properties are in progress.

- Preparation and investigation of NiFeCrMoW based HEAs for high temperature applications in neutron irradiation environment. Four compositions have been prepared (FeCrNiWMo, $Ni_{38.33}Fe_{36}Cr_{13.88}Mo_{6.66}W_{5.15}$, $Ni_{29.5}Fe_{39.8}Cr_{20}Mo_6W_{4.7}$, $Ni_{35}Fe_{30}Cr_{20}Mo_{10}W_5$) and delivered to Budapest Neutron Center for neutron irradiation test. The ductile-brittle transition as a function of phase composition was investigated.

- Preparation and investigation of the **stainless steel** like HEAs doped with sp elements (NiCoFeCrGa, NiCoFeCrGe, NiCoFeCrSn, NiCoFeCrAl) are based on Ni, Co, Fe and Cr with equimolar composition ratio. The result high entropy alloy, NiCoFeCr is the most famous and the most studied alloy. This alloy is a four-component solid solution a single-phase FCC. Due to the doping of sp elements the alloy becomes multiphase structured and the magnetic properties also turn to be exotic according to its BBC phase.
In the Cr containing HEAs a very interesting needle like BCC precipitations in the FCC grains was observed.

- Preparation and investigation of HEAs designed for twining induced plasticity (TWIP) effect (Fe40Mn40Cr10Co10, Fe30Mn40Cr15Co15, Fe40Mn40Cr5Co15, Fe30Mn45Cr15Co10 and Fe35Mn42.5Cr12.5Co10). These compositions have been designed

basing on ab-initio calculations of the Stacking Fault Energy's (SFE). The samples were recrystallized after plastic deformation. The tensile tests have shown a dramatic change in SFE with the change of composition. These investigations are in progress and will be continued after the end of project.

Theoretical research

Regarding to the initial work plan, we have completed the theoretical tasks for the ab initio investigation of HEAs. Below we highlight four key research areas studied by us using ab initio modeling. A more complete list of major achievements is provided in the following section.

-Single-phase forming ability of HEAs. One of the most cited paper of us is "Structural stability of NiCoFeCrAlx high-entropy alloy from ab initio theory" by F Tian, L Delczeg, N Chen, LK Varga, J Shen, L Vitos published in Physical Review B 88 (8), 085128 (2013). In this work, we used for the very first-time ab initio tools to study the phase selection rule in doped HEAs. The theoretical predictions demonstrated that the previously established phase limits are robust and show weak dependence on the base alloy composition. The above pioneering work has been cited 57 times. The other highly recognized work is "Empirical design of single phase high-entropy alloys with high hardness", Fuyang Tian Lajos K. Varga, Nanxian Chen, Jiang Shen, and Levente Vitos published in Intermetallics **58**, 1-6 (2015). This paper addresses the forming ability of single-phase HEAs predicting its maximum strength and confirmed the validity of the conjecture about strength (hardness) versus e/a correlation.

-Elastic properties of HEAs. The electronic structure and elastic properties of HEAs were studied for the first time by ab initio methods in "Ab initio investigation of high-entropy alloys of 3 d elements" by F Tian, LK Varga, N Chen, L Delczeg, L Vitos published in Physical Review B 87 (7), 075144 (2013). The above paper received 56 citation in the last few years. This pioneering work was followed by a series of publications, where the theoretical prediction of the elastic properties of various HEAs were contrasted with the available experimental values. In particular, we would like to highlight the recent publication "Calculating elastic constants in high-entropy alloys using the coherent potential approximation: Current issues and errors", by Fuyang Tian, Lajos K. Varga, Jiang Shen, and Levente Vitos, published in Computational Materials Science 111, 350358 (2016)), where we carefully scrutinized the scope of theoretical investigation of HEAs.

-HEA and magnetism. We used first-principles alloy theory and Monte-Carlo simulations to investigate the magnetic properties of HEAs. Results show that face-centered-cubic (fcc) and body-centered-cubic (bcc) structures possess significantly different magnetic behaviors uncovering that the alloy's Curie temperature is controlled by the stability of the alloying-induced single phase or fcc-bcc dual-phase. We show that the appearance of the bcc phase brings about the observed transition from the paramagnetic state to the ferromagnetic state for several HEAs (e.g., FeCrCoNiAl) at room-temperature. The great success of our pioneering work "Mechanism of magnetic transition in FeCrCoNi-based high entropy alloys" by Shuo Huang, Wei Li, Xiaoqing Li, Stephan Schonecker, Lars Bergqvist, Erik Holmstrom, Lajos Varga, and Levente Vitos, published in Materials & Design 103, 7174 (2016) led us to go on and establish the only database of magnetic phase diagrams of HEAs. The database is presented in a new manuscript ("Magnetic transition in equiatomic medium- and high-entropy alloys with solid solution phases" by Shuo Huang, Erik Holmström, Olle Eriksson, and Levente Vitos) which is under consideration (unpublished).

-**Plasticity of HEAs.** Twinning is the fundamental mechanism behind the increased strength and ductility in medium- and high-entropy alloys. The beneficial effect of twinning was recognized in commercial high-strength steels (see for instance our recent theoretical work on First-Principles prediction of the deformation modes in austenitic Fe-Cr-Ni alloys by Wei Li, Song Lu, Dongyoo Kim, Kalevi Kokko, Staffan Hertzman, Se Kyun Kwon, Levente Vitos, published in Applied Physics Letters 108, 081903 (2016).), but its presence in the new family of multi-component alloys is not yet comprehended, which limits their optimal exploitation. Since many high-entropy alloys showing outstanding mechanical properties are actually thermodynamically unstable at ambient and cryogenic conditions, the observed twinning challenges the existing phenomenological and theoretical plasticity models. We adopted a transparent approach based on first principles calculations to shed light on the origin of twinning in high-entropy alloys. First, we used our tools to establish the SFE in FeCrCoNiMn as a function of temperature and showed that this alloy goes through various deformation modes with increasing temperature. These results were published in "Temperature dependent Stacking Fault Energy of FeCrCoNiMn High Entropy Alloy" by Shuo Huang, Wei Li, Song Lu, Fuyang Tian, Jiang Shen, Nanxian Chen, Erik Holmstrom, and Levente Vitos, in Scripta Materialia 108, 44-47 (2015) and received more than 80 citations in only three years!

Next, using the effective energy barriers we demonstrated that twinning can be an active deformation mode in metastable face-centered cubic alloys with a fraction that surpasses the previously established upper limit. The small inherent affine shear strain prior to slip further promotes twinning in these alloys. Although decreasing temperature efficiently drives the system across various deformation modes, the particular chemistry is primarily responsible for the emergence of the exceptional twinning in metastable alloys. The advance in understanding the plasticity revealed new opportunities for tailoring the mechanical response in engineering materials involving high-entropy alloys. These new results are published in Nature Communications **9**, 2381 (2018).

Detailed research results within the project

Below we list several research achievements including both experimental and theoretical works, and which closely follow the research plan. For a more complete list, the reader is referred to the list of publications.

2013-2014
We used first-principles alloy theory to investigate the atomic-level properties of HEAs composed of 3d metals [Physical Review. B 87, 075144 (2013), Physical Review B 88, 085128 (2013).] and refractory elements [Journal of Alloys and Compounds 599, 19-25 (2014).]. Our study provided the first ab initio phase diagram for the 3d-HEAs doped with Al, and confirms the previously established experimental and estimated phase selection rules. Furthermore, we show that the face centered cubic solid solutions are typically highly anisotropic, whereas the body centered cubic solid solutions made of refractory elements turn completely isotropic when the valence electron concentration becomes 4.72.These findings illustrate how first-principles quantum theory combined with modern alloy theory can promote our understanding about the complex chemical and magnetic interactions in novel HEAs. Our results were highlighted at Advances in Engineering http://advanceseng.com/

Looking for light metal components a new high entropy (HEA) multicomponent alloy was

developed on Al-Ti base [Materials and Corrosion Volume 65, 691–695 (2014).]. The Al25Ti25Ga25Be25 alloy displays good mechanical strength (HV0,1= 490) and excellent corrosion resistance as compared to the Cu2CrFe2NiMn2 alloy and stainless steel 304 because it has a lower corrosion rate in 1M H2SO4 solutions at room temperature.

Two new refractory high-entropy alloys, Ti20Zr20Hf20Nb20V20 and Ti20Zr20Hf20Nb20Cr20, were produced by induction melting and casting [Int. Journal of Refractory Metals and Hard Materials 47, 131–138 (2014).]. Relatively low temperatures (900 ºC) and short time (10 min.) annealing produced no substantial phase precipitation in accordance with the XRD graphs, preserving the one-phase structure of V containing alloy. The mechanical properties (the Young's modulus E, yield stress, fracture strength, plastic strain) were determined by compression test and compared with the theoretical predictions based on ab initio calculations. The calculated large positive Cauchy pressure (c12–c14) suggests that these refractory HEAs have strong metallic character and enhanced ductility in accordance with experimental findings.

The activation of plastic deformation mechanisms determines the mechanical behavior of crystalline materials. However, the complexity of plastic deformation and the lack of a unified theory of plasticity have seriously limited the exploration of the full capacity of metals. Current efforts to design high-strength structural materials in terms of stacking fault energy have not significantly reduced the laborious trial and error works on basic deformation properties. To remedy this situation, we have recently put forward a comprehensive and transparent theory for plastic deformation of face-centered cubic metals [PNAS 111, 6560-6565 (2014).]. The new theory is based on a microscopic analysis that, without ambiguity, reveals the various deformation phenomena and elucidates the physical fundaments of the currently used phenomenological correlations. We have identified an easily accessible single parameter derived from the intrinsic energy barriers (IEBs), which fully specifies the potential diversity of metals. Based entirely on this parameter, a simple deformation mode diagram was shown to delineate a series of convenient design criteria, which clarifies a wide area of material functionality by texture control.

Using the ab initio exact muffin-tin orbitals method in combination with the coherent potential approximation, we calculated the γ surface for the disordered Cu–Al, Cu–Zn, Cu–Ga, Cu–Ni, Pd–Ag and Pd–Au alloys [Journal of Physics: Condensed Matter 26, 265005 (2014).]. Studying the effect of segregation of the solute to the stacking fault planes shows that only the local chemical composition affects the γ surface. Based on our γ surface results, we demonstrated that the previous revealed ‘universal scaling law’ between the intrinsic energy barriers (IEBs) is well obeyed in random solid solutions. This achievement greatly simplifies the calculations of the twinning measure parameters or the critical twinning stress. Adopting two twinability measure parameters derived from the IEBs, we find that in binary Cu alloys, Al, Zn and Ga increase the twinability, while Ni decreases it. Aluminum and gallium yield similar effects on the twinability.

Within the same failure mode, iron has the lowest ideal tensile strength among the transition metals crystallizing in the body-centered cubic structure. We have demonstrated that this anomalously low strength of Fe originates partly from magnetism and is reflected in unexpected alloying effects in dilute Fe-M (M = Al, V, Cr,Mn, Co, Ni) binaries [Physical Review B 90, 024201 (2014).]. We employed the structural energy difference and the magnetic pressure to disentangle the magnetic effect on the ideal tensile strength from the chemical effect. We found that the investigated solutes strongly alter the magnetic response of

the Fe host from the weak towards a stronger ferromagnetic behavior, which is explained based on single-particle band energies. Our achievements on binary disordered alloys opened new possibilities to study the ideal strength of bcc HEAs using modern computational alloys theory.

2014-2015:
During this year, two MSc theses were prepared and defended successfully. Both students were admitted to the PhD school of Eötvös Loránd University –Material Science Department.

The thesis of Molnár Dávid ("Investigation of the properties of high entropy alloys by ab initio calculations") focused on ab initio calculations of mechanical properties of single phase high-entropy alloys. In the theoretical part the principal points of the EMTO Program Package. The QNA density functional scheme was found more accurate than the PBE one. .First, as a practice, the theoretical method was applied for simple metallic elements which are the components of high entropy alloys. The equilibrium volume, bulk modulus and charge density have been calculated for a number of elements and compared with experimental values. Next, the same characteristics have been calculated for a number of single phase high entropy alloys and compared with experimental values. Since the experimental values are given at 300 K, they should be extrapolated to 0 K - an extrapolation method was employed. The relationship between the charge density and the bulk modulus and the shrinkage of the alloys compared to the ideal hard sphere structure are discussed in detail.

The thesis of Vida Ádám ("Preparation and investigation of high entropy alloys") deals with preparation and characterization of a number of high entropy alloys having at least four major elements in 5-35 at.% concentration range. These alloys are referred by the elements names arranged in decreasing order of their atomic number (e.g NiCoFeCrAl). The samples were prepared by induction melting in cold copper mould and homogenized by 5 times re-melting. Typical sample size and mass was ~ 7 cm length, 1.5 cm diameter and 25 g, respectively. The density was measured with a He pycnometer (AccuPic II 1340, USA). Vickers hardness was obtained using a dynamic hardness tester, (UMIS CSIRO, Australia) with 1 kg load. The mechanical characteristics (elastic, shear and bulk moduli, Poisson ratio) have been determined from longitudinal and transversal ultrasound propagation speed (Olympus 45 MG, Japan). These equipments have been purchased with the financial help of the present OTKA project. The phase and crystalline structures have been followed by scanning electron microscope (FEI Quanta 3D, USA) and x-ray diffraction (Bruker D8), respectively. Finally, we prepared micropillars from some HEAs and compressed them with the dynamic micro hardness tester, which is a novelty in the case of these types of alloys. We have observed some crucial points from the theory of the HEAs, namely the changes in crystalline structure according to the valence electron concentration (VEC), the cocktail effect, the correlation between the hardness and bulk modulus and the dendrite texture of some as-cast samples. We compared all of our results with theoretical predictions by Dávid Molnár and co-workers, based on ab initio calculations. Comparing the results, we got both negative and positive matches depending on HEA families.

Using ab initio alloy theory, we revealed [Scientific Report 5, 12334 (2015).] the alloying effect on the elastic properties and the ideal tensile strength (ITS) in the [001] direction of four body-centered cubic (bcc) refractory HEAs based on Zr, V, Ti, Nb, and Hf. We found that these HEAs show high elastic anisotropy and large positive Cauchy pressure, suggesting good extrinsic ductility. Starting from ZrNbHf, it is found that the ITS decreases with equimolar Ti addition. On the other hand, if both Ti and V are added to ZrNbHf, the ITS is

enhanced by about 42%. An even more captivating effect is the ITS increase by about 170%, if Ti and V are substituted for Hf. The alloying effect on the ITS was explained by the d-band filling. An intrinsic brittle-to-ductile transition was found in terms of the failure mode under uniaxial tension. These investigations suggest that intrinsically ductile HEAs with high ideal strength can be achieved by controlling the proportion of group four elements to group five elements.

It is well known that stacking fault energy (SFE) affects the propensity to form deformation twins, and low-SFE materials are more likely to deform by twinning, with increased strain hardening rate, dislocation storage capacity, and ductility. Due to the complexity of the problem related to the chemical and magnetic disorder present in many HEAs, so far no ab initio investigations of the SFE of the HEAs have been published. Using ab initio alloy theory, we put forward [Scripta Materialia 108, 44-47 (2015).] the first comprehensive investigation of the SFE of paramagnetic FeCrCoNiMn high entropy alloy. We divided the SFE into three major contributions: chemical, magnetic and strain parts. Structural energies, local magnetic moments and elastic moduli were used to estimate the effect of temperature on each term. Our results explain the recently reported twinning observed below room-temperature and predict the occurrence of the hexagonal phase at cryogenic conditions.

The AlxMoNbTiV (x = 0–1.5) high-entropy alloys (HEAs) adopt a single solid-solution phase, having the body centered cubic (bcc) crystal structure. We employed [J. Phys.: Condens. Matter 27, 075401 (2015).] the ab initio exact muffin-tin orbitals method in combination with the coherent potential approximation to investigate the equilibrium volume, elastic constants, and polycrystalline elastic moduli of AlxMoNbTiV HEAs. A comparison between the ab initio and experimental equilibrium volumes demonstrates the validity and accuracy of the present approach. Our results indicate that Al addition decreases the thermodynamic stability of the bcc structure with respect to face-centered cubic and hexagonal close packed lattices. For the elastically isotropic Al0.4MoNbTiV HEAs, the valence electron concentration (VEC) is about 4.82, which is slightly different from VEC ~ 4.72 obtained for the isotropic Gum metals and refractory HEAs.

We collected [Intermetallics 58, 1-6 (2015).] the available basic properties of nearly 100 high-entropy alloys (HEAs) with a single face centered cubic (fcc) or body centered cubic (bcc) phase. HEAs crystallizing in the fcc structure are mainly composed of the late 3d elements (LTM-HEAs), whereas HEAs consisting of the early (refractory) transition elements and the LTM-HEAs containing an increased level of bcc stabilizer form the bcc structure. Guided by the solid solution theory, we investigate the structure and hardness of HEAs as a function of the valence electron concentration (VEC) and the atomic size difference (d). The fcc structure is found for VEC between 7.80 and 9.50, whereas the structure is bcc for VEC between 4.33 and 7.55. High strength is obtained for an average valence electron number VEC ~ 6.80 and for an average atomic size difference d~6%. Based on these empirical correlations, one can design the high-entropy alloys with desired hardness.

First-principles alloy theory, formulated within the exact muffin-tin orbital method in combination with the coherent-potential approximation, was used [Physical Review B 91, 224203 (2015).] to study the mechanical properties of ferromagnetic body-centered cubic (bcc) Fe1−xMx alloys (M=Mn or Ni with less than 10% solute concentration). We considered several physical parameters accessible from ab initio calculations and their combinations in various phenomenological models to compare the effect of Mn and Ni on the properties of Fe. Alloying was found to slightly alter the lattice parameters and produce noticeable influence on

elastic moduli. Both Mn and Ni decrease the surface energy and the unstable stacking fault energy associated with the {110} surface facet and the {110}<111> slip system, respectively. Nickel was found to produce larger effect on the planar fault energies than Mn. The semi-empirical ductility criteria by Rice and Pugh consistently predict that Ni enhances the ductility of Fe but give contradictory results in the case of Mn doping. The origin of the discrepancy between the two criteria was discussed and an alternative measure of the ductile-brittle behavior based on the theoretical cleavage strength and single-crystal shear modulus G{110}<111> was proposed. These above pioneering studies were later extended to the case of refractory HEAs.

2015-2016:
In the third year the work was continued according to the project work plan. During this period of time, the two former master students (Dávid Molnár and Ádám Vida) have been admitted to the PhD school of Eötvös University – Department of Materials Physics, where they followed the first year program of the school and worked on their thesis within the present OTKA project. For as much they have got state scholarship, the amount of money in the 1.2.1 raw of the budget sheet (full time or part-time researcher employment) was given for another young researcher, Zsolt Maksa) who also worked for the present OTKA project.

Three high entropy alloys have been prepared by inductive melting and casting: Ni29.5Fe39.8Cr20Mo6W4.7, Ni38.33Fe36Cr13.88Mo6.66W5.15, TiZrHfFeVNb. The composition was carefully selected in order to avoid elements which will be radioactive after neutron irradiation. Unfortunately, the investigation of the irradiated samples had to be postponed due to the sample protocol of the Neutron Irradiation Department of Wigner RCP.

We have collected all the empirical design criteria for single - phase high entropy alloys based on the tabulated data of the elements and small software helps using it in predicting the properties of a new composition.

The equimolar NiCoFeCr is an FCC type single-phase HEA. Four sp elements were added in equimolar ratios: NiCoFeCrAl, NiCoFeCrGa, NiCoFeCrGe and NiCoFeCrSn. The initially non-magnetic and single-phase structure turned into multiphase magnetic alloy. Investigations done using first-principles calculations and key experimental measurements revealed that the equimolar FeCrCoNiGe system is decomposed into a mixture of face-centered cubic and body-centered cubic solid solution phases. The increased stability of the ferromagnetic order in the as-cast FeCrCoNiGe composite, with measured Curie temperature of 640 K, is explained using the exchange interactions. (Huang, S., Vida, Á., Molnár, D., Kádas, K., Varga, L. K., Holmström, E., & Vitos, L. (2015). Phase stability and magnetic behavior of FeCrCoNiGe high-entropy alloy. Applied Physics Letters, 107(25), 251906.)

Continuing the structural investigations of the four sp element doped HEA's X-ray diffraction combined with scanning electron microscopy SEM measurements were performed. The nanoindentation test revealed a 'fingerprint" of the two-phase structure. The Young's and shear moduli of the investigated HEAs were also determined using ultrasound methods. The correlation between these two moduli suggests a general relationship for metallic alloys (Vida, A., Varga, L. K., Chinh, N. Q., Molnar, D., Huang, S., & Vitos, L. (2016). Effects of the sp element additions on the microstructure and mechanical properties of NiCoFeCr based high entropy alloys. Materials Science and Engineering: A, 669, 14-19.)

The correlation between the strength, ductility and phase structures of two new NiFeCrMoW type alloys was investigated. The ductile or brittle behavior is strongly influenced by the volume fraction of FCC and BCC phases. This allows for optimizing the combination of strength and ductility by varying the alloy composition. (A. Vida, Nguyen Q. Chinh, J. Lendvai, A Hetzel, L.K. Varga, "Microstructure and transition from brittle to ductile behavior of NiFeCrMoW high entropy alloy", submitted)

Three new alloys Al25Ti25Ni25Cu25, Al22.5Ti22.5Ni20Cu20Fe15 and Al20Ti20Ni20Cu20Fe20 were produced by induction-melting and casting. Only a simple FCC phase was observed for the Al25Ti25Ni25Cu25 alloy after annealing at 573, 773, 973 and 1173 K. FCC1 and FCC2 solid solutions structures appear in the as-cast and as-annealed Al22.5Ti22.5Ni20Cu20Fe15 and Al20Ti20Ni20Cu20Fe20 alloys. Elemental segregation can be observed with the dendrite region enriched in Al, Ti and Ni while the interdendrite region is enriched in Cu and Fe. This kind of alloys exhibits high resistance to annealing softening, similar to the CoCrFeNiTiAlx high entropy alloys, but are less expensive. (É. Fazakas, V. Zadorozhnyy, D.V. Louzguine-Luzgin, "Effect of iron content on the structure and mechanical properties of Al25Ti25Ni25Cu25 and (AlTi)60-xNi20Cu20Fex (x=15, 20) high-entropy alloys", Applied Surface Science 358 (2015) 549–555)

Five new alloys have been prepared from high purity (99.99%) elements by induction melting under inert atmosphere: Ni24Co24Fe24Cr8.7Al18Zr1B0.3 and Ni34.43Co16.39Fe16.39Cr16.39Al16.39 Ni55Fe5Cr22Mo5Nb5Al8 and Ni24Co24Fe24Al18Cr10 and Ni25Fe25Mn15Cr10Nb5Ti5Al15. The aim of the selection is to replace the toxic Co powder, and find HEAs with similar properties. The as cast HEA samples were ball milled and a composite was prepared from 20 wt% HEA + 80 wt% NbC. mixed by further ball milling. The "green" cylindrical sample (Φ = 8 mm, H = 5 mm) was prepared by compaction under 10 T. The sintering temperature was near the melting point of the HEA (binder) 1400 oC for 120 min. The obtained 1000 HV (at 0.3 kg) is promising and further investigations of the structure and properties are in progress.

We used first-principles alloy theory and Monte-Carlo simulations to investigate the magnetic properties of FeCrCoNiAlx high entropy alloys. Results show that face-centered-cubic (fcc) and body-centered-cubic (bcc) structures possess significantly different magnetic behaviors uncovering that the alloy's Curie temperature is controlled by the stability of the Al-induced single phase or fcc-bcc dual-phase. We show that the appearance of the bcc phase with increasing Al content brings about the observed transition from the paramagnetic state for FeCrCoNi to the ferromagnetic state for FeCrCoNiAl at room-temperature. Similar mechanism is predicted to give rise to room-temperature ferromagnetism in FeCrCoNiGa high entropy alloy. (Shuo Huang, Wei Li, Xiaoqing Li, Stephan Schonecker, Lars Bergqvist, Erik Holmstrom, Lajos Varga, and Levente Vitos Mechanism of magnetic transition in FeCrCoNi-based high entropy alloys, Materials & Design 103, 7174 (2016)).

HEAs present a great challenge for conventional ab initio calculations and the few available theoretical predictions involve a large degree of uncertainty. An often adopted theoretical tool to study HEAs from first-principles is based on the exact muffin-tin orbitals (EMTO) method in combination with the coherent potentials approximation (CPA), which can handle both chemical and magnetic disorders. Here we assess the performance of EMTO-CPA method in describing the elastic properties of HEAs based on Co, Cr, Fe, Mn, and Ni. We carefully scrutinize the effect of numerical parameters and the impact of various magnetic states on the calculated properties. The theoretical results for the elastic moduli are compared to the

available experimental values. (Fuyang Tian, Lajos K. Varga, Jiang Shen, and Levente Vitos, calculating elastic constants in high-entropy alloys using the coherent potential approximation: Current issues and errors, Computational Materials Science 111, 350358 (2016)).

First-principles alloy theory was used to establish the c-surface of Fe-Cr-Ni alloys as function of chemical composition and temperature. The theoretical stacking fault energy (SFE) versus chemistry and temperature trends agree well with experiments. Combining our results with the recent plasticity theory based on the c-surface, the stacking fault formation is predicted to be the leading deformation mechanism for alloys with effective stacking fault energy below 18 mJ/m2. Alloys with SFE above this critical value show both twinning and full slip at room temperature. Interestingly, twinning remains a possible deformation mode in addition to full slip even at elevated temperatures, in line with observations. (Wei Li, Song Lu, Dongyoo Kim, Kalevi Kokko, Staffan Hertzman, Se Kyun Kwon, Levente Vitos, First-Principles prediction of the deformation modes in austenitic Fe-Cr-Ni alloys, Applied Physics Letters 108, 081903 (2016).)

2016-2017:

Together with our colleagues, we have prepared a book chapter entitled “Applications of Coherent Potential Approximation to HEAs” by Fuyang Tian, Yang Wang, Douglas L. Irving, and Levente Vitos in High-Entropy Alloys: Fundamentals and Applications, Edited by Michael C. Gao, Jien-Wei Yeh, Peter K. Liaw, Yong Zhang Springer (2016). The chapter details the coherent potential approximation (CPA) to describe the chemically and magnetically disordered phases for systems of arbitrary number of components. Two widely used CPA implementations, namely the exact muffin-tin orbitals (EMTO) and the Korringa Kohn Rostoker (KKR) methods were reviewed. Applications to predict lattice stability, electronic and magnetic structure, elasticity properties and stacking fault energies of single-phase HEAs were presented.

First-principle alloy theory and key experimental techniques were applied to determine the thermal expansion of FeCrCoNiGa high-entropy alloy. The magnetic transition, observed at 649 K, is accompanied by a significant increase in the thermal expansion coefficient. The phase stability is analyzed as a function of temperature via the calculated free energies accounting for the structural, magnetic, electronic, vibrational and configurational contributions. The single- and polycrystal elastic modulus for the ferro- and paramagnetic states of the face-centered and body-centered cubic phases are presented. By combining the measured and theoretically predicted temperature-dependent lattice parameters, we reveal the structural and magnetic origin of the observed anomalous thermal expansion behavior. The results are now published in “Thermal expansion in FeCrCoNiGa high-entropy alloy from theory and experiment” by Shuo Huang, Ádám Vida, Wei Li, Dávid Molnár, Se Kyun Kwon, Erik Holmström, Béla Varga, Lajos Károly Varga, and Levente Vitos, in Appl. Phys. Lett. 110, 241902 (2017).

The severe local lattice distortion, induced mainly by the large atomic size mismatch of the alloy components, is one of the four core effects responsible for the unprecedented mechanical behaviors of high-entropy alloys (HEAs). We proposed a supercell model, in which every lattice site has similar local atomic environment, to describe the random distributions of the atomic species in HEAs. Using these supercells in combination with *ab initio* calculations, we investigated the local lattice distortion of refractory HEAs with body-

centered-cubic structure and 3*d* HEAs with face-centered-cubic structure. Our results demonstrated that the local lattice distortion of the refractory HEAs is much more significant than that of the 3*d* HEAs. We showed that the atomic size mismatch evaluated with the empirical atomic radii is not accurate enough to describe the local lattice distortion. Both the lattice distortion energy and the mixing entropy contribute significantly to the thermodynamic stability of HEAs. However, the local lattice distortion has negligible effect on the equilibrium lattice parameter and bulk modulus. The results are now published in "Local lattice distortion in high-entropy alloys" Hongquan Song, Fuyang Tian, Qing-Miao Hu, Levente Vitos, Yangdong Wang, Jiang Shen, Nanxian Chen Physical Review Materials 1, 023404 (2017).

Using ab initio alloy theory, we investigated the lattice stability of paramagnetic AlxCrMnFeCoNi (x between ö and 5) high-entropy alloys considering the competing body-centered cubic (bcc) and face-centered cubic (fcc) crystal structures. The theoretical lattice constants increase with increasing x, in good agreement with experimental data. Upon Al addition, the crystal structure changes from fcc to bcc with a broad two-phase field region, in line with observations. The magnetic transition temperature for the bcc structure strongly decreases with x, whereas that for the fcc structure shows weak composition dependence. Within their own stability fields, both structures are predicted to be paramagnetic at ambient conditions. Bain path calculations support that within the duplex region both phases are dynamically stable. As compared to AlxCrFeCoNi, equiatomic Mn addition is found to shrink the stability range of the fcc phase and delay the appearance of the bcc phase in terms of Al content, thus favoring the duplex region in 3d-metals based high-entropy alloys. The results are published in "Phase selection rule for Al-doped CrMnFeCoNi high-entropy alloys from first-principles" Xun Sun, Hualei Zhang, Song Lu, Yunzhi Wang, and Levente Vitos, Acta Materialia 140, 366-374 (2017).

We used the Hume-Rothery rules and ab initio mixing enthalpies to design novel high entropy alloys composed of late 3d metal (Mn, Fe, Co, Ni, Cu) and CrMoW. Results predict that CrMoW, CrMoWMn, CrMoWCo and CrMoWNi adopt single body-centered cubic (bcc) crystal structure. The ab initio calculations of elastic moduli and ideal strengths indicate that the bcc phase is more stable thermodynamically than the face-centered cubic (fcc) crystal structure for CrMoW, CrMoWMn, CrMoWNi HEAs, but the late 3d elements decreases the mechanical stability of the bcc phase. In particular Ni addition increases the intrinsic ductility and decreases the intrinsic strength of CrMoW alloy. The results are published in "Predicting single phase CrMoWX high entropy alloys from empirical relations in combination with first-principles calculations" Fuyang Tian, Lajos Károly Varga, and Levente Vitos, Intermetallics 83, 9-16 (2017).

Ab initio total energy calculations were used to determine the elastic properties of TiZrVNb, TiZrNbMo and TiZrVNbMo high-entropy alloys in the body centered cubic (bcc) crystallographic phase. Calculations were performed using the Vienna Ab initio Simulation Package and the Exact Muffin-Tin Orbitals methods, and the compositional disorder is treated within the frameworks of the special quasi-random structures technique and the coherent potential approximation, respectively. Special emphasis is given to the effect of local lattice distortion and trends against composition. Significant distortion can be observed in the relaxed cells, which result in an overlap of the first and second nearest neighbor (NN) shells represented in the histograms. When going from the four-component alloys TiZrVNb and TiZrNbMo to the five-component TiZrVNbMo, the changes in the elastic parameters follow the expected trends, except that of *C*44 which decreases upon adding equiatomic Mo to

TiZrVNb despite of the large shear elastic constant of elemental Mo. Although the rule of mixtures turns out to be a useful tool to estimate the elastic properties of the present HEAs, to capture the more delicate alloying effects one needs to resort to *ab initio* results. Results published in "Alloying effect on the elastic properties of refractory high-entropy alloys" Li-Yun Tian, Gui-Sheng Wang, Joshua S. Harris, Douglas L. Irving, Ji-Jun Zhao, Levente Vitos, Materials & Design 114, 243-252 (2017).

The effects of V, Cr and Mn on the magnetic, elastic and thermal properties of FeCoNiCu high-entropy alloy were studied by using the exact muffin-tin orbitals method in combination with the coherent potential approximation. The calculated lattice parameters and Curie temperatures in the face-centered cubic structure are in line with the available experimental and theoretical data. A significant change in the magnetic behavior is revealed when adding equimolar V, Cr and Mn to the host composition. The three independent single crystal elastic constants are computed using a finite strain technique, and the polycrystalline elasticity parameters including shear modulus, Young's modulus, Pugh ratio, Poisson's ratio and elastic anisotropy are derived and discussed. The effects of temperature on the structural parameters are determined by making use of the Debye-Grüneisen model. It was found that FeCoNiCuCr possesses slightly larger thermal expansion coefficient than the other alloys considered here. These results are published in "Thermal Expansion, Elastic and Magnetic Properties of FeCoNiCu-Based High-Entropy Alloys Using First-Principle Theory, Shuo Huang, Ádám Vida, Anita Heczel, Erik Holmström, and Levente Vitos, JOM, The Journal of The Minerals, Metals & Materials Society (TMS) **9**, 2107-2112 (2017).

2017-2018:

Recently we published a book on the theoretical description of high entropy alloys. The book collects our joint efforts to understand and model from quantum theory the fundamental properties of a series of complex alloys. The book is available at "Theoretical design of single phase high-entropy alloys" Fuyang Tian, Lajos Karoly Varga, and Levente Vitos, ISBN: 978-3- 330-08506-0, LAP Lambert Academic Publishing (2017).

The postponed three entropy alloys ($Ni_{29.5}Fe_{39.8}Cr_{20}Mo_6W_{4.7}$, $Ni_{38.33}Fe_{36}Cr_{13.88}Mo_{6.66}W_{5.15}$, TiZrHfFeVNb), which were carefully selected for neutron irradiation were irradiated in the Neutron Irradiation Department of Wigner RCP. These samples are now waiting their compulsory rest in order to pass the possible activation, further measurements will be applied after the rest.

The PhD Thesis of Ádám Vida was submitted for consideration at Eötvös University in the beginning of June.
The thesis is concentrated to multiphase HEAs, which means that all the results presented there, are meant to multiphase systems. The chronological order of progression and the results are shown through the published papers in this topic.
On the first step, the most important and most famous HEA is presented, which consists of Ni, Co, Fe and Cr elements. This one crystallizes in Face Centered Cubic (FCC) lattice and it is solid solution with paramagnetic properties.
The doping effect of *sp* element on this d system were studied. Based on the results, more alloys were prepared, where Al, Ga, Ge and Sn doping were followed. The single-phase alloy became multiphase when doping and the second phase is Body Centered Cubic (BCC) with ferromagnetic properties. This result was in accordance with a generally accepted core effect called cocktail effect. Furthermore, it is shown that the phase separation is not only the

function of the so-called Valence Electron Concentration (VEC), but it depends much also on enthalpies of mixing.
In the next sections the investigation of the individual alloys of this family were started. First, we have explained the magnetic nature of the new born BCC phase of NiCoFeCrGe.
In the case of Ga containing sample, the magnetic behavior of this alloy has also been explained, so the anomalous thermal expansion.
During targeted heat treatments it has been shown that the as-cast state has to be considered as metastable. Based on the results, the phase ratios and morphologies can be varied, and nano scale chemical inhomogeneities can be created with different heat treatments and different cooling speeds.
The results also suggest that the system chooses the easiest way to crystallize, not the lowest energy state and it remains in metastable state at ambient conditions. Both chemical and structural metastable behavior were identified during this research. In conclusion, one can conclude that the cooling speeds, applied at different castings, are rapid enough for these types of HEAs to regard them quick cooled.
In the last part, a different family is presented, which was created in hope of capability for high temperature applications. One can find Ni, Fe, Cr, Mo and W elements with varying concentration in the two alloys. First, equimolar one, was designed for maximal entropy and the second, non-equimolar was designed for maximal solubility based only on knowledge achievable from binary phase diagrams. After casting three phases can be observed in equimolar and two phases in the non-equimolar compositions. These results were in good accordance with the theoretical predictions. Micropillars were made on the samples by focused ion beam and then compressed with nanoindentation, while recording the stress-strain data. Through these results we have shown that by varying the nominal composition the phase structure and morphology - thus the mechanical properties can be tuned significantly.

The non-equilibrium nature of a two-phase NiCoFeCrGa high entropy alloy (HEA) was studied by analyzing its microstructures after different heat-treatment conditions. The microstructure - containing a mixture of well-separated FCC and BCC regions – of the as-cast alloy has changed strongly by heat-treatment for 1 h at 1150 K, significantly changing the ratio of the volume fraction of the FCC and BCC phases. The microstructure - containing a mixture of well-separated FCC and BCC regions of the as-cast alloy has changed significantly by heat-treatment for 1 h at 1150 K. Needle like BCC phase particles evolved inside the original FCC regions when cooling the heat-treated samples to room temperature by rapid or medium rates. The chemical composition of the BCC needles is the same than that of the original BCC regions in the alloy.
Further, in the case of slow cooling, at around the Curie-point, all of the BCC regions decomposed into a mixture of BCC matrix and cube- like BCC phase precipitates, indicating that the transition between para- and ferromagnetism may have significant role on the microstructure evolution of the high entropy NiCoFeCrGa alloys.
In summary, there is an unambiguous correlation between the cooling rate and the microstructure of the heat-treated alloy. Thus, such type of HEAs shows great potential on tuning both mechanical and magnetic properties by different annealing conditions. These results were presented as *Evolution of the phase structure after different heat treatments in NiCoFeCrGa high entropy alloy* by Vida Á., Maksa, Zs., Molnár, D., Huang, S., Kovac, J., Varga, L. K., L Vitos & Chinh, N. Q. in *Journal of Alloys and Compounds*, *743*, 234-239. (2018)

The Ni-Co-Fe-Cr based, “stainless steel” like HEA alloy composition was further extended towards the Al and Ti doping, expecting an oxidation resistant high temperature and high

strength alloy. The valence electron concentration (VEC) was chosen just below 8 selecting the following non equimolar concentrations $Ni_{34}Co_{25}Fe_{15}Cr_8Al_{10}Ti_6$ (VEC= 7,87). After adequate heat treatment a two-phase structure is obtained which confer both toughness and hardness to the material beside to the oxidation resistance. The alloy is still under investigation.

The elastic parameters and ideal tensile strength in the [001] direction for the body-centered cubic solid solution phase of $FeCrCoMnAl_x$ ($0.6 \leq x \leq 1.5$) high-entropy alloys are determined using first-principle alloy theory. Based on the estimated theoretical Curie temperatures, all alloys considered here are predicted to order ferromagnetically at room temperature. The mechanical behaviors are analyzed through the single crystal and polycrystalline elastic moduli, Pugh ratio, and Debye temperature by making use of a series of phenomenological models. High ideal tensile strength is found for the equi-atomic FeCrCoMnAl system, and the intrinsic strength increases with decreasing Al content. The results are collected in "Mechanical performance of FeCrCoMnAl*x* high-entropy alloys from first-principle" by Shuo Huang, Xiaoqing Li, He Huang, Erik Holmström, and Levente Vitos, Materials Chemistry and Physics **210**, 37-42(2018).

Alloys with adjustable mechanical performance are of fundamental interest in materials design. We investigated the magnetic and chemical ordering behavior of ferromagnetic $FeCrCoNiAl_x$ ($1 \leq x \leq 2.5$) high-entropy alloys with the help of first-principle alloy theory. The lattice constants, and the single- and polycrystalline elastic parameters for partially ordered and random structures are considered. In contrast to the trend found for the completely disordered phase, we demonstrate that Al-induced ordering results in an enhanced Young's modulus, especially at high Al concentrations, which brings about the observed increase of the hardness for systems with body-centered cubic underlying lattice. The results suggest that metals with outstanding strength and ductility can be design by a proper control of the ordering level in single- and multiphase high-entropy alloys. These results are now collected in a new manuscript "Magneto-chemical transition induced strengthening in Al-doped FeCrCoNi high-entropy alloys" Shuo Huang, Wei Li, Erik Holmström, and Levente Vitos which is under consideration (unpublished).

Tailorable magnetic state near room temperature is very promising for several technological, including magnetocaloric applications. Using first-principle theory, we focud on the Curie temperature (T_C) of a number of equiatomic medium- and high-entropy alloys. All calculations were performed at the computed lattice parameters, which are in line with the available experimental data. Theory predicts a large crystal structure effect on T_C, which explains the experimental observations under specified conditions. The analysis of alloying additions on T_C allows us to explore composition-dependent trends with adjustable magnetic properties. These results are now published in "Mapping the magnetic transition in equiatomic medium- and high-entropy alloys with solid solution phases" Shuo Huang, Erik Holmström, Olle Eriksson and Levente Vitos, Intermetallics **95**, 80-84 (2018).

The CrCoNi-based medium and high entropy alloys (MHEAs) have drawn much attention due to their exceptional mechanical properties at cryogenic temperatures. The twinning critical resolved shear stress (CRSS) is a fundamental parameter for evaluating the strength-ductility properties of MHEAs. We constructed and applied an extending twinning nucleation Peierls-Nabarro (P-N) model to predict the twinning CRSSes of face-centered cubic (FCC) CrCoNi-based MHEAs. The order of the twinning CRSSes of the selected alloys is CrCoNi>CrCoNiMn>CrCoNiFe>CrCoNiFeMn and the values are 291, 277, 274 and 236

MPa, respectively. These theoretical predictions agree very well with the experimental twinning CRSSes of CrCoNi and CrCoNiFe accounting for 290±30 and 235±10 MPa, respectively and are perfectly consistent with the strength-ductility properties including yield stress, ultimate tensile stress and uniform elongation for fracture of the FCC CrCoNi-based MHEAs obtained at cryogenic temperatures. The presented method offers a first-principle quantum-mechanical tool for optimizing and designing new MHEAs with exceptional mechanical properties. The results are published in "Critical stress for twinning nucleation in CrCoNi-based medium and high entropy alloys" He Huang, Xiaoqing Li, Zhihua Dong, Wei Li, Shuo Huang, Daqiao Meng, Xinchun Lai, Tianwei Liu, Shengfa Zhu, and Levente Vitos Acta Materialia **149**, 388-396 (2018).

Twinning is the fundamental mechanism behind the increased strength and ductility in medium- and high-entropy alloys. The beneficial effect of twinning was recognized in commercial high-strength steels, but its presence in the new family of multi-component alloys is not yet comprehended, which limits their optimal exploitation. Since many high-entropy alloys showing outstanding mechanical properties are actually thermodynamically unstable at ambient and cryogenic conditions, the observed twinning challenges the existing phenomenological and theoretical plasticity models. We adopted a transparent approach based on effective energy barriers in combination with first principles calculations to shed light on the origin of twinning in high-entropy alloys. We demonstrate that twinning can be an active deformation mode in metastable face-centered cubic alloys with a fraction that surpasses the previously established upper limit. Our advance in understanding the plasticity reveals new opportunities for tailoring the mechanical response in engineering materials involving high-entropy alloys. The results are presented in "Twinning in metastable high-entropy alloys beyond the limit" by Shuo Huang, He Huang, Wei Li, Dongyoo Kim, Song Lu, Xiaoqing Li, Erik Holmström, Se Kyun Kwon and Levente Vitos, Nature Communications **9**, 2381 (2018).

A tungsten carbide based hard metal cemented with a high entropy alloy was studied. The material consist of WC, cubic carbides (Ti,Ta,Nb)(C,N), and a CoCrFeNi alloy binder phase. The hard metal is pressed in a standard cutting tool geometry, sintered to have a 25μm binder phase enriched surface zone that is free from cubic carbides, and coated with protective layers of Ti(C.N) and Al2O3. The resulting cutting insert was tested in a machining operation and compared to an equivalent reference that has Co as binder phase. The cutting tool with high entropy binder had a very high resistance to plastic deformation that did not change with cutting speed in the machining test whereas the reference insert showed a linear increase in edge depression when the cutting speed was increased. The results are presented as "High entropy alloys: Substituting for cobalt in cutting edge technology. *Applied Materials Today, 12*, 322-329." by Erik Holmström, Raquel Lizarraga, David Linder, Armin Salmasi, Wei Wang, Huahai Mao, Henrik Larsson, and Levente Vitos. (2018).