Final Project Report OTKA No. K 128229, (2018.09.01-2023.08.31)

Abstract

The target of the project was to design, develop and optimize two functional High Entropy Materials (HEMs) for magnetocaloric and high temperature thermoelectric materials. Since its discovery in 2004, this new class of alloys seems to promise a low-cost solution for many applications where high strength combines with good ductility and where rich functional properties are required. The selection of multicomponent and multi-phase HEMs has been made using ab initio theoretical calculations. We prepared several HEMs using experimental facilities, and characterized them with respect to the structural, chemical, magnetic and thermal properties in the Wigner laboratories and also at our partners. In particular, we studied the ferro-paramagnetic and structural transition and the thermopower of HEMs, which are the material parameters necessary for designing the above mentioned two applications. During the five-year project, we investigated a large number of magnetic HEMs and proposed alloy solutions for further investigations for scaling up.

Introduction

The performed research is based on the synergy of first-principles quantum mechanical calculations by the principal investigator and the experimental investigations of the participant researchers at the Wigner Research Centre for Physics (WRCP) and Eötvös University (ELTE). The electronic structure calculations carried out in the last ten years on multicomponent, high-entropy materials (HEMs) based on a properly chosen average crystalline structure has now been extended towards two application-oriented properties: 1. magnetocaloric effect (MCE) and 2. thermoelectric effect (TEE).

HEMs are multicomponent alloys (containing at least 5 elements), where the configurational entropy is maximized by equiatomic concentrations, leading to an extension of solid solubility and to the formation of single-phase or two-phase simple structures (BCC, FCC and HCP). Compared to metallic glasses, actually both are chemically disordered structures with high strength but the advantage of HEMs is their good ductility due to the appropriate crystalline structure whereas bulk metallic glasses are inherently brittle due to their amorphous structure which show both chemical and topological disordering. Thus, HEMs are low-cost structural materials, combining high strength and good plasticity, and the Cr- and Al-containing HEM alloys show excellent corrosion resistance. The extension of solid solubility can be understood by considering the free energy $\Delta G = \Delta H - T\Delta S$, where both terms are usually negative. As a rule of thumb, an amorphous structure (or an intermetallic phase) forms when ΔH is large and a high-entropy alloy forms when $T\Delta S$ dominates. In general, the enthalpy of mixing and the atomic-size mismatch should be smaller than -15 kJ/mole and 10 %, respectively, for the formation of HEMs. The conditions for the formation of single-phase HEMs were amply studied in our papers published prior to the present project.

In the last four decades, the WRCP laboratory successfully studied amorphous and nanocrystalline alloys. Within this project, we turned to exploit these experiences to the study the functionality of HEMs. From the vast possibilities, we have selected two accessible functions of HEMs, promising both for theoretical and experimental investigations, namely designing HEMs (i) with good MCE characteristics and (ii) with promising thermoelectric

properties. The first group of HEMs are supposed to be used as rare-earth-free magnetocaloric materials, while the second group of HEMs can be applied in high-temperature thermoelectric generators (HT-TEG). These theory-based exploratory research activities aimed at unresolved problems and questions. The facilities for the preparation of these alloys and the majority of the equipments needed for studying their structure and relevant properties are available in the WRCP and/or ELTE laboratories. With the resources provided by our three previous OTKA grants (034666, 72451 and 109570), we have modernized some of the preparation facilities.

Concerning the *ab initio* quantum mechanical calculations, we have demonstrated over the last 15 years the applicability of density functional theory (DFT) to chemically and magnetically disordered alloys. This was possible because we put forward a basically new implementation of the coherent potential approximation within the framework of the exact muffin tin orbitals (EMTO) theory. This new tool makes it possible to extend the accurate DFT calculations from ordered structures to the case of concentrated random alloys and treat multicomponent systems having chemical and magnetic disorder on any kind of underlying crystal lattice.

The main objective was to accumulate critical knowledge of selected HEMs with potential applications in high-technology designs based on MCE and TEE. This goal has been reached by integrating first-principles atomic-level quantum mechanical modeling of complex alloys and compounds with world-leading theoretical and experimental expertise on MCE, TEE and HEMs. Novel HEMs has been produced by casting via induction melting, melt-spinning and mechanical alloying.

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

2018-2019:

Our primary goal is to assess the performance of our theoretical method based on ab initio density functional theory for the calculation of functional properties of HEAs, like ferro-paramagnetic and structural transitions and estimation of thermoelectric power. We employ the exact muffin-tin orbitals (EMTO) method in combination with the coherent potential approximation (CPA) and investigate a few selected HEAs based on 3d, 4d and 5d transition metals.

-Preparation by induction melting and vacuum casting of novel PdxCoCrFeNiPd and AlxCoCrFeNi alloys where the properties are tuned by Pd and Al concentrations.

-Preparation by mechanical alloying " n" type Mg(Be, Ca,Al, Bi)2Si and "p" type Mn(Fe,Cr, Co) Si1.75 metal silicides samples for high temperature thermopower couple.

- Preparation of foamed HEA by yeast method and development of home- made apparatus for thermal conductivity measurement of the cellular HEA.

2019-2020:

The first results of ab initio calculations will be published on MCE and some of the predictions will be tested experimentally. The electrical transport properties, (resistivity and thermopower) together with the thermal conductivity will be measured as a function of temperature.

The figure of merit of the cellular solid sample will be calculated from the measured data. 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.

2020-2021:

The results of MCE experiments will be summarized in a patent application. Investigation of the resistance against oxidation of high temperature foamed HEA used for thermoelectric generator. The results on the model thermoelectric generator will be summarized in an application for protection of industrial designs. These applications must precede the publications in scientific journals. The results on ferro-paramagnetic and structural transitions will be published in scientific journals.

2021-2022:

The theoretical and experimental results obtained on functionalizing HEA alloys will be published in a review article. A student will defend his master thesis on MCE of high entropy alloys and the new PhD student who will be hired on the expenses of present project will present his thesis on foamed HEA based thermoelectric generator. The output of the project from theoretical point of view will be the design and estimation of two functional properties of the HEAs and from experimental point of view, two tested compositions and preparation technologies will be proposed for large-scale production in MCE and TEG applications.

2022-2023:

Since the project was originally planned for 4 years (2018-2022), our research for the fifth year focused on finishing several subproject and working on questions and problems which directly emerged from the research during the first four years.

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.

Regarding to the initial work plan, we have completed both the theoretical and experimental tasks for the study of magnetic HEMs. Wherever it was possible, we closely coordinated the theoretical works with the experimental efforts. Below we highlight a few key research areas studied by us using ab initio modeling, experimental or joint investigations.

-Magnetocaloric effect in HEMs. We have explored the magnetocaloric application for a series of $Mn_xCr_{0.3}Fe_{0.5}Co_{0.2}Ni_{0.5}Al_{0.3}$ (0.8 < x < 1.1) HEAs by integrated theoretical and experimental methods. Both theory and experiment indicate that the designed HEAs have Curie temperatures close to room temperature and are tunable with Mn concentration. A non-monotonic evolution is observed for both the entropy change and the relative cooling power with changing Mn concentration. The underlying atomic mechanism is found to primarily emerge from the complex impact of Mn on magnetism. We conclude that promising magnetocaloric properties can be achieved by tuning the Mn concentration in combination

with controlling structural phase stability (*MnxCr0.3Fe0.5Co0.2Ni0.5Al0.3 high entropy alloys for magnetocaloric refrigeration near room temperature*, Z. Dong, S. Huang, V. Ström, G. Chai, L. K. Varga, O. Eriksson, L. Vitos, Journal of Materials Science & Technology **79**, 15-20 (2021)).

We performed ab initio electronic structure calculations of the phase stability and magnetic transition temperature of AlxCr0.25MnFeCo0.25-yNiy (x=0-0.5, y=0-0.25) alloys to screen for compositions showing promising magnetocaloric properties in the vicinity of room temperature. The selected Al0.44Cr0.25MnFeCo0.05Ni0.2 alloy was synthesized via a rapid solidification technique and systematically characterized with respect to its structural and magnetocaloric properties. The results indicate that this alloy possesses a homogeneous microstructure based on an underlying body-centered cubic lattice and has a Curie temperature of 340 K. The temperature dependence of the adiabatic temperature change was evaluated using both direct and indirect methods. The ab initio-assisted design of 3d-metal-based high-entropy alloys is intended to contribute to the development of magnetic refrigerators for room-temperature applications (*Magnetocaloric properties of melt-spun MnFe-rich high-entropy alloy*, S. Huang, Z. Dong, W. Mu, V. Strom, G. Chai, L. K. Varga, O. Eriksson, and L. Vitos, Appl. Phys. Lett. **119**, 141909 (2021)).

We investigated how the V content in a series of A150Vx(Cr0.33Mn0.33Co0.33)(50-x) (x = 12.5, 6.5, 3.5, and 0.5 at.%) high-entropy alloys affects the local magnetic moment and magnetic transition temperature as a step towards developing high-entropy functional materials for magnetic refrigeration. This has been achieved by carrying out experimental investigations on induction melted alloys and comparison to *ab initio* and thermodynamic calculations. Structural characterization by x-ray diffraction and scanning electron microscopy indicates a dual-phase microstructure containing a disordered body-centered cubic (BCC) phase and a B2 phase with long-range order, which significantly differ in the Co and V contents. Ab initio calculations demonstrate a weaker magnetization and lower magnetic transition temperature (TC) of the BCC phase in comparison with the B2 phase. We find that lower V content increases the B2 phase fraction, the saturation magnetization, and the Curie point, in line with the calculations. This trend is primarily connected with the preferential partition of V in the BCC phase, which however hinders the theoretically predicted antiferromagnetic B2 phase stabilizing effect of V. On the other hand, the chemistry-dependent properties of the ferromagnetic B2 phase suggest that a careful tuning of the composition and phase fractions can open the way towards promising high-entropy magnetic materials (On the structural and magnetic properties of Al-rich high entropy alloys: a joint experimental-theoretical study, E. Dastanpour, S. Huang, S. Schonecker, H. Mao, V. Strom, O. Eriksson, L. K. Varga and L. Vitos, J.Phys. D: Appl. Phys. 56 015003 (2023)).

-Spin fluctuation in paramagnetic HEMs. High entropy alloys (HEAs) based on 3d transition metals display rich and promising magnetic characteristics for various high-technology applications. Understanding their behavior at finite temperature is, however, limited by the incomplete experimental data for single-phase alloys. We used first principles alloy theory to investigate the magnetic structure of polymorphic CoCrFeMnNi in the paramagnetic state by accounting for the longitudinal spin fluctuations (LSFs) as a function of temperature. In both face-centered cubic (fcc) and hexagonal close-packed (hcp) structures, the LSFs induce sizable magnetic moments for Co, Cr and Ni. The impact of LSFs was demonstrated on the phase stability, stacking fault energy and the fcc-hcp interfacial energy. The hcp phase is energetically preferable to the fcc one at cryogenic temperatures, which results in negative stacking fault energy at these conditions. With increasing temperature, the

stacking fault energy increases, suppressing the formation of stacking faults and nano-twins. Our predictions are consistent with recent experimental findings (*Thermal spin fluctuations in CoCrFeMnNi high entropy alloy*, Z. Dong, S. Schönecker, W. Li, D. Chen, and L. Vitos, Scientific Reports **8**, 12211 (2018)).

The magnetic structure of polymorphic Cr-Co-Ni medium entropy alloys was investigated as a function of temperature and chemical composition by *ab initio* calculations. Besides the thermal lattice expansion, the longitudinal spin fluctuations (LSFs) were accounted for in determining the magnetic state at finite temperature. We showed that sizable local magnetic moments persist on all alloy components in the paramagnetic state for both face-centered cubic and hexagonal close-packed structures, and each alloy species exhibits particular temperature and concentration dependencies. The crucial role of LSFs for the finite temperature magnetic state and its impact on the temperature dependent elastic parameters are demonstrated (*Finite temperature magnetic properties of Cr-Co-Ni medium entropy alloys from first principles*, Z. Dong and L. Vitos, Scripta Materialia **171**, 78-82 (2019)).

-Thermophysical properties of HEMs. We reported the pressure-induced magneto-volume effect in the body-centered-cubic CoCrFeAl HEA coupled with magnetic phase transitions from ferromagnetic to paramagnetic, and to non-magnetic states, originating from the successive collapses of local magnetic moments of Co and Fe. The observed magneto-volume anomalies, occurring in a progressive way, tailor appreciably the coefficient of thermal expansion of CoCrFeAl. These results further strengthen HEAs' anticipated potential for designing multifunctional materials in virtue of their multiple outstanding properties, and reveal possible routes for their future synthesis (*Pressure-Induced magnetovolume Effect in CoCrFeAl high-entropy alloy*, L. Liu, S. Huang, L. Vitos, M. Dong, E. Bykova, D. Zhang, B. S.G. Almqvist, S. Ivanov, J.-E. Rubensson, B. Varga, L. K. Varga, and P. Lazor, Communications Physics **2**, 42 (2019)).

We have investigated the thermo-magnetic and mechanical properties of the chemically disordered solid-solution, Al_{0.6}Cr_{0.2}MnFe_{0.5}Co_{0.3}Ni_{0.5}, which has a body-centered cubic underlying lattice and measured Curie temperature of ~380 K. First-principles alloy theory was employed to investigate the temperature-dependent free energy, elastic constants, and coefficient of thermal expansion at the ferromagnetic and paramagnetic states. Theory and experiment were found to strengthen each other, and the results indicate that the magnetic state has a strong impact on the thermo-elastic properties of the considered alloy. This advance in the thermo-magneto-elasticity enhances the understanding required for controlling the magnetic and mechanical response of multi-component systems (*Thermo-elastic properties of bcc Mn-rich high-entropy alloy*, S. Huang, Z. Dong, W. Mu, V. Ström, G. Chai, and L. Vitos, Applied Physics Letters **117**, 164101 (2020)).

We have introduced a series of Mn-rich Al_xCr_{0.2}MnFe_{0.5}Co_{0.3}Ni_{0.5} ($0.3 \le x \le 0.7$) high-entropy alloys by combining experimental and theoretical techniques. The X-ray diffraction and magnetization measurements indicate that the Al addition significantly alters the crystal structure and the entropy change upon magnetization-demagnetization cycles while keeping the Curie temperature almost unchanged. First-principles alloy theory was used to analyze the individual entropy contributions from the vibrational, magnetic, electronic, and configurational degrees of freedom. The theoretical results indicate that the main entropy change comes from the field-induced changes of the magnetic order and the vibrational entropy. Our work highlights that the presence of the body-centered-cubic phase, showing a sizable elastic softening upon ferromagnetic-paramagnetic transition, brings about the substantial magnetocaloric effect for this family of alloys. (*Thermo-elastic properties of bcc Mn-rich high-entropy alloy*, S. Huang, Z. Dong, W. Mu, V. Ström, G. Chai, and L. Vitos, Applied Physics Letters **117**, 164101 (2020)).

-Plasticity of HEMs. The Invar anomaly is one of the most fascinating phenomena observed in magnetically ordered materials. Invariant thermal expansion and elastic properties have attracted substantial scientific attention and led to important technological solutions. By studying planar faults in the high-temperature magnetically disordered state of Ni-Fe, we disclosed a completely different anomaly. An invariant plastic deformation mechanism is characterized by an unchanged stacking fault energy with temperature within wide concentration and temperature ranges. This anomaly emerges from the competing stability between the face-centered cubic and hexagonal close-packed structures and occurs in other paramagnetic or nonmagnetic systems whenever the structural balance exists. These findings create a platform for tailoring high-temperature properties of technologically relevant materials toward plastic stability at elevated temperatures (*Invariant plastic deformation mechanism in paramagnetic nickel-iron alloys*, Z. Dong, W. Li, S. Schonecker, B. Jiang, and L. Vitos,Proceedings of the National Academy of Sciences PNAS **118**, e2023181118 (2021)).

Superelasticity associated with the martensitic transformation has found a broad range of engineering including magnetocaloric applications. However, the intrinsic hysteresis and temperature sensitivity of the first-order phase transformation significantly hinder the usage of smart metallic components in many critical areas. We have reported a large superelasticity up to 15.2% strain in [001]-oriented NiCoFeGa single crystals, exhibiting non-hysteretic mechanical responses, a small temperature dependence and high-energy-storage capability and cyclic stability over a wide temperature and composition range. In situ synchrotron X-ray diffraction measurements show that the superelasticity is correlated with a stress-induced continuous variation of lattice parameter accompanied by structural fluctuation. Neutron diffraction and electron microscopy observations reveal an unprecedented microstructure consisting of atomic-level entanglement of ordered and disordered crystal structures, which can be manipulated to tune the superelasticity. The discovery of the large elasticity related to the entangled structure paves the way for exploiting elastic strain engineering and development of related functional materials (Unprecedented non-hysteretic superelasticity of [001]-oriented NiCoFeGa single crystals, H. Chen, Y.-D. Wang, Z. Nie, R. Li, D. Cong, W. Liu, F. Ye, Y. Liu, P. Cao, F. Tian, X. Shen, R. Yu, L. Vitos, M. Zhang, S. Li, X. Zhang, H. Zheng, J. F. Mitchell, Y. Ren, Nature Materials 19, 712-718 (2020)).

Combined theoretical and experimental efforts were put forward to study the critical factors influencing deformation mode transitions in face-centered cubic materials. We revisited the empirical relationship between the stacking fault energy (SFE) and the prevalent deformation mechanism. With ab initio calculated SFE, we established the critical boundaries between various deformation modes in the model Cr-Co-Ni solid solution alloys. Satisfying agreement between theoretical predictions and experimental observations were reached. Our findings shield light on applying quantum mechanical calculations in designing transformation-induced plasticity and twinning-induced plasticity mechanisms for achieving advanced mechanical properties (*Theoretical and experimental study of phase transformation and twinning behavior in metastable high-entropy alloys*, Z. Yang, S. Lu, Y. Tian, Z. Gu, J. Sun, L. Vitos, Journal of Materials Science and Technology **99**, 161-168 (2022)).

High-density and nanosized deformation twins in face-centered cubic (fcc) materials can effectively improve the combination of strength and ductility. However, the microscopic

dislocation mechanisms enabling a high twinnability remain elusive. Twinning usually occurs via continuous nucleation and gliding of twinning partial dislocations on consecutive close-packed atomic planes. Here we unveil a completely different twinning mechanism being active in metastable fcc materials. The transformation-mediated twinning (TMT) is featured by a preceding displacive transformation from the fcc phase to the hexagonal close-packed (hcp) one, followed by a second-step transformation from the hcp phase to the fcc twin. The nucleation of the intermediate hcp phase is driven by the thermodynamic instability and the negative stacking fault energy of the metastable fcc phase. The intermediate hcp structure is characterized by the easy slips of Shockley partial dislocations on the basal planes, which leads to both fcc and fcc twin platelets during deformation, creating more twin boundaries and further enhancing the prosperity of twins. The disclosed fundamental understanding of the complex dislocation mechanism of deformation twinning in metastable alloys paves the road to design novel materials with outstanding mechanical properties (*Theory of transformation-mediated twinning*, S. Lu, X. Sun, Y. Tian, X. An, W. Li, Y. Chen, H. Zhang, and L. Vitos, PNAS Nexus **2**, 111 (2022)).

-Thermoelectric HEMs. Among various thermoelectric base materials (TEMs), the XYZ type of half Heusler (HH) alloys have been scrutinized. These alloys form a degenerate semiconductor although consists of three metallic elements: X = early transition metal (ETM), Y =late TEM and Z = P-block, post transition metal. They become stable closed shell ions, i.e. a d10 configuration for Y and a s2p6 configuration for Z. This procedure requires 18 valence electrons and empties formally the valence atomic orbitals of X. Low cost, nontoxicity, excellent thermal and mechanical properties of these alloys make them promising candidates for thermoelectric applications.

The optimal orders of magnitude for the different properties of TEMs are: 10^{18} - 10^{19} cm⁻³ for the carrier concentration (n) 100μ V/K for thermopower coefficient (*S*), 1000 Ohm⁻¹cm⁻¹ for electrical conductivity (σ) and the minimum phonon thermal conductivity should be no greater than 0.003 Wcm⁻¹K⁻¹ at room temperature. In order to meet these conditions, a complete transport lab had to be built to measure these transport properties at room temperature and at higher temperature where the proposed TEG are supposed to operate. We intended to obtain these optimal electronic parameters by a high-entropy strategy using inductive melting and reducing the thermal conductivity by a foam structure obtained by 3D deposition. A large set of TEG materials have been prepared by inductive melting. The XRD spectra and the Seebeck coefficients were measured at room temperature. We demonstrated that the deviation from VEC = 18, in general, destroys the single phase FCC structure of the selected XYZ type half Heusler alloys (*These results will soon be published in international journals and also in a PhD thesis by Gábor Gulyás*).

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. We should mention that during our research along the initial work plan, a series of new and interesting questions emerged. Although these questions could not be foreseen in the original plan, we addressed them and there are a few published results from this additional works as well.

2018-2019

Alloys with adjustable mechanical performance are of fundamental interest in material designs. We investigated the magnetic- and chemical-ordering behavior of the ferromagnetic Fe-Cr-Co-Ni-Alx ($1 \le x \le 2.5$) 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 were considered. In contrast to the trend found for the completely disordered phase, we demonstrated that ordering driven primarily by Al results in an enhanced Young's modulus, especially at high-Al concentrations, which is in line with the observed increase of the hardness for systems with a body-centered-cubic underlying lattice. The results suggest that outstanding strength and ductility can be realized by proper control of the ordering level in single- and multiphase high-entropy alloys.

High-entropy alloys (HEAs) consisting of multi-principal elements have demonstrated many interesting structural, physical, and chemical properties for a wide range of applications. We reviewed the current theoretical research on the elastic parameters of HEAs. The performance of various ab initio-based computational models (effective medium and supercell approaches) is carefully analyzed. Representative theoretical elastic parameters of different HEAs, including single-crystal elastic constants, polycrystalline elastic moduli, elastic anisotropy, and Debye temperature, were presented and discussed. For comparison, simple mixtures of the elastic moduli of pure elements were calculated and contrasted with the ab initio results. Our work provides a reference for future theoretical investigation of the micromechanical properties of systems based on HEAs.

High entropy alloys based on 3d transition metals display rich and promising magnetic characteristics for various high-technology applications. Understanding their behavior at finite temperature is, however, limited by the incomplete experimental data for single-phase alloys. We used first principles alloy theory to investigate the magnetic structure of polymorphic CoCrFeMnNi in the paramagnetic state by accounting for the longitudinal spin fluctuations (LSFs) as a function of temperature. In both face-centered cubic (fcc) and hexagonal close-packed (hcp) structures, the LSFs induce sizable magnetic moments for Co, Cr and Ni. The impact of LSFs was demonstrated on the phase stability, stacking fault energy and the fcc-hcp interfacial energy. The hcp phase is energetically preferable to the fcc one at cryogenic temperatures, which results in negative stacking fault energy at these conditions. With increasing temperature, the stacking fault energy increases, suppressing the formation of stacking faults and nano-twins. Our predictions are consistent with recent experimental findings.

The competition between plastic deformation mechanisms in FeCrCoNiAlx high-entropy alloys was explored as a function of temperature by first-principle theory. Investigating the generalized stacking fault energy, we identified a strong interplay between the magnetic and chemical effects. At cryogenic conditions (ferromagnetic state), full-slip is accompanied by martensitic transformation, whereas increasing temperature towards room-temperature (paramagnetic state) changes the deformation mechanism to full-slip plus twinning. Alloying with Al reduces the susceptibility for stacking fault formation in the ferromagnetic state and promotes twinning in the paramagnetic state. Our advance in magneto-plasticity reveals new opportunities for tailoring the mechanical response in high-entropy alloys.

Using ab initio calculations, we investigated the elastic properties of paramagnetic AlxCrMnFeCoNi (0 < x < 5) high-entropy alloys (HEAs) in both body-centered cubic (bcc) and face-centered cubic (fcc) structures. Comparison with available experimental data demonstrates that the employed approach describes accurately the elastic moduli. The

predicted lattice constants increase monotonously with Al addition, whereas the elastic parameters exhibit complex composition dependences. The elastic anisotropy is unusually high for both phases. The brittle/ductile transitions formulated in terms of Cauchy pressure and Pugh ratio become consistent only when the strong elastic anisotropy is accounted for. The negative Cauchy pressure of CrMnFeCoNi is due to the relatively low bulk modulus and C12 elastic constant, which in turn are consistent with the relatively low cohesive energy. These findings in combination with the experimental data suggest anomalous metallic character for the HEAs system.

High-entropy alloys (HEAs) composed of multiple-principal elements with (nearly) equimolar ratio establish a new conceptual framework for alloy design and hold a promise for extensive applications in industry, akin to the controlled expansion alloys (CEAs), such as Invar alloys. Spontaneously, one question emerges - would it be possible to synthesize a novel class of alloys combining the virtues of both CEAs and HEAs? We reported the pressure-induced magneto-volume effect in the body-centered-cubic CoCrFeAl HEA coupled with magnetic phase transitions from ferromagnetic to paramagnetic, and to non-magnetic states, originating from the successive collapses of local magnetic moments of Co and Fe. The observed magneto-volume anomalies, occurring in a progressive way, tailor appreciably the coefficient of thermal expansion of CoCrFeAl. These results further strengthen HEAs' anticipated potential for designing multifunctional materials in virtue of their multiple outstanding properties, and reveal possible routes for their future synthesis.

The observation of the hexagonal-closed-packed (hcp) phase in CoCrFeNi-based multicomponent alloys has reopened the question of phase stability in these alloys. We investigated the alloying effect of tungsten on the crystal and magnetic structures of (CoCrFeNi)1-xWx high entropy alloys using density functional theory by means of the exact muffin-tin orbital method. The body-centered-cubic (bcc), face-centered-cubic (fcc), and hcp phases are investigated in two magnetic states: ferrimagnetic and paramagnetic. Below 8 at. % W the ground state of (CoCrFeNi)1-xWx is the ferrimagnetic hcp phase and above that, the ferrimagnetic bcc phase is stabilized. Our calculations show that the fcc and hcp phases are energetically very close in the whole range of studied W compositions and because CoCrFeNi and (CoCrFeNi)0.93W0.07 are observed in the fcc phase at room temperature, the hcp-fcc structural phase transition is expected to occur at lower temperatures. The total magnetic moment in bcc is almost double the value calculated for the fcc and hcp structures, which is due to that Cr moments are nearly quenched in bcc but are coupled antiferromagnetically to Fe, Ni, and Co in both hcp and fcc.We calculated also the Curie temperature of these alloys using the mean-field approximation. The calculated value was found to be 155 K for fcc CoCrFeNi, in excellent agreement with experiments, and the addition of W decreases this value. Our results contribute to the development of these relatively unknown corrosionresistant materials into industrial applications, such as cemented carbides.

The magnetic structure of polymorphic Cr-Co-Ni medium entropy alloys was investigated as a function of temperature and chemical composition by *ab initio* calculations. Besides the thermal lattice expansion, the longitudinal spin fluctuations (LSFs) were accounted for in determining the magnetic state at finite temperature. We showed that sizable local magnetic moments persist on all alloy components in the paramagnetic state for both face-centered cubic and hexagonal close-packed structures, and each alloy species exhibits particular temperature and concentration dependencies. The crucial role of LSFs for the finite temperature magnetic state and its impact on the temperature dependent elastic parameters are demonstrated. First principles calculations were performed to study the effects of alloying elements (X=Al, Si, Sc, V, Cr, Mn, Cu, Zn, Y,Mo, Ta,Wand Re) on the phase stability and elastic properties of TiZrHfNb refractory high entropy alloys. Both equimolar and non-equimolar alloys were considered. It was shown that the calculated lattice parameters, phase stability and elastic moduli of equimolar TiZrHfNbX are consistent with the available experimental and theoretical results. The substitutions of alloying elements at Ti, Zr, and Hf sites with various contents show similar effects on the phase stability and elastic properties of the TiZrHfNb-based alloys. The substitutions on Nb site are found to generally decrease the stability of body centered cubic phase. Close connections between the charge densities at the Wigner-Seitz cell boundary and the bulk moduli of TiZrHfNb-based alloys are found. These results provide a quantitative model for exploring the phase stability and elastic properties of TiZrHfNb-based alloys from the electronic structure viewpoint.

2019-2020

We have introduced a series of Mn-rich Al_xCr_{0.2}MnFe_{0.5}Co_{0.3}Ni_{0.5} ($0.3 \le x \le 0.7$) high-entropy alloys by combining experimental and theoretical techniques. The X-ray diffraction and magnetization measurements indicate that the Al addition significantly alters the crystal structure and the entropy change upon magnetization-demagnetization cycles while keeping the Curie temperature almost unchanged. First-principles alloy theory was used to analyze the individual entropy contributions from the vibrational, magnetic, electronic, and configurational degrees of freedom. The theoretical results indicate that the main entropy change comes from the field-induced changes of the magnetic order and the vibrational entropy. Our work highlights that the presence of the body-centered-cubic phase, showing a sizable elastic softening upon ferromagnetic-paramagnetic transition, brings about the substantial magnetocaloric effect for this family of alloys.

The stability of constituent phases in multi-component system plays a key role in tailoring their properties. Our recent alloy families demonstrate that in order to reach optimal magnetocaloric performance, one should be able to control the alloy phases. We selected the prototypic AlTiVCr_{1-x} Nb_x ($0 \le x \le 1$) alloy with body-centered cubic crystal structure to study the chemical ordering feature. First-principle investigations of the elemental distribution identify a family of B2 type of partially ordered configurations. We have mapped out the elastic parameters in detail as a function of composition and temperature for disordered and partially ordered phases. A great sensitivity to the order-disorder transformation was revealed, especially for the Cr-rich system. These results demonstrate that a proper control of the ordering level can facilitate the optimal tuning of their mechanical performance while keeping the density almost unchanged. Our study further predicts that these alloys possess high specific stiffness, low thermal expansion, and large elastic softening resistance. It is demonstrated that the considered alloys have thermal and mechanical properties that compete with superalloys and other high temperature structural materials.

Superelasticity associated with the martensitic transformation has found a broad range of engineering including magnetocaloric applications. However, the intrinsic hysteresis and temperature sensitivity of the first-order phase transformation significantly hinder the usage of smart metallic components in many critical areas. We have reported a large superelasticity up to 15.2% strain in [001]-oriented NiCoFeGa single crystals, exhibiting non-hysteretic mechanical responses, a small temperature dependence and high-energy-storage capability and cyclic stability over a wide temperature and composition range. In situ synchrotron X-ray diffraction measurements show that the superelasticity is correlated with a stress-induced

continuous variation of lattice parameter accompanied by structural fluctuation. Neutron diffraction and electron microscopy observations reveal an unprecedented microstructure consisting of atomic-level entanglement of ordered and disordered crystal structures, which can be manipulated to tune the superelasticity. The discovery of the large elasticity related to the entangled structure paves the way for exploiting elastic strain engineering and development of related functional materials.

Motivated by the phase stability studies, we have carried out specific investigations to understand the deformation mechanisms in refractory HEAs. Density-functional theory simulations and a continuum mechanics analysis have been conducted to investigate the competition between cleavage decohesion and dislocation emission from a crack tip in the body-centered cubic HfNbTiZr, MoNbTaVW, MoNbTaW, MoNbTiV, and NbTiVZr. This crack-tip competition is evaluated for tensile loading and a totality of 15 crack configurations and slip systems. Our results predict that dislocation plasticity at the crack tip is generally unfavorable, although the competition is close for some crack orientations, suggesting intrinsic brittleness and low crack-tip fracture toughness in these five HEAs at zero temperature. Fluctuations in local alloy composition, investigated for HfNbTiZr, can locally reduce the resistance to dislocation emission for a slip system relative to the configuration average of that slip system, but do not change the dominant crack-tip response. In the case of single-crystal MoNbTaW, where an experimental, room-temperature fracture-toughness value is available for a crack on a {100} plane, theoretical and experimental results agree favorably. We have surveyed the effect of material anisotropy on preferred crack tip orientations, which are found to be alloy specific. Mixed-mode loadings were found to shift the competition in favor of cleavage or dislocation nucleation, depending on crack configuration and amplified by the effect of material anisotropy on crack tip stresses.

The ordered phase of the FeNi system is known for its promising magnetic properties that make it a first-class rare-earth free permanent magnet. Mapping out the parameter space controlling the order-disorder transformation is an important step towards finding growth conditions that stabilize the $L1_0$ phase of FeNi. We have studied the magnetic properties and chemical order-disorder transformation in FeNi as a function of lattice expansion by utilizing *ab initio* alloy theory. The largest volume expansion considered was 29% which corresponds to a pressure of -25 GPa. The thermodynamic and magnetic calculations were formulated in terms of a long-range order parameter, which was subsequently used to find the ordering temperature as a function of pressure. We have shown that negative pressure promotes ordering, meaning that synthetic routes involving an increase of the volume of FeNi are expected to expand the stability field of the $L1_0$ phase.

2020-2021

We investigated the AlxCr0.2MnFe0.5Co0.3Ni0.5 (0.3 < x < 0.7) high-entropy alloys (HEAs) by combining experimental and theoretical techniques. X-ray diffraction and magnetization measurements indicated that Al alters the crystal structure and the entropy change upon magnetization–demagnetization while keeping the Curie temperature almost unchanged. First-principles calculations of the vibrational, magnetic, electronic, and configurational entropies showed that the leading entropy change is due to the magnetic and vibrational degrees of freedom. We demonstrated that the presence of the body-centered-cubic phase, showing a sizable elastic softening upon magnetic transition, brings about the substantial magnetocaloric effect in this family of alloys.

We screened for magnetocaloric application a series of MnxCr0.3Fe0.5Co0.2Ni0.5Al0.3 (0.8 < x < 1.1) HEAs. Both theory and experiment indicate that the designed HEAs have Curie temperature close to room temperature and is tunable with Mn concentration. A non-monotonic evolution was observed for both the entropy change and the relative cooling power with changing Mn concentration. The underlying atomic mechanism was found to primarily emerge from the complex impact of Mn on magnetism.

We reported a chemically disordered solid solution, Al0.6Cr0.2MnFe0.5Co0.3Ni0.5, based on a body-centered cubic underlying lattice with the measured Curie temperature of 380 K. First-principles alloy theory was employed to investigate the temperature-dependent free energy, elastic constants, and coefficient of thermal expansion at the ferromagnetic and paramagnetic states. Theory and experiment were found to strengthen each other, and the results indicate that the magnetic state has a strong impact on the thermo-elastic properties of the considered alloy.

Using ab initio calculations, we studied the effect of magnetism and chemical composition on the generalized stacking fault energy surface (γ -surface) of Cr-Co-Ni medium entropy alloys and showed that both chemistry and the coupled magnetic state strongly affect the γ -surface, consequently, the primary deformation modes. The relations among various stable and unstable stacking fault energies were revealed and discussed. These findings are useful for studying the deformation behaviors of Cr-Co-Ni alloys and facilitate a density functional theory based control of the mechanical and magnetic properties of Cr-Co-Ni alloys.

In the next step, we accounted for the longitudinal spin fluctuations in the paramagnetic state of Cr–Co–Ni alloys. The longitudinal spin fluctuations were demonstrated to be important for the quantitative description of the thermo-mechanical properties and the corresponding chemical and temperature dependences. Replacing Ni with Cr and Co was found to yield opposite influence on the mechanical properties at finite temperature. A high thermal stability in plasticity was predicted in the low Cr regime in Cr–Co–Ni alloys, while a good thermal stability in elasticity could be achieved in the high Cr and low Co regime.

Tetragonal (L10) FeNi is a promising material for high-performance rare-earth-free permanent magnets. Pure tetragonal FeNi is very difficult to synthesize due to its low chemical order–disorder transition temperature (593 K), and thus one must consider alternative non-equilibrium processing routes and alloy design strategies that make the formation of tetragonal FeNi feasible. We investigated by ab initio calculations whether alloying FeNi with a suitable element can have a positive impact on the phase formation and ordering properties while largely maintaining its attractive intrinsic magnetic properties. We found that small amount of non-magnetic (Al and Ti) or magnetic (Cr and Co) elements increase the order–disorder transition temperature. Adding Mo to the Co-doped system further enhances the ordering temperature while the Curie temperature is decreased only by a few degrees. These results show that alloying is a viable route to stabilizing the ordered tetragonal phase of FeNi.

The Invar anomaly is one of the most fascinating phenomena observed in magnetically ordered materials. Invariant thermal expansion and elastic properties have attracted substantial scientific attention and led to important technological solutions. By studying planar faults in the high-temperature magnetically disordered state of Ni-Fe, we disclosed a completely different anomaly. An invariant plastic deformation mechanism is characterized by an unchanged stacking fault energy with temperature within wide concentration and temperature ranges. This anomaly emerges from the competing stability between the face-centered cubic and hexagonal close-packed structures and occurs in other paramagnetic or nonmagnetic systems whenever the structural balance exists. These findings create a platform for tailoring high-temperature properties of technologically relevant materials toward plastic stability at elevated temperatures.

The hysteresis that occurs during superelasticity caused by the stress-induced first-order martensite transformation is sometimes detrimental to the properties of superelastic materials. First-principles calculations were performed to investigate the effect of chemical composition and crystal disorder on the superelasticity of Ni50-*x*Co*x*M25Ga25 (M = Mn, Fe) Heusler alloys. Calculations of the stress-strain relation in the studied alloys reproduce the recent experimental findings for non-hysteretic superelasticity within an acceptable range of composition and ordering. We evaluated the Bloch spectral function to study the Fermi surface topology in connection with non-hysteretic superelasticity. We proposed the Landaude Gennes model-dependent critical parameter *P*c, which can be used to predict the composition range of non-hysteretic superelastic materials. For the ferromagnetic L2_1 Ni50-*x*Co*x*Mn25Ga25 and B2 Ni50-*x*Co*x*Fe25Ga25 alloys, the non-hysteretic superelasticity phenomenon theoretically occurs for Co contents over x = 16 at.% and x = 28 at.%, respectively.

Using first-principles alloy theory, we performed a systematic study of the Co-Cu phase diagram. Calculations are carried out for ferromagnetic and paramagnetic Co1-xCux solid solutions with face-centered-cubic (fcc) crystal structure. We found that the equilibrium volumes and magnetic states are crucial for a quantitative description of the thermodynamics of the Co-Cu system at temperatures up to 1400 K. In particular, the paramagnetic state of Cu-rich alloys with persisting local magnetic moments is shown to be responsible for the solubility of a small amount of Co in fcc Cu whereas the excess entropy in the ferromagnetic Co-rich region critically depends on the adopted lattice parameters. None of the common local or semilocal density functional theory approximations have the necessary accuracy for the lattice parameters when compared to the experimental data. The predicted *ab initio* Co-Cu phase diagram is in good agreement with the measurements and CALPHAD data, making it possible to gain a deep insight into the various contributions to the Gibbs free energy. Our study provides an atomic-level description of the thermodynamic quantities controlling the limited mutual solubility of Co and Cu and highlights the importance of high-temperature magnetism.

2021-2022

High-entropy functional materials are of great interest in materials science and engineering community. We performed ab initio electronic structure calculations of the phase stability and magnetic transition temperature of AlxCr0.25MnFeCo0.25_yNiy (x=0-0.5, y=0-0.25) alloys to screen for compositions showing promising magnetocaloric properties in the vicinity of room temperature. The selected Al0.44Cr0.25MnFeCo0.05Ni0.2 alloy was synthesized via a rapid solidification technique and systematically characterized with respect to its structural and magnetocaloric properties. The results indicate that this alloy possesses a homogeneous microstructure based on an underlying body-centered cubic lattice and has a Curie temperature of 340 K. The temperature dependence of the adiabatic temperature change was evaluated using both direct and indirect methods. The ab initio-assisted design of 3d-metal-based high-entropy alloys is intended to contribute to the development of magnetic refrigerators for room-temperature applications.

We employed quantum mechanics modeling to investigate the effects of Ge and Si solute elements on the physical properties and plastic deformation modes in two families of highentropy alloys, CoCrFeMnNi and CoCrFeNi, and medium-entropy alloy, CoCrNi. The static lattice constants and single-crystal elastic parameters were calculated for these three facecentered-cubic random solid solutions as a function of composition. Using the elastic constants, we analyzed mechanical stability, derived polycrystalline modulus, and evaluated solid-solution strengthening for these multi-component alloys. We fabricated (CoCrFeNi)100xSix (x=0, 4, 6) and measured the polycrystalline modulus and hardness. The calculated trends for Young's and shear modulus as well as lattice parameters were verified by our measurements. The dependence of generalized stacking fault energy on Ge and Si was studied in detail for the considered multi-component alloys. The competition between various plastic deformation modes was revealed based on effective energy barriers. Our calculations predict that the activated deformation modes in all the above alloys are the stacking fault mode (dominant) and the full-slip mode (secondary), and as the concentrations of Ge and Si increase, twining becomes favored.

Developing high-strength and ductile face-centered cubic (fcc) high-entropy alloys (HEAs) has attracted significant attention. The generalized stacking fault energy (GSFE) is a very useful concept to describe stable and unstable planar defects and their energies on a slip plane. It plays an essential role in designing high performance fcc HEAs and understanding the nanoscale plasticity phenomena. Using first-principles simulations, we investigated the configuration-averaged GSFEs of 29 single-phase fcc HEAs and identified indicators that can be used to tune stacking fault energies. First we determined the equilibrium structural parameters for all considered alloys and compared them with available experimental data. With the obtained GSFEs, we analyzed the relationship between the stacking fault energies and materials properties, and investigated scaling relations between planar fault energies and the tendencies to exhibit deformation twinning and transformation to hexagonal close-packed martensite. We found that unstable SFE and shear modulus correlates strongly. Moreover, we revealed that the ratio of intrinsic SFE to unstable SFE, yisf/yusf, is a characteristic materials measure, and the tendencies to twinning and martensitic transformation rank with it. Our results are expected to be useful for an efficient alloy design and selection of solutes in fcc HEAs.

Combined theoretical and experimental efforts were put forward to study the critical factors influencing deformation mode transitions in face-centered cubic materials. We revisited the empirical relationship between the stacking fault energy (SFE) and the prevalent deformation mechanism. With ab initio calculated SFE, we established the critical boundaries between various deformation modes in the model Cr-Co-Ni solid solution alloys. Satisfying agreement between theoretical predictions and experimental observations were reached. Our findings shield light on applying quantum mechanical calculations in designing transformation-induced plasticity and twinning-induced plasticity mechanisms for achieving advanced mechanical properties.

The hexagonal close-packed (hcp) phase of iron is unstable under ambient conditions. The limited amount of existing experimental data for this system was obtained by extrapolating the parameters of hcp Fe–Mn alloys to pure Fe. On the theory side, most density functional theory (DFT) studies on hcp Fe considered non-magnetic or ferromagnetic states, both having limited relevance in view of the current understanding of the system. We investigated the equilibrium properties of paramagnetic hcp Fe using DFT modelling in combination with alloy theory. We showed that the theoretical equilibrium c/a and the equation of state of hcp Fe become consistent with the experimental values when the magnetic disorder is properly

accounted for. Longitudinal spin fluctuation effects further improve the theoretical description. Our study provides useful data on hcp Fe at ambient and hydrostatic pressure conditions, contributing largely to the development of accurate thermodynamic modelling of Fe-based alloys.

Recent advances in tuning the long-standing strength-ductility tradeoff have drawn attention to high-entropy alloys (HEAs), and the appearance of hexagonal close-packed (hcp) structures has been emphasized. However, few studies have explored the elastic moduli of hcp HEAs, which is of prime importance for improved understanding of the outstanding mechanical properties. We focused on a set of equiatomic rare-earth-free HEAs with hcp structures, i.e. ScTiZr, ScTiHf, ScZrHf, TiZrHf, and ScTiZrHf, and their thermo-elastic properties were studied using quantum mechanical first-principles methods. It was found that, for all considered HEAs, the hexagonal axial ratio shows a weak dependence on the temperature effect, and the thermal expansion coefficient remains almost unchanged above room temperature. From the calculated temperature-dependent single-crystal elastic constants, we analyzed the mechanical stability, elastic anisotropy, and derived polycrystalline moduli. Results indicate that the above HEAs exhibit rather high elastic isotropy and large elastic softening resistance. The *ab initio* predicted Young's modulus, shear modulus, and specific modulus do not obey the rule of mixture, which indicates that there exists a strong intrinsic hardening effect in all of the considered HEAs. The calculated results are in good agreement with the available experimental measurements.

A high-priority target in the design of new metallic materials for load-bearing implant applications is the reduction of Young's modulus approximating that of cortical bone in the predominant loading direction. We explored how directionally preferential bulk elastic properties of implant materials are achieved by harnessing elastic anisotropy. Specifically focusing on recently proposed biocompatible refractory high-entropy alloys (RHEAs) in the body-centered cubic structure, we conducted systematic density functional theory calculations to investigate the single-crystal elastic properties of 21 Ti-containing RHEAs. Our results provide evidence that the valence electron count has a dominant influence on elastic anisotropy and crystal directions of low Young's modulus and high torsion modulus in the RHEAs. By means of modeling the orientation distribution function for crystallographic texture, we examined the effect of non-random texture on the anisotropic poly-crystalline Young's modulus and torsion modulus with varying texture sharpness. We adopted fiber textures that can result from rolling and distinct texture orientations that can form during rapid directional solidification. We discussed the potential for lowering Young's modulus in the RHEAs by using single crystals or textured aggregates. Furthermore, we prepared four of the theoretically considered alloys by arc-melting and reported their lattice parameters, quasi isotropic Young's moduli, and Wickers hardnesses.

The {100} and (110) cleavage energies of body-centered cubic TiZrNbHf high-entropy alloy were calculated using two alloy models: special quasi-random structures (SQSs) and the coherent potential approximation (CPA). The projector augmented wave method, as implemented in the Vienna ab initio simulation package (VASP), in combination with SQSs was adopted to evaluate the impact of local lattice distortions, whereas the exact muffin-tin orbitals (EMTO) method was used in combination with both SQSs and CPA to study the effect of chemical disorder using rigid underlying lattices. The variations of the cleavage energy as a function of surface chemistry and structure from the EMTO and VASP calculations were consistent with each other. The cleavage energies from CPA are in good agreement with those from SQSs, confirming that an averaged supercell approach reproduces well the mean-field CPA results. The alloy's cleavage energies estimated by the rule of

mixtures compare well with those from the direct calculations, and the surface chemistry dependence of the cleavage energies is mainly controlled by the number of Nb atoms in the surface terminal layers owing to the large cleavage energy of Nb metal.

We used density-functional theory to assess the electronic structure, elastic properties and planar fault energies of the B2 Ti(AlxNb1-x) ($0.2 \le x \le 0.8$) phase in relation to the composition and chemical ordering. We found that the covalent bonding becomes stronger for B2 Ti(AlxNb1-x) with higher Al concentration and long range order (LRO) parameter. Based on a universal ductile-to-brittle criterion by integrating Pettifor's Cauchy pressure with Pugh's modulus ratio, the deformability becomes less for Ti(AlxNb1-x) with higher Al concentration and LRO parameter, which is well correlated with the bonding character. Rice's ratio has an anti-correlation with Pugh's modulus ratio for Ti(AlxNb1-x). According to Rice's criterion, Ti(AlxNb1-x) with various Al concentration and LRO parameter are brittle in pure mode I loading, however, Nb-enriched disordered and low-ordered Ti(AlxNb1-x) may satisfy Rice's criterion for nucleation of dislocation and thus, are ductile in mode II or III loading. The hardness increases but the fracture toughness decreases obviously with increasing the degree of covalent bonding in Ti(AlxNb1-x).

2022-2023

The present work investigates how the vanadium (V) content in a series of Al50Vx(Cr0.33Mn0.33Co0.33)(50-x) (x = 12.5, 6.5, 3.5, and 0.5 at.%) high-entropy alloys affects the local magnetic moment and magnetic transition temperature as a step towards developing high-entropy functional materials for magnetic refrigeration. This has been achieved by carrying out experimental investigations on induction melted alloys and comparison to *ab initio* and thermodynamic calculations. Structural characterization by x-ray diffraction and scanning electron microscopy indicates a dual-phase microstructure containing a disordered body-centered cubic (BCC) phase and a B2 phase with long-range order, which significantly differ in the Co and V contents. Ab initio calculations demonstrate a weaker magnetization and lower magnetic transition temperature (TC) of the BCC phase in comparison with the B2 phase. We find that lower V content increases the B2 phase fraction, the saturation magnetization, and the Curie point, in line with the calculations. This trend is primarily connected with the preferential partition of V in the BCC phase, which however hinders the theoretically predicted antiferromagnetic B2 phase stabilizing effect of V. On the other hand, the chemistry-dependent properties of the ferromagnetic B2 phase suggest that a careful tuning of the composition and phase fractions can open the way towards promising high-entropy magnetic materials.

We have conducted an in-depth study of the magnetic phase due to a spinodal decomposition of the BCC phase of a CrFe-rich composition. This magnetic phase is present after casting (arc melting) or water quenching after annealing at 1250 °C for 24 h but is entirely absent after annealing in the interval 900–1100 °C for 24 h. Its formation is favored in the temperature interval ca 450–550 °C and loses magnetization above 640 °C. This ferromagnetic-paramagnetic transition is due to a structural transformation from ferromagnetic BCC into paramagnetic σ and FCC phases. The conclusion from measurements at different heating rates is that both the transformation leading to the increase of the magnetization at 640 °C are diffusion controlled.

The relationship between the tendencies towards rigidity (measured by shear modulus, G) and hardness (measured by Vickers hardness, HV) of early transition metal (ETM)-based

refractory high-entropy alloys (RHEA) and bond parameters (i.e., valence electron concentration (VEC), enthalpy of mixing (DHmix)) was investigated. These bond parameters, VEC and DHmix, are available from composition and tabulated data, respectively. Based on our own data (9 samples) and those available from the literatures (47 + 27 samples), it seems that for ETM-based RHEAs the G and HV characteristics have a close correlation with the bonding parameters. The room temperature value of G and HV increases with the VEC and with the negative value of DHmix. Corresponding equations were deduced for the first time through multiple linear regression analysis, in order to help design the mechanical properties of ETM refractory high-entropy alloys.

Multi-component alloys have received increasing interest for functional applications in recent years. Here, we explore the magnetocaloric response for Al–Cr–Mn–Co medium-entropy alloys by integrated theoretical and experimental methods. Under the guidance of thermodynamic and ab initio calculations, a dual-phase system with large magnetic moment, i.e., Al50Cr19Mn19Co12, is synthesized, and the structural and magnetocaloric properties are confirmed via characterization. The obtained results indicate that the selected alloy exhibits a continuous mixture of a disordered body-centered cubic and an ordered B2 phase. The ab initio and Monte Carlo calculations indicate that the presence of the ordered B2 phase is responsible for the substantial magnetocaloric effect. The magnetization measurements demonstrated that this alloy undergoes a second-order magnetic transition with the Curie temperature of 300 K. The magnetocaloric properties are examined using magnetic entropy change, refrigeration capacity, and adiabatic temperature change. The property-directed strategy explored here is intended to contribute to the study of potential multi-component alloys in magnetocaloric applications.

In a previous work [El-Tahawy et al., J. Magn. Magn. Mater. 560, 169660 (2022)], we reported that from a sulfate type bath, hcp-Co can be electrodeposited at high pH and low current density and investigated the structure and magnetoresistance (MR) characteristics of such hcp-Co electrodeposits. Based on this earlier work, Co-rich Co-Cu and Co-Ni alloy electrodeposits were prepared under the same conditions by adding varying amounts of CuSO4 and NiSO4, respectively, to the CoSO4 bath. According to the results of detailed structural studies by various X-ray diffraction (XRD) geometries, in both the Co-Cu and Co-Ni systems an hcp phase formed exclusively up to about 2 at% of the alloying element. Above this concentration, a significant fcc phase fraction appeared in Co-Cu and a minor fcc fraction in Co-Ni up to about 8 at%. This means that the destabilization effect of Cu on hcp-Co is higher than that of Ni. Although the reduction of the stability of hcp-Co with increasing Cu and Ni content is a well-known phenomenon, a quantitative comparison of this effect in Co-Cu and Co-Ni alloys is missing from the literature. The measured lattice constants are analyzed in comparison with Vegard's law for the Co-Cu and Co-Ni element pairs deduced from data previously reported for the hcp and fcc phases of all three pure elements. For Corich Co-Ni alloys, the concentration dependence of the lattice parameters was found to follow Vegard's law for both the hcp and fcc phases due to the miscibility of the two components. For the Co-rich Co-Cu alloys, the data indicate a positive deviation from Vegard's law for both the hcp and fcc phases in agreement with the known similar behavior of fcc Co-Cu alloys for the whole composition range. The positive deviation from Vegard's law in the Co-Cu system is due to the excess mixing volume required for solid solution alloy formation of these immiscible elements in either phases. The MR data are discussed in the light of the observed phases and of the MR parameters reported in our previous work on the hcp and fcc phases of pure Co.

High-density and nanosized deformation twins in face-centered cubic (fcc) materials can effectively improve the combination of strength and ductility. However, the microscopic dislocation mechanisms enabling a high twinnability remain elusive. Twinning usually occurs via continuous nucleation and gliding of twinning partial dislocations on consecutive close-packed atomic planes. Here we unveil a completely different twinning mechanism being active in metastable fcc materials. The transformation-mediated twinning (TMT) is featured by a preceding displacive transformation from the fcc phase to the hexagonal close-packed (hcp) one, followed by a second-step transformation from the hcp phase to the fcc twin. The nucleation of the intermediate hcp phase is driven by the thermodynamic instability and the negative stacking fault energy of the metastable fcc phase. The intermediate hcp structure is characterized by the easy slips of Shockley partial dislocations on the basal planes, which leads to both fcc and fcc twin platelets during deformation, creating more twin boundaries and further enhancing the prosperity of twins. The disclosed fundamental understanding of the complex dislocation mechanism of deformation twinning in metastable alloys paves the road to design novel materials with outstanding mechanical properties.

Giant magnetocaloric (GMC) materials constitute a requirement for near-room-temperature magnetic refrigeration. (Fe,Mn)2(P,Si) is a GMC compound with strong magnetoelastic coupling. The main hindrance towards application of this material is a comparably large temperature hysteresis, which can be reduced by metal site substitution with a nonmagnetic element. However, the (Fe,Mn)2(P,Si) compound has two equally populated metal sites, the tetrahedrally coordinated 3 f and the pyramidally coordinated 3g sites. The magnetic and magnetocaloric properties of such compounds are highly sensitive to the site-specific occupancy of the magnetic atoms. Here we have attempted to study separately the effect of 3 f and 3g site substitution with equal amounts of vanadium. Using formation energy calculations, the site preference of vanadium and its influence on the magnetic phase formation are described. A large difference in the isothermal entropy change (as high as 44%) with substitution in the 3 f and 3g sites is observed. The role of the lattice parameter change with temperature and the strength of the magnetocalastic coupling on the magnetic properties are highlighted.