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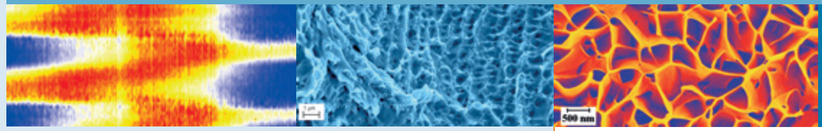

Treasure maps for magnetic high entropy alloys

The new class of high entropy alloys (HEA) holds potential for advanced manufacturing and possesses hardness and resistance to wear and corrosion. Recently magnetic HEAs and their magnetic properties such as the magnetic Curie temperature have attracted attention. However, due to the immense configurational phase space of these alloys (Fig. 1) theoretically guided materials design becomes critically important. Our present work represents an experimentally validated computational guide for the discovery and design of materials with specifically desired properties.

For the computational approach we combine *ab initio* based density-functional theory with a mean field magnetic model to allow efficient Curie temperature predictions. The predictive power of this theory is validated with experimental data from a variety of CoFeNi-based HEAs. Our approach allows us to screen a wide compositional range of HEAs, which essentially provides "treasure maps" of the enormous and unexplored parameter space occupied by four and five component alloys.

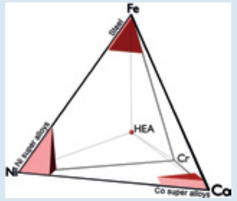

Fig. 1: *3D representation of the quaternary FeCoNiCr phase diagram. Regions explored in conventional material design are indicated by the red areas. The idea behind HEAs is to explore the large, so far unexplored region, e.g., by starting at the indicated equiatomic composition in the middle of the diagram.*

To verify the performance of our approach, we computed Curie temperatures for a number of different alloys for which Curie temperature values have been reported in literature (black and red bars in Fig. 2). The trend in the measured Curie temperatures is in very good agreement with our theoretical results indicating the predictive strength of the approach.

Our theoretical predictions were further tested by fabricating alloys of CoFeNiCrPdX ranging from x=0 to 0.5. Fig. 3 shows the experimental Curie temperatures (red stars), which are in excellent agreement with the theoretical predictions. In addition to the previously experimentally identified alloying strategies to achieve room temperature ferromagnetism in CoCrFeNi alloys, we suggest three alternative alloying candidates,

EDITORIAL

Dear Colleagues and Friends of the MPIE,

The combination of high strength and ductility becomes more and more important for industrial applications. In this issue we present our theoretical and experimental work on high entropy alloys (HEA) – alloys which combine exactly those targeted properties. Please also have a look at our recently published Nature paper on HEA.

In the section "Scientists at the MPIE" we present two of our researchers who specialize in steels and steel related topics such as kappa carbides, hydrogen embrittlement and coatings.

Enjoy reading and best regards,

Prof. Dr. Dierk Raabe, Chief Executive, MPIE

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News and Events

Selected Past Events

28 Apr 2016: Girls' Day

A group of schoolgirls had the chance to get an exclusive insight on being a materials' researcher for one day. Students and trainees of the MPIE showed them the fields of surface science, materials testing and nano science. At the Girls' Day companies and research institutions invite female pupils once per year for one day. The girls learn about possible trainings and courses of study in fields usually dominated by men.

20 Apr 2016: Cooperation with the Heinrich Heine University Düsseldorf

In a joint meeting of the Heinrich Heine University Düsseldorf and the MPIE both sides agreed on intensifying their cooperation in terms of research and strategy. Topics like the welcoming of international researchers, the networking with other research institutions in North Rhine Westphalia and joint research projects especially in the fields of chemistry and physics were discussed.

9 Jun 2016: Career Event with Infineon Technologies AG

The PhD representatives of the MPIE organized another career event, this time with Infineon Technologies. Infineon presented its work fields and career perspectives. The PhD and postdoctoral students of the MPIE had the chance to ask about job opportunities and possible research projects. This event is part of a new series of one-day events on career perspectives of Max Planck scientists. The series is jointly organized by the PhD representatives and the MPIE's board of directors. The intention of these events is to bring together leading experts from industry and the MPIE's early career researchers to have in depth discussions about career possibilities after the time at the MPIE.

Selected Upcoming Events

4 Jul 2016: Workshop on "Alloys for Additive Manufacturing"

The workshop focusses on materials, in particular metals, alloys and metal-based composites for additive manufacturing (AM), i.e. on materials that are optimised for use in AM processes, and on materials by AM, i.e. materials that can be synthesised only or only cost-effectively by AM. The entire process chain from alloy design and powder making to processing and post-processing will be addressed. The workshop will take place at the MPIE.
http://www.mpie.de/aamws2016

1 – 2 Sep 2016: 5th International Symposium on Computational Mechanics of Polycrystals and 1^{rst} DAMASK User Meeting

The symposium gives an up-to-date overview on the multi-scale modelling and simulation of polycrystal plasticity of metals. Special attention shall be given to industrially relevant multi-phase materials and materials showing mechanical twinning and phase transformations. This year the symposium is combined with the first DAMASK User Meeting. DAMASK is the multi-physics simulation software developed at the MPIE. The workshop will take place at the MPIE.
http://www.mpie.de/cmcn2016

2 – 7 Oct 2016: Workshop "*Ab initio* Description of Iron and Steel" (ADIS2016): Mechanical Properties

This 6th ADIS workshop will be focussed on the prediction and understanding of mechanical properties, incl. the description of precipitate formation, dislocations, stacking faults, deformation and failure mechanisms. It will take place at the Ringberg Castle (Tegernsee, Germany).

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Selected Talks

Computational Materials Design:

J. Neugebauer: *Ab Initio Thermodynamics: Understanding the fundamental mechanisms behind H embrittlement in metals: An ab initio guided multiscale approach*. Joint HYDROGENIUS and I2CNER International Workshop on Hydrogen-Materials Interactions 2016, Fukuoka, Japan, 3 – 4 Feb 2016

J. Neugebauer: *Database concepts and ICME links for atomistic simulations*. 2nd International Workshop on Software Solutions for Integrated Computational Materials Engineering ICME 2016, Barcelona, Spain, 12 – 15 Apr 2016

Interface Chemistry and Surface Engineering:

M. Rohwerder: Conducting Polymers for Intelligent Self-Healing Coatings. EMN Meeting on Polymer, Hongkong, 12 – 15 Jan 2016

S. Wippermann: Interface-controlled materials for solar energy conversion: semiconducting nanocrystal-solids, Colloquium at the Department of Physics at the Tsinghua University, Beijing, China, 7 Apr 2016

Microstructure Physics and Alloy Design:

R. Kuzmina, B. Gault, M. Herbig, D. Ponge, S. Sandlöbes, D. Raabe: *From grains to atoms: ping-pong between experiment and simulation for understanding microstructure mechanisms*. Res Metallica Symposium, Department of Materials Engineering, KU Leuven, Belgium, 11 May 2016

D. Ponge, M. Herbig, C. Tasan, D. Raabe: *Integrated experimental and simulation analysis of dual phase steels*. Workshop on Possibilities and Limitations of Quantitative Materials Modeling and Characterization 2016, Bernkastel, Germany, 23 May 2016

Structure and Nano-/Micromechanics of Materials:

M. Palm: *Development and processing of advanced iron aluminide alloys for application at high temperatures*. 62. Metallkunde Kolloquium, Lech am Arlberg, Austria, 11-13 Apr 2016

C. Kirchlechner, N. Malyar, P.J. Imrich, G. Dehm: *X-ray μLaue Diffraction to understand plasticity at interfaces*. DPG Spring Meeting 2016, Regensburg, Germany, 8 Mar 2016

Selected Publications

Computational Materials Design:

G. P. M. Leyson, B. Grabowski, J. Neugebauer: *Multiscale modeling of hydrogen enhanced homogeneous dislocation nucleation*, Acta Mat, 107, 144-151 (2016)

B. Dutta, A. Cakir, C. Giacobbe, A. Al-Zubi, T. Hickel, M. Acet, J. Neugebauer: *Ab initio prediction of martensitic and intermartensitic phase boundaries in Ni-Mn-Ga*, Phys. Rev. Lett., 116, 025503 (2016)

Interface Chemistry and Surface Engineering:

C. H. Choi, M. Kim, H. C. Kwon, S. J. Cho, S. Yun, H.-T. Kim, K. J. J. Mayrhofer, H. Kim, M. Choi: *Tuning selectivity of electrochemical reactions by atomically dispersed platinum catalyst*. Nat Commun, 7, 10922, (2016)

S. Kato, S. K. Matam, P. Kerger, L. Bernard, C. Battaglia, D. Vogel, M. Rohwerder, A. Züttel: *The Origin of the Catalytic Activity of a Metal Hydride in CO_2 Reduction*. Angew. Chem. Int. Ed, 55, 20, 6028–6032 (2016)

Microstructure Physics and Alloy Design:

J.-K. Kim, W.-S. Ko, S. Sandlöbes, M. Heidelmann, B. Grabowski, D. Raabe: *The role of metastable LPSO building block clusters in phase transformations of an Mg-Y-Zn alloy*, Acta Mat, 112, 171-183 (2016)

Z. Li, K. G. Pradeep, Y. Deng, D. Raabe, C. C. Tasan: *Metastable high-entropy dual-phase alloys overcome the strength–ductility trade-off*, Nature (2016)

Structure and Nano-/Micromechanics of Materials:

S. Djaziri, S. Gleich, H. Bolvardi, C. Kirchlechner, M. Hans, C. Scheu, J.M. Schneider, G. Dehm: *Are Mo_2BC nano-crystalline coatings damage resistant? Insights from comparative tension experiments*, Surface and Coatings Technology, 289, 213-218 (2016)

X. Li, A. Scherf, M. Heilmaier, F. Stein: *The Al-Rich Part of the Fe-Al Phase Diagram*, J. Phase Equilib. Diffus., 37, 162-173 (2016)

Scientists at the MPIE

Dr. Poulumi Dey works as a postdoctoral fellow in the group "Adaptive Structural Materials" in the department "Microstructure Physics and Alloy Design". His research focusses on multi-principal element alloys; on the microstructure, properties and processing of bulk metallic materials & on metallic and ceramic coatings. His latest publication is about high-entropy alloys which combine high ductility and strength and consist of similar quantities of five or more different metals. The high-entropy alloy investigated by Li and his colleagues shows a metastable dual-phase structure with a substantial work-hardening ability. After these results were published in Nature (see below), Li is going to further tune the composition and microstructure to make the alloy even more applicable for industrial use.

Before his research stay at the MPIE, he did his PhD at the Shanghai Jiao Tong University in Shanghai, China, and was a visiting scholar for one year at the University of California in Davis, USA.

Selected Publications:

Z. Li, K. G. Pradeep, Y. Deng, D. Raabe, C. C. Tasan: *Metastable high-entropy dual-phase alloys overcome the strength-ductility trade-off*. Nature (2016), DOI: 10.1038/nature17981

Z. Li, X. Yang, J. Zhang, A. Shan: *Interfacial Mechanical Behavior and Electrochemical Corrosion Characteristics of Cold-sprayed and Hot-rolled Titanium/Stainless-Steel Couples*. Adv Eng Mater (2016), DOI: 10.1002/adem.201500567

Dr. Zhiming Li works as a postdoctoral fellow in the group "Computational Phase Studies" in the department "Computational Materials Design". Her main research interests are in the fields of theoretical condensed matter with a special focus on unconventional superconductors, *ab initio* determination of phase composition and *ab initio* based design of materials resistant to hydrogen embrittlement. At the MPIE she works on the *ab initio* prediction of the composition of κ carbides in FeMnAlC alloys. These steels containing κ precipitates, are especially interesting for many industrial applications as they combine high strength, ductility and corrosion resistance. Additionally, Dey investigates ways to resist hydrogen embrittlement which limits the applicability of high strength steels. In this regard, κ carbides are found to be potential hydrogen traps in Al containing high Mn steels. The interplay of hydrogen and microstructure in Ni-based superalloys is also being investigated thoroughly.

Dey got her PhD in physics in 2011 from the Indian Institute of Technology in Guwahati, India. Her thesis was about the "Disorder and spin balance induced exotic phases in weakly coupled s-wave superconductors".

Selected Publications:

M. Yao, P. Dey, J.B. Seol, P.-P. Choi, M. Herbig, R.K.W. Marceau, T. Hickel, J. Neugebauer, D. Raabe: *Combined atom probe tomography and density functional theory investigation of the Al off-stoichiometry of κ-carbides in an austenitic Fe-Mn-Al-C low density steel*. Acta Mater, 106, 229-238 (2016)

P. Dey, R. Nazarov, B. Dutta, M. Yao, M. Herbig, M. Friák, T. Hickel, D. Raabe, J. Neugebauer: *Ab initio explanation of disorder and off-stoichiometry in Fe-Mn-Al-C κ carbides*. Under review in PRB

Awards and Achievements

Dr. Martin Diehl, postdoctoral researcher in the group "Theory and Simulation", won the Young Academics Award of the Deutsche Gesellschaft für Materialkunde.

Dr. Jeongho Han, postdoctoral researcher from South Korea, was awarded a scholarship of the Alexander von Humboldt Foundation and is now working in the MPIE group „Alloy Design and Thermomechanical Processing".

Dr. Fritz Körmann, postdoctoral researcher in the group "Computational Phase Studies", received a research fellowship of the Deutsche Forschungsgemeinschaft and is now a visiting researcher at the Delft University of Technology, Netherlands.

Dr. Jianjun Li, postdoctoral researcher from China, received an Alexander von Humboldt scholarship and now works in the MPIE department "Microstructure Physics and Alloy Design".

Dr. Tong Li, worked as a visiting scholar at the University of Sydney, Australia, and is now working in the MPIE group "Atom Probe Tomography" with a scholarship of the Alexander von Humboldt Foundation.

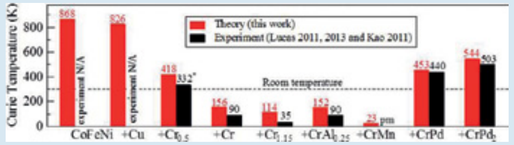

Fig. 2: *Theoretical (red bars) and experimental (black bars) Curie temperatures for various CoFeNi-based HEAs. The Curie temperatures marked with the star have been derived from an empirical linear interpolation (J. Appl. Phys. 113, 17A923 (2013)).*

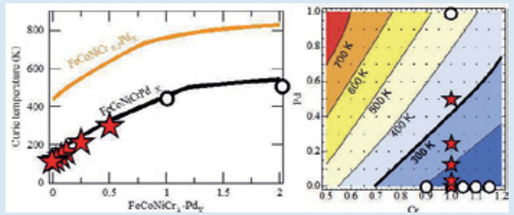

Fig. 3: *Left: Comparison between theoretically predicted (solid lines) and experimentally measured (symbols) Curie temperatures. The stars denote experimental results obtained in the present study. The agreement with the new theoretical approach is very good allowing to faithfully scan experimentally unexplored regions, e.g., the orange line showing a modified Cr content or the contour plot in the right panel showing a 2D 'treasure map'.*

namely Ag, Au, and Cu, each of which has a variety of compositions that should exhibit room temperature ferromagnetism. The developed treasure maps provide an extensive set of compounds that have not yet been synthesized and we have identified hundreds of new alloy combinations that could be useful.

This work has been done in a broad collaboration with research teams at the Rochester Institute of Technology, Air Force Research Laboratory and Delft University of Technology in the Netherlands.

Authors: Dr. Fritz Körmann, Dr. Duancheng Ma & Dr. Blazej Grabowski

Original reference: F. Körmann, D. Ma, D. D. Belyea, M. S. Lucas, C. W. Miller, B. Grabowski, M. H. F. Sluiter, Applied Physics Letters 107, 142404 (2015).

Alloy development to the nth-dimension: high entropy alloys

High entropy alloys (HEA) are multicomponent (5 or more) alloys with an equiatomic or a near equiatomic composition (e.g. $Fe_{20}Mn_{20}Co_{20}Cr_{20}Ni_{20}$). The HEA concept was introduced based on the hypothesis that the high configurational entropy (many ways to place atoms in a crystal lattice, Fig. 1) would stabilize a solid solution phase over competing intermetallic phases. This represents a new alloy exploration strategy, where instead of starting from a corner of a phase diagram with one prevalent base element, such as steels or aluminium alloys, completely new equiatomic compositions can be made. This new alloy development concept opens many doors to new alloy systems, which could be used in numerous applications and for fundamental research.

From an engineering point of view, exploring the vast compositional space of a HEA system is a significant challenge. The conventional trial and error approach is impractical for rapidly screening hundreds of new alloys. Therefore the accelerated discovery and development of HEAs relies on physical-based modelling and other simulation tools. For rapid screening and development, these tools should not only be limited to the prediction of the constituent phases, but they must also be able to predict the functional and mechanical properties of new alloys for various applications.

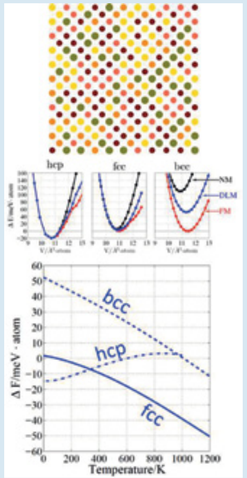

Fig. 1: *Thermodynamics of $Fe_{20}Mn_{20}$-$Co_{20}Cr_{20}Ni_{20}$ at ground state and finite temperature.*

Our HEA design team consists of members from different backgrounds, ranging from metallurgists to physicists, and the team encompasses a wide spectrum of scientific and engineering expertise. We strive for a bottom-up approach where state-of-the-art atomistic calculations (Fig. 1) guide alloy design. The team is applying and developing state-of-art theoretical, synthesis, and characterization methods. The combination of *ab initio* calculations and rapid alloy prototyping (see 01/2013 newsletter) will provide a high-throughput method for rapidly screening, producing, and characterizing new materials.

At the moment, we are developing new HEAs in three areas: (1) structural alloys exhibiting unique strengthening mechanisms, (2) tuneable magnetic cooling alloys, and (3) ultra-high-temperature structural materials.

Unique strengthening mechanisms in FeMnCoCrNi system

The $Fe_{20}Mn_{20}Co_{20}Cr_{20}Ni_{20}$ alloy was the first HEA system discovered that exhibited a single fcc solid solution phase in the as-cast state. The FeMnCoCrNi alloy exhibits high fracture toughness (200 MPa $m^{1/2}$) down to cryogenic temperatures due to the increasing stability of the hcp phase at lower temperatures, as shown in Fig. 1. The increasing stability of the hcp phase promotes the formation of mechanical twinning, which prevents crack propagation.

Following this design strategy of enhancing the fracture toughness, the composition can be further tailored for targeted properties and economic benefits. By varying the Mn content in $Fe_{80-x}Mn_xCo_{10}Cr_{10}$ alloys, we can control the fcc and hcp phase stability in order to alter the deformation mechanisms under tension (Fig. 2). *Ab initio* calculations reveal that the hcp phase becomes more stable with increasing Fe content substituted by Mn. From these efforts, we can provide alloy design guidelines for promoting hcp phase formation, which enhances strength through the TWIP and TRIP deformation mechanisms.

Tuneable magnetic refrigeration materials

Compared with the conventional gas compression-evaporation cooling process, magnetic refrigeration has drawn great attention due to its higher energy efficiency and ozone / greenhouse gas-free operation. Employing *ab initio* methods, we are able to explore a broader composition range beyond experimental compositions in order to obtain a desirable working temperature, such as room temperature for house hold refrigerators, and at the same time maximize its cooling capacity. Compared with current room temperature magnetic refrigeration materials, these alloys offer significant benefits including cheaper and less toxic elements and easy fabrication for mass production.

Refractory-based high temperature alloys

New refractory-based high entropy alloys have recently been investigated for use as high temperature materials in future gas turbine engines and hypersonic vehicles. While Mo- and Nb-based alloys have been proposed as alternative high temperature materials for gas turbine engines, these alloys do not possess an adequate balance of properties. For this reason, new refractory-containing alloys based on the HEA concept are being developed at the MPIE.

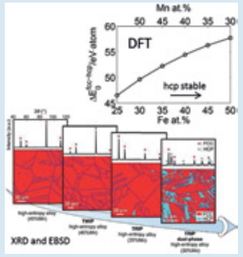

Fig. 2: *Design of Fe80-xMnxCo10Cr10 for TWIP or TRIP.*

We choose an alloy element palette consisting of Hf, Mo, Nb, Ta, Ti, V, W, and Zr in order to promote the formation of a single high temperature body-centred cubic (bcc) phase. Al, Cr, and Si are also considered in the palette to improve oxidation resistance and to promote the formation of intermetallic (IM) phases that can help strengthen the alloys. Thermodynamic calculations have been carried out for four-component alloys over a wide range of compositions in order to rapidly predict phase stability. For four-component alloys, 87,568 unique compositions over 36 alloy systems were identified.

In five- and six-component alloys, millions of unique alloy compositions among hundreds of alloy systems are possible from this elemental palette because we do not limit alloy compositions to equiatomic ratios. To analyse the data, we are utilizing advanced computational methods that include data mining, cluster analysis, and principal component analysis in order to rapidly assess higher-dimensional composition space. For example, principal component analysis can easily group alloy systems based on the predicted phase equilibria at the melting temperature, as shown in Fig. 3. From this clustering, we can easily identify alloy systems that contain similar IM phases that can be used to strengthen the alloys.

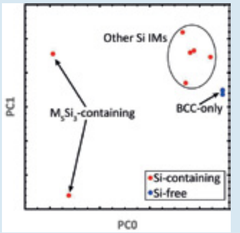

Fig. 3: *Principal component analysis of phases present in 36 alloy systems.*

The relatively new idea of high entropy alloys has motivated researchers to explore previously unknown composition space, and this drive for identifying new and useful alloys materials will undoubtedly impact the transportation and energy industries by providing novel alloys that exhibit unique properties. The proposed composition space for high entropy alloys and their derivatives is massive, and the tools and techniques we are developing here at the MPIE will help engineers to rapidly screen and further develop new material systems.

Authors: Dr. Duancheng Ma & Dr. Michael Titus

Awards and Achievements

Dr. Hong Luo, postdoctoral researcher from China, won an Alexander von Humboldt scholarship and now works in the MPIE group „Alloy Design and Thermomechanical Processing".

Prof. Dr. Jörg Neugebauer, director of the department "Computational Materials Design", was awarded the Ernst Mach Medal of the Czech Academy of Sciences.

Dr. Sai Tang, postdoctoral researcher from China, works in the MPIE group "Theory and Simulation", financed by an Alexander von Humboldt scholarship.

Dr. Michael Titus, postdoctoral researcher from the USA, received an Alexander von Humboldt fellowship and now works in the MPIE groups "Adaptive Structural Materials" and "Combinatorial Metallurgy and Processing".

Dr. Markus Valtiner, head of the group "Interaction Forces and Functional Materials", received a Starting Grant of the European Research Council and is financed with 1.5 million euros for five years.