Max-Planck-Institut für Eisenforschung GmbH

Influence of carbon on stacking fault energy

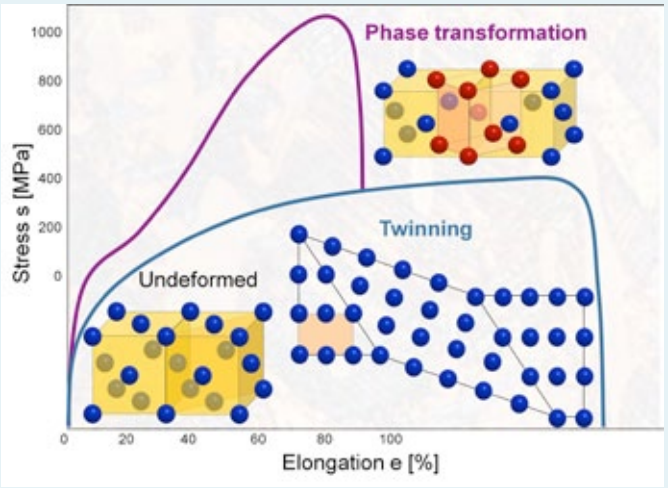
Modern steels are under a rapid development: 2500 different kinds already exist, many of them developed during the last decade. Steel grades that are strong and ductile at the same time are of particular interest for automotive applications. In order to achieve a tailored design of modern steels quantum mechanical methods in combination with modern experiments play a key role.

High manganese steels are a major focus of research activities at the MPIE because of their high strength and ductility. These properties are crucial for the safety of modern cars. Detailed understanding of mechanisms occurring on the atomic scale during transformation processes is of main interest.

Depending on their chemical composition high manganese steels can compensate mechanical loads by sophisticated mechanisms on the atomic scale: On the one hand, twins can be formed in the crystal lattice (TWIP effect = twinning induced plasticity). On the other hand, the crystal structure can change locally from austenite to martensite (TRIP effect = transformation induced plasticity). Which of these effects occur depends on the energy required to shift the atomic layers with respect to another: the stacking fault energy (SFE).

The role of carbon in the SFE

High manganese steels usually have a carbon content of up to 1 wt.%, but in the literature contradictory data are reported for the dependence of the SFE on the carbon concentration. TEM experiments show only little correlation whereas XRD indicates a strong correlation between SFE and carbon content. With novel theoretical methods developed in the department Computational Materials



Stress-strain curves for steels showing the TRIP and TWIP mechanism.

EDITORIAL

Dear Reader,

In this newsletter all three MPIE departments present a current research project. The influence of carbon on the stacking fault energy is one of the major topics as well as the foundation of a new scientific group that develops adaptive structural materials. "ECCO$_2$" - a new project funded through the federal ministry of education and research is also presented. The project deals with the electrochemical conversion of carbon dioxide. Additionally, some recent achievements of our scientists are presented.

Enjoy reading and best regards,

Prof. Dr. Dierk Raabe
(Chief Executive, MPIE)

Awards and Achievements

Dr. Oana Cojocaru-Mirédin successfully applied for the competition "NanoMatFutur" arranged by the German Federal Ministry of Education and Research. She now has the opportunity to lead her own research group about the optimisation of solar cells based on 3D chemical analysis on the atomic scale.

Björn Lange, Josef Meier and **Albert Glensk** (from the left) participated in this year's 62nd Lindau Nobel Laureate Meeting.

Christiane Jacobs received the Azubipreis of the Max Planck Society as the best trainee in material testing in the region Duisburg and Solingen 2011.

Dr. Fritz Körmann was awarded the Otto Hahn Medal for his dissertation titled "Magnetic systems studied by first-principles thermodynamics" at the University of Paderborn.

Dr. Sumantra Mandal from the Indira Gandhi Centre for Atomic Research (India) received an Alexander von Humboldt scholarship and works on the evaluation of the 3D interfacial segregation behaviour using site specific local electrode atom probe tomography and 3D EBSD-EDX studies.

Design of Prof. Jörg Neugebauer, the physics of steel can be modelled accurately on the computer. With *ab initio* methods (*ab initio* = starting from the beginning) scientists can calculate energies of crystal lattices without any experimental input.

By solving an approximation of the quantum-mechanical Schrödinger equation, which is the basis of *ab initio* methods, information about the physical, chemical and electronic origin of atomic interactions is obtained. "The numerical complexity is enormous", states Dr. Tilmann Hickel, group leader in the department, "but we can manage systems of up to several hundred atoms now." And calculations in Hickel's group indeed show that there is a strong increase of the SFE with the carbon content. It is a definite advantage of ab initio methods that one can consider single effects separately, which is often not possible with experiments. Nevertheless, experimental validation of the theoretical results was highly desirable.

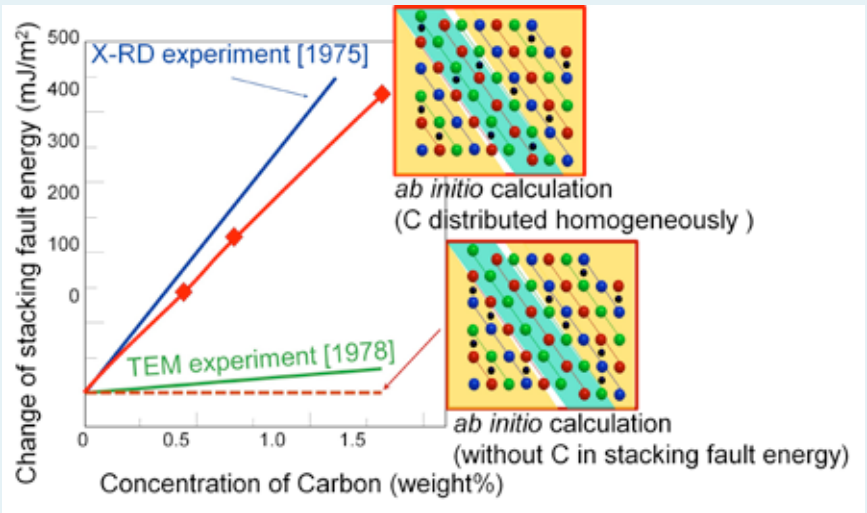
Theory and experiment go hand in hand

The ab initio calculations were performed under the assumption that carbon is homogeneously distributed in the crystal structure. This assumption is correct at room temperature, where carbon cannot diffuse between iron and manganese atoms.

Things change, of course, when an electron beam hits the surface during TEM measurements. This can easily transfer energy to the carbon atoms, causing a local temperature increase of up to 200-350 °C and drastically changing the diffusion rate of carbon atoms. *Ab initio* calculations showed that stacking fault regions caused by twinning are energetically less favourable environments for carbon, so at higher temperatures carbon diffuses a few atomic layers away and thus its influence on the SFE is diminished. This diffusion is only feasible if the energy of the carbon atoms is high enough to overcome the kinetic barriers, as is the case if the surface is bombarded with a high-energy electron beam during TEM measurements. Under normal conditions, as assumed in the calculations, the carbon atoms are immobile.

In order to prove this hypothesis, TEM measurements were performed by Dr. Stefanie Sandlöbes in which the samples were cooled with liquid nitrogen. As soon as the cooling was removed, the SFE clearly decreased, which proves the hypothesis. Repeated cooling did not change the SFE value, because the carbon atoms do not return to their former positions, which remain energetically unfavourable.

The experimental validation was thus successful and proves once more the efficient combination of experiment and theory.



Data obtained from experiments and ab initio calculations on the dependence of the SFE on the carbon content.

Smart Alloys

To create smart alloys you need even smarter scientists - Dr. Cem Tasan and Dr. Blazej Grabowski are the heads of the new group “Adaptive Structural Materials“, funded by the European Research Council (ERC) Advanced Grant „SmartMet“. In this interview they talk about the target of their research and explain why two group leaders are necessary for this project.

Dr. Loschen (L): What does “Adaptive Structural Materials“ actually mean?

Dr. Tasan (T): Structural means that materials are used for generating structures, e.g. automotives, bridges, buildings etc. “Adaptive“ is the actual key word here: we aim at designing materials that are able to adapt to varying external conditions.

L: How do you achieve this adaptive behaviour?

T: We plan to introduce metastable phases into the material that transform when they experience e.g. stress.

Dr. Grabowski (G): Imagine a crack propagating in a material: when the crack tip, which exerts a lot of stress to its environment, reaches one of those metastable nanoparticles, the stress causes the metastable nanoparticle to transform to a stronger phase and thus stops the crack from expanding.

L: Why are there two scientists as a head of this group?

G: Cem, the experimentalist and me, the theoretician, will work complementarily. Metastable phases are experimentally difficult to analyse, but with DFT methods, these are methods based on quantum-mechanical principles, we can set the parameters to a point where the system is metastable and calculate the properties under the given conditions. Parameters such as temperature, stress or volume can be changed step by step until the phase transforms. Theory can predefine not only conditions but also compositions and thus reduce time and material needed for finding the optimum alloy. On the other hand, we need the experimentalists to validate our calculations.

L: But DFT methods are usually restricted to 0 Kelvin?

G: The department “Computational Materials Design“ has been developing various methodologies to include finite temperatures into the DFT description, thus enabling us to calculate systems up to their melting point with high accuracy and efficiency.

L: How are the materials produced in the end?

T: We closely collaborate with our metallurgy and processing group. This unique combination is only possible at the MPIE where you have all these facilities under one roof: Design (theoretical and experimental), production and analysis.

L: How does the interplay between theory and experiment work?

G: At first we discuss possible starting points and work in parallel. After a few results we discuss which direction to take, we reach our aim by small iterations.

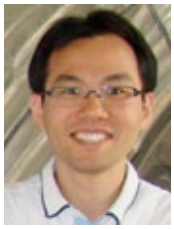
L: What composition do you have in mind to start with?

T: The aim is of course an iron based alloy, but right now we are not restricting ourselves to any specific elements. Our first investigations are dedicated to a specific Ti-based alloy which is known as “gum metal“ because it reveals ideal plasticity. The mechanism is complicated but we try to understand it with in-situ microstructural analysis and simulation and then we transfer this knowledge to other, e.g. iron alloys.

Awards and Achievements

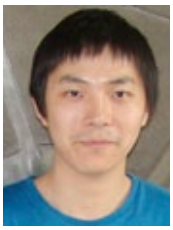
Dr. Ross Marceau from the University of Sydney (Australia) received a fellowship from the Alexander von Humboldt Foundation and chose the MPIE for his research project on the relationship between the atomic structure of TWIP steels and their mechanical properties.

Prof. Dr. Jörg Neugebauer, head of the department Computational Materials Design, was elected into the review board 302 “Chemical solid state and surface research” of the DFG.



Dr. Sang Yong Shin, Korean grantee of a scholarship from the Alexander von Humboldt Foundation, works on deformation and fracture mechanisms in high strength Fe-Mn-Al-C light weight TRIPLEX steels.

Natalie Tillack completed her Master thesis about first-principles investigations of oxide dispersion strengthened steels at the University of Bochum with an excellent result.



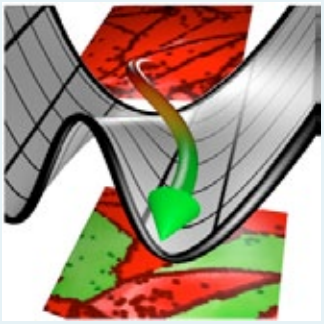
Dr.-Ing. Han Zhang from the Tsinghua University (China) received a stipend from the Alexander von Humboldt Foundation and works on the super plasticity of ultrahigh strength steels and their performance optimisation.

Scientists at the MPIE

Dr. Frank Uwe Renner is head of the group "Interface Structures and High-Temperature Reactions" at the department "Interface Chemistry and Surface Engineering" since 2007. During his PhD Renner started to look at initial stages of electrochemical corrosion mainly employing in-situ X-ray diffraction using synchrotron light. Currently, he focuses on nanometer and atomic-scale structural studies of surfaces and interfaces in contact with electrolytes and corrosive gas atmospheres. His current research projects include amongst others dealloying reactions and selective dissolution of alloys, corrosion of amorphous and nanocrystalline steels, and experiments at synchrotron light sources.

Dr. Mira Todorova, born in Sofia (Bulgaria), joined the department "Computational Materials Design" at the end of 2006. During her dissertation "Oxidation of palladium surfaces" she worked in Berlin, before going to Sydney (Australia) for a two years postdoc, partly funded by a fellowship from the Fritz-Haber-Institut of the Max-Planck-Society. Todorova's studies combine electronic structure calculations with thermodynamic concepts, focusing among others on surface structures and their stability, oxidation and corrosion.

L: What is the biggest challenge for each of you within the project?



Logo of the group showing the intimate coupling between experiment and theory: The red fields show EBSD images of a material before and after phase transformation. The black/grey surface shows the energy dependence of a stable and unstable phase.

G: Taking into account magnetic structures especially when it comes down to Fe-based alloys is a challenge, but our department has already been working on several approaches. Another challenge is finding the most accurate and efficient approach for simulating instable phases and calculating the chemical disorder, as typical DFT calculations are limited to only several 100 atoms. Advantageous in this respect is the expertise I have developed over the recent years in computing DFT based phase diagrams.

T: Analysing transformation processes is always a challenge. We have the advantage that we can employ many in-situ techniques here, but still the time resolution of the analytic instruments is not always sufficient. The second challenge is the spatial resolution: nanoparticles are difficult to analyse, but fortunately here at the MPIE we have strong tools available such as the atom probe tomography. In a nutshell, it is a risky project, but it seems that we have all the necessary tools at hand here to overcome these challenges.

Short CVs:

Dr. Blazej Grabowski: diploma in physics at University of Paderborn, 2005-2009 doctorate in the department "Computational Materials Design" of Prof. Neugebauer, focusing on finite temperature DFT, 2-year scholarship from the "Nachwuchsakademie" of the Deutsche ForschungsGesellschaft, one year post-doc at Lawrence Livermore National Laboratory, CA, USA, return to the MPIE in April 2012.

Dr. Cem Tasan: degree in materials science and metallurgical engineering and master in polymer nanocomposites from Middle East Technical University Ankara, until 2010 PhD in TU Eindhoven in the group of Prof. Mark Geers (on micro-mechanics of damage and in-situ testing), post-doc at MPIE in the department "Microstructure Physics and Alloy Design" of Prof. Raabe, then accepting the current position.

Imprint

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CO_2 can do
Investigating catalysts for the electrochemical conversion of carbon dioxide

More than 832 million tons of carbon dioxide (CO2) were emitted in Germany alone in 2010. Even if Germany was able to fulfill the Kyoto protocol in 2008 there is still a lot to be done. Besides avoiding the emission or capturing and storing CO2 waste, one could also commence to use it as a precious chemical resource.

Converting CO2 into methanol and other valuable chemicals (Cn products) is still a major challenge. The electrochemical reduction of CO2 to useful fuel or chemical feedstock molecules is associated with severe problems such as low activity, deterioration of the catalyst over time and lack of product selectivity. Finding potential electrocatalytic materials to improve the reaction is considered as the most crucial point, but simple trial and error approaches with conservative and separated investigations have not been successful so far. Dr. Karl Mayrhofer and his "Electrocatalysis" group at the MPIE make an innovative, combinatorial approach: by combining several insitu investigation techniques they are searching for new catalyst materials with good activity, selectivity and stability.

The scanning flow cell

The SFC allows a high-throughput electrochemical surface analysis.

"The heart of the set-up is the scanning flow cell", states Mayrhofer, who was just recently awarded a grant of more than 1 Mio € by the Federal Ministry of Education and Research (BmBF). The scanning flow cell (SFC) allows for a high-throughput electrochemical surface analysis down to the micro-meter range. The SFC is made up of a microfluidic system with tiny channels in which the counter and the reference electrode are placed. The capillary is positioned onto the sample, which is at the same time the working electrode, thus forming a micrometer size electrochemical cell. Automatically the capillary moves to the next position where the next measurement is taken under the exact same conditions. "With the SFC we cannot only determine optimal reactor operation conditions in a fast way, or quickly screen for active material compositions - we can even analyse the reaction products online to predict stability and selectivity in parallel ", says Mayrhofer.

Online investigation of reaction products

The electrolyte flowing through the capillary contains the mixture of products, side products and components from catalyst deterioration. They are investigated by coupling the SFC with a Differential Electrochemical Mass Spectrometer (DEMS) and an Inductively Coupled Plasma Mass Spectrometer (ICP-MS), both highly sensitive techniques. With the DEMS it is possible to obtain data on the sensitivity of the reduction of CO2 and the dependence of the efficiency of the process vs. time. Coupling SFC-ICP/MS enables the online investigation of the potential-dependent stability of the electrodes, the most crucial part for electrocatalyst development. The combinatorial screening will allow a flexible approach with respect to the anticipated materials, which includes several material libraries of binary and ternary material combinations. Screening 20 full libraries per month - this is the ambitious goal. In the end the best performing materials will be used for further investigations and up-scaling processes within industrial cooperations, which will ideally bring utilisation of CO2 one step closer to implementation.

Selected Publications

Computational Materials Design:

T. Hickel, B. Grabowski, F. Körmann, J. Neugebauer: Advancing density functional theory to finite temperatures: methods and applications in steel design, Journ. Of Phys. Cond. Matter, 24, 5, 053202, (2012).

U. Aydin, L. Ismer, T. Hickel, J. Neugebauer: Solution enthalpy of hydrogen in fourth row elements: Systematic trends derived from first principles, Phys. Rev., B85, 155144, (2012).

Interface Chemistry and Surface Engineering:

J. C. Meier, C. Galeano, I. Katsounaros, A. A. Topalov, A. Kostka, F. Schüth, K. J. J. Mayrhofer: Degradation mechanisms of Pt/C Fuel Cell Catalysts under simulated start – stop conditions, ACS Catalysis, 2, 832-843, (2012).

F. U. Renner, G. N. Ankah, A. Pareek: In-situ surface-sensitive X-ray diffraction study on the influence of iodide over the selective electrochemical etching of Cu3Au (111), Surf. Sci., 606, 9-10, L37-L40, (2012).

Microstructure Physics and Alloy Design:

S. Sandlöbes, M. Friak, S. Zaefferer, A. Dick, S. Yi, D. Letzig, Z. Pei, L.-F. Zhu, J. Neugebauer, D. Raabe: The relation between ductility and stacking fault energies in Mg and Mg-Y alloys, Acta Mat, 60, 6-7, 3011-3021 (2012).

H. Springer, D. Raabe: "Rapid alloy prototyping: Compositional and thermp-mechanical high throughput bulk combinatorial design of structural materials based on the example of 30Mn-1.2C-xAl triplex steels", Acta Materialia 60, 4950-4959, (2012).

News and Events

Dr. Kai de Weldige new head of administration

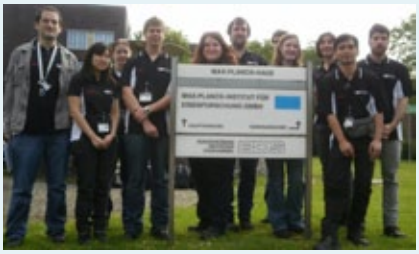
Dr. Kai de Weldige is the new administrative head and executive at the MPIE. He studied physics at the University of Bonn and did his PhD at the MPIE and the University of Dortmund in 1996. His PhD dealt with the surface analysis of the self-organisation of N-alkanethiols under potential control. After that he worked for the "Deutsches Stiftungszentrum", a consultancy centre for establishing and administrating scientific foundations. Dr. De Weldige is also specialised in project and change management as well as in optimisation of workflows.

Workshop on hydrogen embrittlement in steels

On June 25th the MPIE organised a workshop on hydrogen embrittlement in steels as part of a series of topical one-day meetings at the institute. The intention is to bring together leading experts from academia and industry to enable in-depth discussions of fundamental and applied research regarding both current and potential research areas. The programme included topics such as modelling of plasticity mechanisms, hydrogen-dislocation interactions and advances in the characterisation of alloy design as well as a lab session.
If you would like to be informed about upcoming workshops, please write an e-mail to research.coordination@mpie.de

International student visits at the MPIE

Bachelor students of chemistry, applied physics and metallurgy from the Netherlands and Australia paid a visit to the MPIE in the first half of this year. The groups were interested in seeing how an international research institute works and in getting into contact with scientists in the field of material sciences. Several highlights were presented such as kinetic Monte-Carlo methods for electrical steels, the transmission electron microscope and the high temperature laboratory. In addition to that, the MPIE scientists explained how material corrosion and fundamental electrocatalysis work.



Group photo of the students from the Western Australian School of Mines, who visited the MPIE in June.

MPIE took part at the Thyssen Krupp Ideenpark in August

The MPIE and the RWTH Aachen took part at the ThyssenKrupp Ideenpark from August 11th-23rd. The SFB "Steel – *ab initio*" was presented to a broad public showing how computer simulations contribute to the development of new steels. Visitors had the chance to build models of crystals and to do experiments with different types of steel wires. The Ideenpark is a technical fair for everybody and took place at the Grugapark in Essen.

Upcoming Events

Materials SurMat Day in November

The MPIE doctoral programme SurMat and the Materials Research Department of the Ruhr University Bochum (RUB) are organising a workshop from November 8th-9th in the event centre of the RUB. The programme includes talks covering all range of topics dealing with materials science, such as physical properties of materials, materials for sustainable energy, microstructure and phase transitions and surface engineering. A poster session will show research activities from all involved research groups.
The programme is available on: www.mpie.de or here http://www.rd.ruhr-uni-bochum.de/mrd

For registration please write an e-mail to: surmat@mpie.de

Selected Lectures

J. Neugebauer: "Fully Ab Initio Determination of Free Energies - Where Do We Stand?", TMS, March 13th 2012, Orlando, USA.

J. Neugebauer: "Vacancy concentrations from 0K to the melting temperature in unary fcc metals: Discovery of large non-Arrhenius effects". Calphad Conference June 3th-8th 2012, Berkeley, USA.

D. Raabe, D. Ponge, P. Choi, J. Millán, S. Sandlöbes, L. Yuan, C. Tasan, E. Planchet, S. Zaefferer, T. Hickel, M. Friak, A. Dick, G. Inden, J. Neugebauer: "Designing nanostructured metallic bulk alloys via first principles simulations and atomic scale characterization: The basis of modern manufacturing". Plenary Lecture, NIMS Conference June 4th 2012, Tsukuba, Japan.

D. Ponge, J. Millán, L. Yuan, S. Sandlöbes, A. Kostka, P. Choi, T. Hickel, J. Wittig, G. Inden, H. Assadi, R. Kirchheim, J. Neugebauer, D. Raabe: "Nanostructuring of 1 Mio tons: Designing ultrastrong and ductile steels". Plenary Lecture, DPG Spring Meeting (Deutsche Physikalische Gesellschaft) March 28th 2012, Berlin, Germany.

M. Stratmann: "Electrochemistry – rebirth of a science". Physics colloquium, institute for experimental physics and institute for quantum optics and -informatics, University of Innsbruck, Österreichische Akademie der Wissenschaften, May 15th 2012, Innsbruck, Austria.

M. Stratmann: "Electrocatalysis – How to answer major questions in fundamental research". Keynote Lecture, Closing Symposium of the Collaborative Research Centre SFB 558 "Metal-substrate interactions in heterogeneous catalysis", April 16th-18th 2012, Bochum, Germany.