## Scientists at the MPIE

**Dr. Baptiste Gault** is the new head of the group *Atom Probe Tomography*. Atom probe tomography is a cutting-edge microscopy and microanalysis technique that maps compositional variations in three-dimensions with near-atomic resolution. The group is investigating an array of materials that includes e.g. ferrous, aluminium, titanium, nickel & cobalt alloys as well as semiconductors that find application in photovoltaic applications. Insights from atom probe tomography help advance understanding the direct link between a material's nanostructure, e.g. the composition of phases, the segregation of species at *crystalline defects*, the distribution of dopants in semiconductors, and its intrinsic physical and mechanical properties. This understanding can then be used to guide the design of new, or optimise existing materials.

Before being group leader at the MPIE, Gault has pursued research in the institutions that have most contributed to the development of the technique: he obtained his PhD in Rouen in France (2006), followed by research scientist and research fellow positions at the University of Sydney and the University of Oxford (2007-2012). In 2012, he obtained a faculty position at McMaster in Canada, but then moved onto a position of senior publisher and associate editor of Materials Today at Elsevier Ltd. During his time in publishing, Gault was also a visiting academic at the University of Oxford, UK, where he remained involved in atom probe research.

Gault's contribution spans the development of new instrumentation with the implementation of ultrafast laser onto atom probes, new methods to enhance the spatial integrity of atom probe and extract structural information from the data, as well as the microstructural study of a range of engineering alloys (Al, Zr, steel), semiconductors (Si, III-V) and oxides.

**Prof. Jochen M. Schneider** is professor and chair of Materials Chemistry at the RWTH Aachen University since 2002. He has been appointed Fellow of the Max Planck Society and leads since October 2015 a group on self-reporting materials at the MPIE. The group's aim is to combine theoretical as well as experimental methods to design materials which report a change in performance through property changes. This property alteration is based on changes in their chemical composition at the atomic level and/or structure and will be detected during application, enabling direct damage assessment. Initially, materials with periodic charge density distributions are in the research focus. Based on these investigations and quantum mechanical calculations, self-reporting materials will be developed by substituting and adding elements to the material in question. The realization of this concept will enable industry 4.0 on an atomic scale.

Schneider studied materials engineering in Germany, the United Kingdom and the USA and received his PhD in 1998. Subsequently, he worked as post doc at the Lawrence Berkeley National Laboratory in Berkeley, California, USA, and as an assistant professor and docent at the Linköping University, Sweden. He was awarded the Sofja Kovalevskaya Prize for outstanding materials research by the president of the Alexander von Humboldt Foundation in 2001. Moreover, he was appointed fellow of the American Vacuum Society (AVS) in 2013.

## Selected Publications

**Computational Materials Design:**

X. Zhang, T. Hickel, J. Rogal, S. Fähler, R. Drautz, J. Neugebauer: *Structural transformations among austenite, ferrite and cementite in Fe-C alloys. A unified theory based on ab initio simulations*, Acta Mat, 99, 281-289 (2015)

M. Friák, D. Tytko, D. Holec, PP Choi, P. Eisenlohr, D. Raabe, J. Neugebauer: *Synergy of atom-probe structural data and quantum-mechanical calculations in a theory-guided design of extreme-stiffness superlattices containing metastable phases*. New J. Phys., 17, 093004 (2015)

**Interface Chemistry and Surface Engineering:**

H.-W. Cheng, P. Stock, B. Moeremans, T. Baimpos, X. Banquy, F. U. Renner, M. Valtiner: *Characterizing the Influence of Water on Charging and Layering at Electrified Ionic-Liquid/Solid Interfaces*. Adv. Mat. Interf., 2, 1500159 (2015)

C.H. Choi, C. Baldizzone, J. Grote, A.K. Schuppert, F. Jaouen, K.J.J. Mayrhofer: *Stability of Fe-N-C Catalysts in Acidic Medium Studied by Operando Spectroscopy*. Angew. Chem. Int. Ed., 54, 43, 12753 – 12757 (2015)

**Microstructure Physics and Alloy Design:**

M. Kuzmina, M. Herbig, D. Ponge, S. Sandloebes, D. Raabe: *Linear complexions: Confined chemical and structural states at dislocations*. Science, 349, 1080-1083 (2015)

A. Stoffers, B. Ziebarth, J. Barthel, O. Cojocaru-Mirédin, C. Elsässer, D. Raabe: *Complex Nanotwin Substructure of an Asymmetric Σ9 Tilt Grain Boundary in a Silicon Polycrystal*. Phys. Rev. Lett., 115, 235502 (2015)

**Structure and Nano-/Micromechanics of Materials:**

S. Brinckmann, G. Dehm: *Nanotribology in austenite: Plastic plowing and crack formation*. Wear, 338/339, 436–440 (2015)

R. Raghavan, J.M. Wheeler, T.P. Harzer, V. Chawla, S. Djaziri, K. Thomas, B. Philippi, C. Kirchlechner, B.N. Jaya, J. Wehrs, J. Michler, G. Dehm: *Transition from shear to stress-assisted diffusion of copper–chromium nanolayered thin films at elevated temperatures*. Acta Mat, 100, 73–80 (2015)



## Selected Talks

**Computational Materials Design:**

J. Neugebauer: *Ab initio guided design of structurally and thermodynamically complex materials*. PSIK Conference, San Sebastian, Spain, 9 – 10 Aug 2015

J. Neugebauer: *Towards automated toolsets for computing high-precision free energies by ab initio approaches*. MS&T, Columbus, USA, 4 – 8 Oct 2015

**Interface Chemistry and Surface Engineering:**

M. Valtiner: *Direct Measurement of Single Molecule Interaction Free Energies at Solid/Liquid Interfaces*. AICHE 2015 meeting, Salt Lake City, USA, 11 Nov 2015

C. H. Choi: *In-situ investigations of electrocatalyst degradation*. 66th meeting of the International Society of Electrochemistry, Taipei, Taiwan, 4- 9 Oct 2015

**Microstructure Physics and Alloy Design:**

R. Kuzmina, M. Herbig, D. Ponge, S. Sandlöbes, D. Raabe: *Linear Complexions: Confined Chemical and Structural States at Dislocations in Metallic Alloys*. MRS Fall Meeting, Boston, USA, 2 Dez 2015

D. Raabe , P.-P. Choi, O. Cojocaru-Miredin, I. Povstugar, C. Liebscher, Z. Tarzimoghadam, D. Ponge, E. Jägle, C. Scheu, J.-H. Kim, G. Eggeler, M. Herbig, A. Stoffers, S. Sandlöbes: *Big challenges solved by observing small atoms*. Workshop on Helmholtz Materials Characterization Platform, Research Center Jülich, Germany, 20 Nov 2015

**Structure and Nano-/Micromechanics of Materials:**

C. Kirchlechner, P. J. Imrich, B. Völker, N. J. Balila, R. Raghavan, T. P. Harzer, G. Dehm: *Small Scale Mechanical Testing and its Impact on Materials' Applications*. 14th IUMRS - International Conference on Advanced Materials, Jeju Island, Korea, 25 – 29 Oct 2015

G. Dehm, T. P. Harzer, B. Völker, P.J. Imrich, Z. Zhang: T*owards New Insights on Interface Controlled Materials by Advanced Electron Microscopy*. Frontiers of Electron Microscopy in Materials Science Meeting (FEMMS 2015). Lake Tahoe, USA, 13 – 18 Sep 2015

## News and Events

### Selected Past Events

**25 September 2015: Researchers' Night in Düsseldorf**

The Researchers' Night 2015 took place in the heart of the City Düsseldorf. The MPIE presented its research results on titanium niobium hip implants and how computer simulations help in improving these alloys. Moreover, a three dimensional printer was presented as an eye-catcher to explain the MPIE's work on alloys for additive manufacturing and how this relatively new technique could be used both for industrial and medical-technical needs.

**18 November 2015: Career Talk – BASF meets MPIE**

Representatives of BASF Coatings gave a talk on career opportunities for scientists at BASF which is one of the world's largest chemical companies. Dr. Patrick Keil, an MPIE alumni and now working at BASF Coatings, reported on his first-hand experience of joining and working for the company as a research scientist. This event is part of a series of career talks taking place at the MPIE and organized by the PhD representatives giving young researchers the possibility to get in contact with possible future employees in industry.

**25 November 2015: KopfSalat with Prof. Gerd Gigerenzer**

Prof. Gerd Gigerenzer, director of the Max Planck Institute for Human Development, gave a talk about rational decision making and how to deal with risks and uncertainties. Around 140 people from in and outside Düsseldorf took part at this event at the MPIE which is part of a series of events with changing topics named KopfSalat.

### Selected Upcoming Events

**3 May 2016: KopfSalat with Dr. Melanie Wald-Fuhrmann**

Dr. Melanie Wald-Fuhrmann, director at the Max Planck Institute for Empirical Aesthetics will give a talk on the various tastes of music and their relation to character properties of individuals. The talk is part of Kopfsalat – a series of events with changing topics.
http://kopfsalat.mpie.de

**30 May – 3 June 2016: Conference on "Soft Matter at Aqueous Interfaces"**

The conference focusses on the properties of soft matter at interfaces between an aqueous phase and a solid, liquid or gaseous second phase. The event will cover the topics: adsorption of soft matter at aqueous interfaces, in-plane structure and 2D-systems & dynamics and flow at interfaces. The conference takes place in Crete, Greece.
https://somatai.eu/events/somatai-conference-2016/

**4 – 5 July 2016: Workshop on "Alloys for Additive Manufacturing"**

There will be a workshop held at the MPIE about new alloys for Additive Manufacturing (AM). It focuses on the origins for the low processability of some existing alloys as well as the design of new alloys tailor-made for AM such as advanced tool steels, aluminium alloys, nickel-base superalloys and composites. The intention is to bring together scientists from academia and industry in a workshop format to enable in-depth discussions of fundamental and applied research.

**Imprint**

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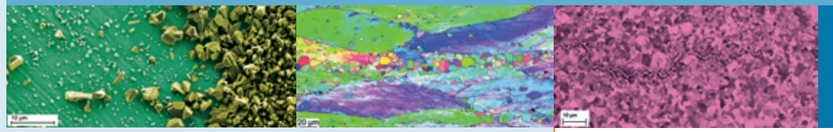

## Where is carbon?

## How dislocations help to decompose cementite and supersaturate ferrite

Mechanical properties of steels are strongly influenced by interactions between dislocations and solute atoms, with carbon (C) being the most important solute atom. A dislocation is a 1-dimensional defect that introduces a strain field into the steel by locally destroying the perfect atomic arrangement. C atoms are attracted by dislocations and, as a consequence, they form an atomic cloud around each dislocation - known as Cottrell atmosphere - critically influencing the mechanical properties of steels. The presence and activity of dislocations also influences the thermodynamic stability of C atoms and changes the local chemical composition within steels.

A steel with great technological importance that critically depends on C-dislocation interactions are severely deformed pearlitic wires with up to 7 GPa strength. Experimental observations have revealed an exponentially increasing density of dislocations and a decomposition of cementite -the central iron carbide in steels- during the severe plastic deformation. The original stoichiometric C-concentration of 25 at.% in cementite substantially decreases (to <10 at.%) and the C atoms redistribute within the ferrite lamellae. This redistribution results in a C supersaturation of ferrite, which is in extreme discrepancy with empirical predictions.

Resolving the discrepancy with experiment and empirical approaches alone is impossible due to the complex microstructure. We have therefore developed and applied a multiscale approach rooted in accurate atomistic simulations to tackle the problem. The main result of our calculations is schematically displayed in Fig. 1. Pearlite consists

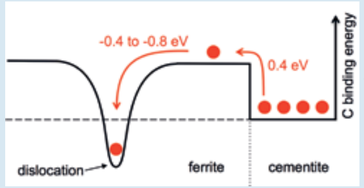


Fig. 1: *Schematic of the C binding energy profile in a deformed pearlite microstructure. A ferrite phase including a dislocation (indicated by the dip in the black solid line) and a cementite phase populated with carbon atoms (red balls) are shown.*

## EDITORIAL

Dear Colleagues and Friends of the MPIE,

One of the strongest engineering materials is pearlite, a material which gains its strength through severe plastic deformation. At the same time the exact mechanisms behind this strength are still not known, thus the design of ultrahigh strength materials is retarded. This newsletter edition provides latest insights on experimental and theoretical approaches to unravel the strengthening mechanisms. Furthermore, we are welcoming two new group leaders, Dr. Baptiste Gault from Oxford University and Prof. Jochen Schneider from RWTH Aachen, who have recently been appointed heads of the groups "Atom Probe Tomography" and "Self-Reporting Materials", respectively. Both colleagues are briefly introduced in the section "Scientists at the MPIE".

Enjoy reading and best regards,

Prof. Dr. Dierk Raabe, Chief Executive, MPIE

## Awards and Achievements

**Dr. Pascal Beese-Vasbender**, post-doctoral student in the group Electrocatalysis, won the Deutsche Studienpreis of the Körber Foundation for his doctoral thesis about bio corrosion and energy conversion / - storage.

**Christian Broß**, apprentice in the field of material testing, won the Apprentice Prize of the Max Planck Society.

**Dr. Christoph Kirchlechner**, leader of the group Nano-/ Microme-chanics of Materials, became member of the Beamtime Re-view Panel of the BESSY synchrotron source.

**Dr. Alena Michalcová**, postdoc in the group Intermetallic Materials, received the "1st Place according to expert public – vox populi" at the competition "The most beautiful colour or black-and-white micrograph of non-ferrous metals" at the Aluminum and Non-Ferrous Metals Conference 2015 in Bystrice nad Pernstejnem, Czech Republic.



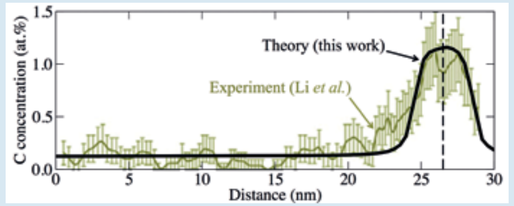


Fig. 2: *Local carbon concentration around a defect (marked by the vertical dashed line) in a supersaturated ferrite phase after wire drawing (true strain ε = 2). Experimental data are from atom probe tomography measurements (Acta Mat 59 (2011) 3965).*

of ferrite (to the left of figure) and cementite (right) with C atoms (red balls) mainly placed in the cementite phase in thermodynamic equilibrium. To bring a C atom into the ferrite phase costs an energy of 0.4 eV which is too large to be overcome at realistic temperatures. However, the situation changes close to the dislocation (indicated by the dip in the solid black curve in Fig. 1), because of the strong C-dislocation binding energy in the range of -0.4 to -0.8 eV. The C-dislocation binding energy can compensate the original cost of bringing a C atom into ferrite, and the dislocation thus acts as an attractive sink for C atoms helping to decompose cementite and supersaturate ferrite.

Knowing the C-dislocation binding energies, we were able to calculate the C concentration profile around the dislocation by using an appropriate statistical (Fermi-Dirac) distribution. The result is shown in Fig. 2 (black line) in comparison to experimental results (green data set) indicating a good agreement. By integrating over the computed C concentration profile in Fig. 2, we have derived the number of C excess atoms per dislocation. The result depends on the total C concentration, but a value of 20 C/nm of dislocation line length reflects a reasonable average. Using additionally the experimentally observed dislocation density, we estimated the increase in C content in the ferrite phase due to dislocations. The result is shown in Fig. 3 by the light gray shaded area. We observe a good agreement of our estimate (black solid line) with the experimentally determined concentrations (green squares), indicating that dislocations play an important role in stabilizing the C supersaturation of the ferrite phase during wire drawing.

Authors: Dr. Gh. Ali Nematollahi & Dr. Blazej Grabowski

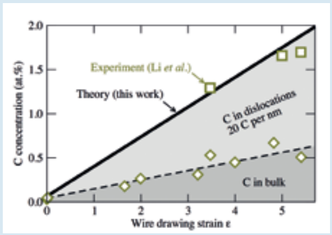


Fig. 3: *Total carbon concentration (green squares and solid black line) in ferrite as a function of the true strain due to wire drawing. The green diamonds and the black dashed curve show the experimentally observed and calculated C concentrations, from the bulk lattice, i.e., excluding the contribution of dislocations.*

# Nanocrystalline bulk steel with near theoretical strength: Revealing the origin of its strength at the atomic scale

There is a steady demand of steel wires with higher strength for engineering applications. Grain refinement through severe plastic deformation (SPD) is among the most promising fabrication techniques to obtain ultrahigh-strength nanostructured materials at the industrial scale. By severe drawing of a pearlitic steel wire an extreme tensile strength of 7 GPa can be reached. The aim of this project is to unravel the strengthening mechanisms in order to understand the exceptional strength of cold-drawn pearlitic steel wire and thus establishing new strategies for the design of ultrahigh strength materials. Two research groups collaborate on this project combining experimental techniques of atom probe tomography (APT) and synchrotron X-ray diffraction (XRD). Dr. Yujiao Li from the Microstructure Physics and Alloy Design (MA) Department uses APT for sub-nanometre scale characterization of pearlitic steel wire microstructure. Dr. Soundes Djaziri from the Structure and Nano-/ Micromechanics of Materials (SN) Department uses synchrotron XRD to study in detail the crystal structure of the pearlitic steel wire during the drawing process.

SPD is a scientifically and technologically important processing technique for producing ultrahigh-strength nanostructured materials, as shown in Fig.1 for the case of pearlitic steel wires where the tensile strength increases with increasing true drawing strain εd from 1 GPa at εd = 0 to nearly 7 GPa at εd = 6.52. The comparison of the maximum tensile strength of nearly 7 GPa with literature data for iron whiskers and other ultrahigh-strength materials reveals that cold-drawn pearlite exhibits the highest tensile strength among all known ductile bulk materials.

Cold drawing reduces the inter-lamellae spacing of pearlite, and consequently reduces the mean free path of lattice dislocations, which governs the Hall-Petch hardening and is mainly responsible for the strength of cold-drawn wires at true wire strains εd < 4. With further drawing, strong cementite decomposition occurs and phase boundaries partially disappear. Surprisingly, the strength of the material yet continuously increases with εd up to the experimental limit of 6.52. Clearly, the strength increase cannot be explained by the refinement of the inter-lamellar spacing any more.

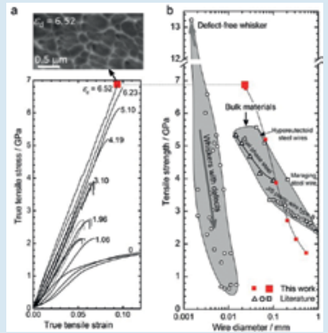


Fig. 1: *Strength of cold-drawn pearlite. (a) True tensile stress-strain curves of cold-drawn wires for various drawing strains. The preceding true wire strain is indicated for each stress-strain curve. The inset shows a SEM image of a fracture surface after the tensile test of the most extremely cold-drawn wire, revealing dimples that indicate plastic deformation prior to fracture. (b) Comparison of tensile strength versus wire diameter for various high strength materials reveals that the most severely cold-drawn ($\epsilon_d$ = 6.52) pearlitic wire is the strongest bulk material known to date.*

Here we explore the strengthening mechanism in this ultra-strong material and its microstructural origin via sub-nanometre scale characterization by atom probe tomography (APT).

Fig. 2 shows 3D carbon atom maps in longitudinal (left) and cross-sectional (right) views of samples drawn to low (εd = 2) and extremely high (εd = 6.52) true wire strains. It can be seen that the initially dominant two-phase lamellar pearlite structure observed at εd = 2 evolves, due to its dissolving cementite layers, into a carbon-decorated ferrite (sub)grain structure, as is visualized by the carbon segregation at the ferrite boundaries (marked by blue arrows) at εd = 6.52. The (sub)grains exhibit a columnar morphology along the drawing direction and a nearly equiaxed shape with sizes below 10 nm in the transverse cross section. It is known that SPD-produced nanostructured materials are prone to dynamic recovery and grain coarsening due to a large density of defects induced by SPD. However, for the present case these softening processes can be suppressed by carbon segregation at grain boundaries due to both the Gibbs adsorption effect and car-bon-drag preventing dislocation relaxation. We found that the relationship between tensile strength and (sub) grain size obeys the same Hall-Petch law in the regime εd > 4.19 as in the low strain regime εd < 4. This indicates that the carbon-stabilized nanoscaled ferrite (sub)



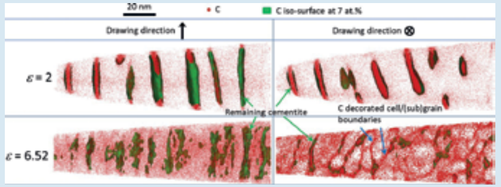


Fig. 2: *Atom probe tomographic characterization of pearlitic steel wires cold drawn to two different true wire drawing strains of 2 and 6.52, respectively. 3D carbon atom maps in both, longitudinal (parallel to the drawing direction) and transverse cross section views (perpendicular to the drawing direction). Green and blue arrows mark the remaining (partially chemically decomposing) cementite and some of the (sub) grain boundaries decorated with carbon atoms, respectively.*

grain structure has replaced the role of lamellar structure in strengthening the present ultra-strong material at high drawing strains.

To stimulate new ideas for the design of ultrahigh strength materials we emphasize the essential role of the second phase, e.g. cementite in pearlite. Via wire-drawing induced mechanical alloying the second phase chemically decomposes and acts as a supplier of solute atoms, which segregates to the (sub) grain boundaries stabilizing the nanoscaled grain structure, thus enabling an enormous strength of the drawn materials.

The key mechanical consequences of severely deformed pearlitic steel wires are including microstructure refinement and cementite decomposition but there are other effects that should be taken into account when high levels of strain are applied. APT measurements have shown that the concentration of carbon is not only increasing in the grain boundaries but also in the ferrite grain interiors and it exceeds the equilibrium solubility limit by far. As a consequence, more and more carbon stemming from the decomposing cementite must be partially accommodated inside the ferrite grains during the wire-drawing process. Thus a fundamental question arises: where do carbon atoms prefer to be located?

One of the experimental goals of the SN Department in this study is to link the observed cementite decomposition with structural evolution of the ferrite phase upon the drawing process. X-ray diffraction techniques provide one of the non-destructive methods for determining structural parameters of materials such as crystal structure, crystallographic texture and residual stresses. In this project, synchrotron radiation is used to probe the wires with much higher accuracy than laboratory X-ray diffraction. Upon wire drawing, high residual internal stresses are produced in the wires and a strong crystallographic texture develops which cause a drastic change in the mechanical behaviour of the steel wires. Furthermore, the study of the mechanical contribution of each phase in the wires is needed in order to characterize the load distribution between the ferrite and the cementite phases. For that purpose, *in situ* tensile tests coupled with synchrotron XRD are performed allowing for directly measuring the lattice strain evolution of the individual phases during deformation. Quantifying the load sharing behaviour of severely drawn pearlitic steel wires makes clearer the contribution of each phase on the global mechanical behaviour and stimulates new ideas for materials strength optimization.

Authors:
Dr. Soundes Djaziri & Dr. Yujiao Li

## Awards and Achievements

**Lutz Morsdorf**, doctoral student in the group Alloy Design and Thermomechanical Processing, received a Postdoctoral Fellowship for North American and European Researchers from the Japan Society for the Promotion of Science.

**Nicolas Peter**, doctoral student in the group Advanced Transmission Electron Microscopy, won the 3rd Place of the Best Talk Award at the 9th International Nanoscience Student Conference in Basel, Switzerland.

**Dr. Cem Tasan**, leader of the group Adaptive Structural Materials (until Dec. 2015) and now working at the Massachusetts Institute of Technology, Cambridge, USA, won the Freigeist Fellowship of the Volkswagen Foundation.

**Jiali Zhang**, doctoral student in the group Adaptive Structural Materials, received the 3rd Best Poster Award at the GDRI CNRS Mecano General Meeting which took place at the MPIE.