Scientists at the MPIE

Dr. Rosaura Aparicio Fernández, postdoctoral researcher in the group "Combinatorial Metallurgy and Processing" in the department „Microstructure Physics and Alloy Design", joined the MPIE in 2013. Her research interests are in the field of metallurgy, materials design, microstructure characterization and solidification analysis on aluminium- and iron- based alloys.

Her actual research is focused on the development of novel methods of synthesis production techniques and characterization of Fe-TiB_2 metal - matrix - composites termed high modulus steels (HMS) in order to increase their mechanical properties as stiffness/density ratio. She places special emphasis on the influence of the solidification rate on the size, morphology and dispersion of the TiB_2 particle as well as the amorphisation of the Fe-B-Ti system and their relation with the mechanical properties.

Rosaura did her PhD in materials science at the Center for Research and Advanced Studies of the National Polytechnic Institute ("Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional") in Querétaro, Mexico. Her thesis was about the "Kinetics analysis of unidirectional solidification of aluminium-silicon alloys".

Selected publications:

R. Aparicio-Fernández, H. Springer, A. Szczepaniak, H. Zhang, D. Raabe: *In-situ metal matrix composite steels: Effect of alloying and annealing on morphology, structure and mechanical properties of TiB_2 particle containing high modulus steels.* Acta Mater, 107, 38 (2016)

R. Aparicio, C. Gonzalez-Rivera, M. Ramirez-Argaez, G. Barrera, G. Trapaga: *Solidification kinetics of a near eutectic Al-Si Alloy, unmodified and modified with Sr.* Met. Mater. Int., 19, 707 (2013)

Dr. Michael Herbig is group leader in the department "Microstructure Physics and Alloy Design". His group "Materials Science of Mechanical Contacts" focusses on the understanding of materials' reaction to contact loads and the design of alloys with prolonged durability. In particular, he is interested in understanding the formation mechanism of white etching cracks that cause severe problems in wind power plants. His research is supported by the German Federal Ministry of Education and Research with 1.5 Mio. euros for five years.

Herbig conducted his PhD at the European Synchrotron Radiation Facility (ESRF), Grenoble / INSA Lyon in France where he investigated short fatigue cracks in titanium by correlated synchrotron phase and diffraction contrast tomography; being fully financed by a scholarship of the French ministry of education. In 2011 he joined the MPIE where he developed in his first year a robust approach that enables the correlative use of transmission electron microscopy and atom probe tomography on the same sample; giving access to combined 3D crystallographic and chemical information at near atomic scale. In the past years his research at the MPIE focused on the investigation of segregation and phase transformation phenomena particularly in steels.

Selected publications:

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

M. Herbig, D. Raabe, Y. Li, P.-P. Choi, S. Zaefferer, S. Goto: *Atomic-scale quantification of grain boundary segregation in nanocrystalline material.* Phys. Rev. Lett., 112, 126103 (2014)

Selected Publications

Computational Materials Design:

L. F. Huang, B. Grabowski, J. Zhang, M. J. Lai, C. C. Tasan, S. Sandlöbes, D. Raabe, J. Neugebauer: *From electronic structure to phase diagrams: A bottom-up approach to understand the stability of titanium-transition metal alloys.* Acta Mat, 113, 311-319 (2016)

G. A. Nematollahi, B. Grabowski, D. Raabe, J. Neugebauer: *Multiscale description of carbon-supersaturated ferrite in severly drawn perlitic wires.* Acta Mat, 111, 321-334 (2016)

Interface Chemistry and Surface Engineering:

N. Hodnik, G. Dehm, K. J. J. Mayrhofer: *Importance and Challenges of Electrochemical in Situ Liquid Cell Electron Microscopy for Energy Conversion Research.* Acc Chem Res, DOI: 10.1021/acs.accounts.6b00330

S. Wippermann, Y. He, M. Vörös, G. Galli: *Novel Silicon Phases and Nanostructures for Solar Energy Conversion.* Appl. Phys. Rev., 3, 040807 (2016)

Microstructure Physics and Alloy Design:

E. D. Welsch, D. Ponge, S. M. H. Haghighat, S. Sandlöbes, P. P. Choi, M. Herbig, S. Zaefferer, D. Raabe: *Strain hardening by dynamic slip band refinement in a high-Mn lightweight steel.* Acta Mat, 116, 188-199 (2016)

G. Stechmann, S. Zaefferer, P. Konijnenberg, D. Raabe, C. Gretener, L. Kranz, J. Perrenoud, S. Buecheler, A.N. Tiwari: *3-Dimensional microstructural characterization of CdTe absorber layers from CdTe/CdS thin film solar cells.* Sol Energ Mat Sol C, 151, 66-80 (2016)

Structure and Nano-/Micromechanics of Materials:

S. Djaziri, Y. Li, G. A. Nematollahi, B. Grabowski, S. Goto, C. Kirchlechner, A. Kostka, S. Doyle, J. Neugebauer, D. Raabe, G. Dehm: *Deformation Induced Martensite: A New Paradigm for Exceptional Steels.* Adv Mater (2016), DOI: 10.1002/adma.201601526

B. N. Jaya, R. Hoffmann, C. Kirchlechner, G. Dehm, C. Scheu, G. Langer: *Coccospheres confer mechanical protection: New evidence for an old hypothesis.* Acta Biomater, 42, 258-264 (2016)

Selected Talks

Computational Materials Design:

J. Neugebauer: *Ab initio determination of lattice stabilities and comparison to CALPHAD.* CALPHAD XLV Conference, Awaji Island, Japan, 29 May - 3 Jun 2016

M. Todorova: *New Insights into Corrosion Mechanisms from Ab Initio Concepts.* Gordon Research Conference "Corrosion - Aqueous", New London, USA, 10 - 15 Jul 2016

Interface Chemistry and Surface Engineering:

M. Rohwerder, V. Dandapani: *A Novel Potentiometric Approach to a Quantitative Characterization of Oxygen Reduction Kinetics at Buried Interfaces.* EMNT 2016, Brussels, Belgium, 16 - 19 Aug 2016

S. Wippermann: *Entropy stabilizes Peierls condensate: phonon-driven charge density wave formation and impurity-induced early condensation.* IBS Surface Atomic Wires, Pohang, South Korea, 17 - 20 Aug 2016

Microstructure Physics and Alloy Design:

D. Ponge, B. Gault, M. Herbig, C. Liebscher, M. Kuzmina, G. Dehm, E. Welsch, M. Yao, T. Hickel, Z. Li, C. Tasan, S. Sandlöbes, C. Scheu, A. Stoffers, S. Sandlöbes, J. Neugebauer, D. Raabe: *Chemo-Mechanics at Lattice Defects: from Mechanisms to Bulk Alloys.* Gordon Research Conference "Thin Film & Small Scale Mechanical Behavior", Bates College Lewiston, USA, 24 – 29 Jul 2016

D. Raabe, O. Cojocaru-Miredin, C. Liebscher, C. Scheu, M. Herbig, A. Stoffers: *Correlative Atom Probe Tomography and Electron Microscopy on Energy Materials.* European Microscopy Congress, Lyon, France, 31 Aug 2016

Structure and Nano-/Micromechanics of Materials:

G. Dehm, S. Djaziri, Y. Li, Gh. Nematollahi, B. Grabowski, S. Goto, C. Kirchlechner, A. Kostka, S. Doyle, J. Neugebauer, D. Raabe: *Mechanically driven martensite formation in ultra-strong pearlitic steel.* Thermec, Graz, Austria, 29 May – 3 Jun 2016

G. Dehm: *Mechanical Testing at Microscopic Length Scale.* European Mechanics of Materials Conference, Brussels, Belgium, 7 – 9 Sep

News and Events

Selected Upcoming Events

2017 will be marked by our 100 years jubilee. Starting from January 2017, we offer various events till our final ceremony in October 2017.

There will be an event each month open to the broad public like a children's university and laboratory day and our well established KopfSalat, a series of lectures with topics reaching from A like Astronomy to Z like Zoology. Please mark in your calendar the following dates for 2017 and we will keep you updated through our website:

26th January: KopfSalat with Prof. Wolf Singer, emeritus director at the Max Planck Institute for Brain Research

February: (planned) Children's University

21st March: KopfSalat with Prof. Dierk Raabe, director at the Max-Planck-Institut für Eisenforschung

27th April: Girls' & Boys' Day

11th May: KopfSalat with Prof. Dr. Metin Tolan, professor for experimental physics at the TU Dortmund University

June: (planned) Children's Laboratory

5th July: KopfSalat with Prof. Andreas Zick, director of the Institute for Interdisciplinary Research on Conflict and Violence, Bielefeld University

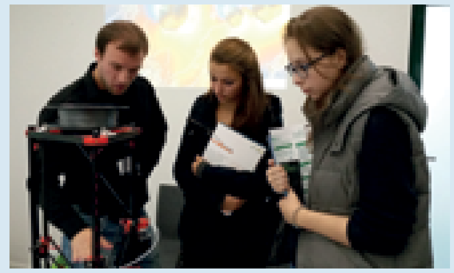
August: (planned) Experimental Lecture

6th September: KopfSalat with Prof. Stefan Hell, nobel laureate and director at the Max Planck Institute for Biophysical Chemistry

5th October: Scientific Symposium

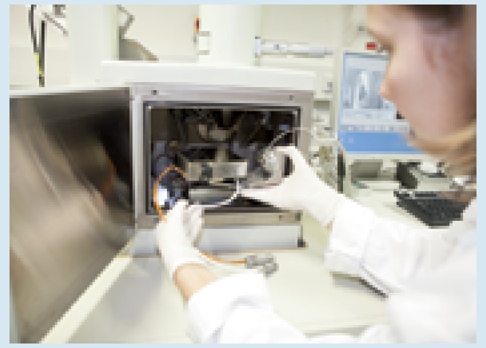
6th October: Final Ceremony

Additionally to the events each month, please keep a close eye on our website which will offer monthly new scientific articles, as well as a film and brochures about life and work at the institute.



At the right: Julian Rechmann (left), doctoral student, explains to pupils how additive manufacturing works.

Below: Nataliya Malyar, doctoral student, at the scanning electron microscope.



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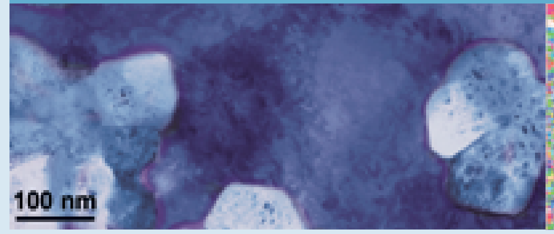
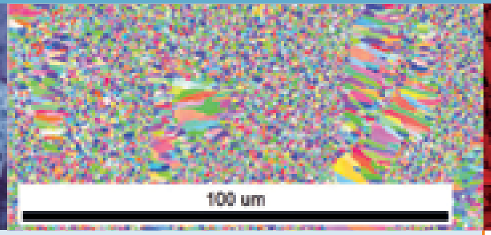
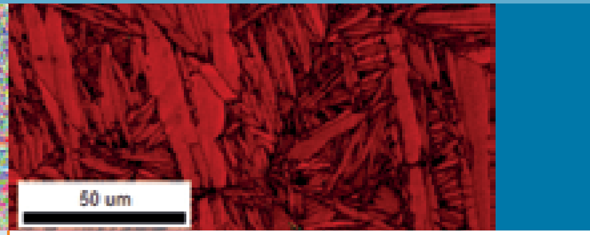
NEWSLETTER 2/2016

Max-Planck-Institut für Eisenforschung GmbH







Reactions at Interfaces: Initial wear

Engineering down to the atomic scale

The performance of engineering materials is typically closely related to their internal structure. Imperfections such as grain boundaries are important for their mechanical strength, since they serve as obstacles for plastic deformations of the atomic lattice. As a consequence, the stability of these structural motives during operation and production is a key concern of materials design. Under harsh conditions, such as e.g. high temperatures, mechanical loads, oxidizing atmospheres, corrosive chemicals and irradiation, these internal interfaces are often affected first. Examining the impacts of production and service conditions on the local chemistry of such defects is important for optimizing material design solutions to meet stringent application demands. One of the major research directions at the MPIE is therefore devoted to diffusion, segregation and oxidation processes along and at internal interfaces, especially grain boundaries. Different experimental as well as simulation groups closely interact on this topic. Here, we address in particular how the interaction of different alloying elements with oxygen influence these processes.

An important example, for instance, is the production of steel. In hot-dip galvanizing of steel – the technologically most important approach for coating steel with zinc – the formation of the so-called inhibition layer at the interface between the zinc coating and the steel surface plays an important role, and it is negatively affected by the presence of oxides on the steel's surface.

An example of the experimentally observed phenomena upon pickling (a metal surface treatment to remove impurities) which takes place after hot rolling, is a significant etching along grain boundaries. It can occur as a consequence of massive grain boundary oxidation during the cooling. Such a network of grain boundary oxide can be nicely seen as dark lines in Fig. 1. The extent of this grain boundary oxidation is sensitively affected by various alloying elements, with some combinations resulting in significantly enhanced grain boundary oxidation. These grain boundary oxides are usually found to consist of layers with varying stoichiometry.

Simultaneously, the physical reasons for the segregation of light elements such as oxygen to grain boundaries has been systematically

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EDITORIAL

Dear Colleagues and Friends of the MPIE,

Reactions at interfaces play a crucial role in the performance of engineering materials. At the same time, these interfaces are influenced by various parameters such as temperature, load etc. In this newsletter edition, we present our work on high temperature oxidation both from the experimental and theoretical point of view.

Besides our scientific articles, please also have a look at our upcoming events for next year which will be marked by our 100 years jubilee. Keep yourself updated through our website.

Enjoy reading and best regards,

Prof. Dr. Dierk Raabe, Chief Executive, MPIE

Reactions at Interfaces: Initial wear..1 - 4

Awards and Achievements................2 & 4

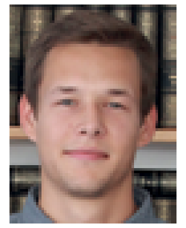
Scientists at the MPIE.............................5

Selected Publications..............................5

News and Events....................................6

Selected Talks...6

Awards and Achievements



Christian Broß, material tester, won the prize for the best trainee in the region Düsseldorf, awarded by the Chamber of Industry and Commerce of the regions Duisburg-Kleve-Wesel.

Vijayshankar Dandapani, doctoral student from India, working in the group "Corrosion", had a selected talk at the Gordon Research Conference 2016 on Aqueous Corrosion in New London, USA.

Dr. Xufei Fang, postdoctoral researcher from China, was awarded a research fellowship of the Alexander von Humboldt Foundation and is now working in the group "Nanotribology".

Herbert Faul, materials tester and training supervisor, was awarded the Silver Badge of Honour for his more than ten years of auditing work from the Chamber of Industry and Commerce Duisburg.

Nataliya Malyar, doctoral student from Russia and working in the group "Nano- and Micromechanics of Materials", received the Best Poster Award at the Gordon Research Conference 2016 in Lewiston, USA.

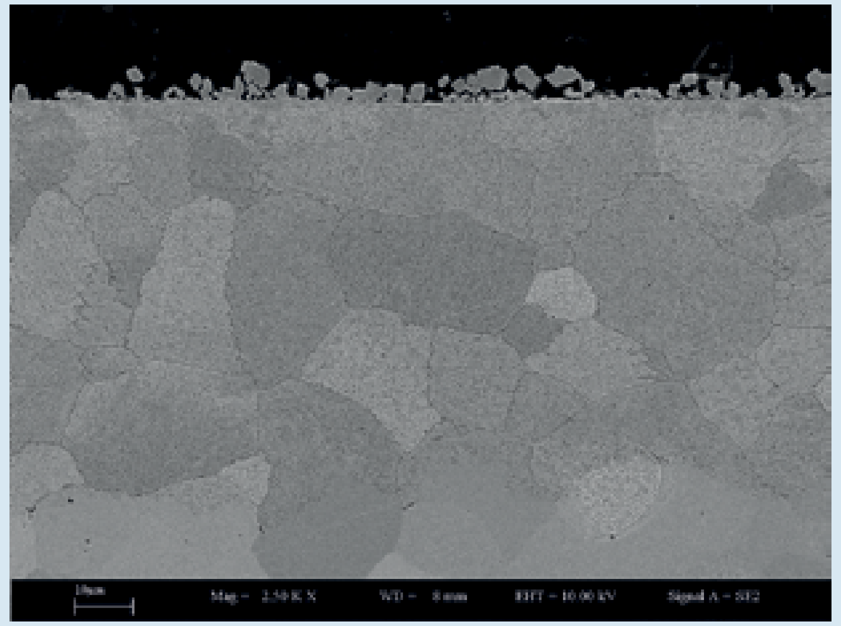


Fig. 1: *SEM image of a Fe-2M%Mn-2%Si model alloy annealed at 700°C for 70 hours at partial pressure of oxygen just below the equilibrium partial pressure of Fe/FeO.*

investigated by *ab initio* calculations. We report here mainly about our research on nanocrystalline Ti, which is – among other applications – one of the most promising materials for human dental implants. Here, oxygen has also a pronounced, but positive impact on Ti properties. A segregation of a certain amount of oxygen is supposed to improve the thermal stability of grain boundaries leading to an increase of the yield strength by a factor of two.

For pure Ti, the symmetry of the atomic neighbourhood turns out to determine the probability that oxygen atoms will segregate to the grain boundary, while the amount of space that is locally available surprisingly plays a secondary role [1].

The observation that C is also a light element that is often found at these kind of defects raised speculations that a collaborative effect of O and C could substantially enhance segregation. We have therefore evaluated more than 70 configurations of O and C in the vicinity of five different grain boundaries (Fig. 2): 25 configurations are energetically more favourable than the solution of O and C in the grain interior (E1<0). The joining of independently segregated O and C atoms is for 33 configurations preferred (E2<0). And this pair formation yields for 42 configurations a larger energy gain than a pair formation in the grain interior (E3<0). In order to have a true co-segregation effect, however, all three energies need to be clearly negative at the same time. Since this turns out to be rarely the case, C does not promote grain boundary oxidation.

On the other hand we revealed by *ab initio* calculations that O strongly prefers Mn-rich environments in high-Mn steels. Therefore, we currently evaluate the hypothesis that the alloying with substitutional metallic atoms is more important for the segregation behaviour of O than the presence of other interstitial atoms.

Degradation mechanisms of mould material in experiments

Another example is precision glass moulding (PGM). PGM is a hot compression moulding process, during which the moulds experiences strong thermal and mechanical forces as well as chemical shock due to the direct contact with the aggressive molten glass. In such harsh conditions, the mould degrades rapidly and we are aiming to understand the fundamental

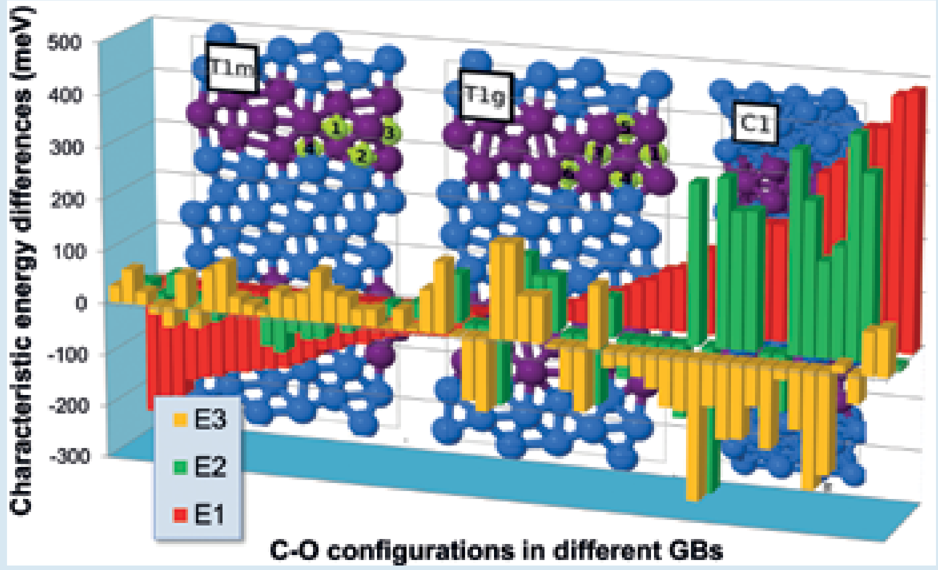


Fig. 2: *Comparison of various C-O configurations in five different grain boundaries (GBs) in hcp Ti with (E1, red) O and C solved in the grain interior; (E2, green) O and C independently segregated to grain boundaries; and (E3) the pair formation in the grain interior (E3, yellow). Negative energy differences favour the formation of these configurations.*

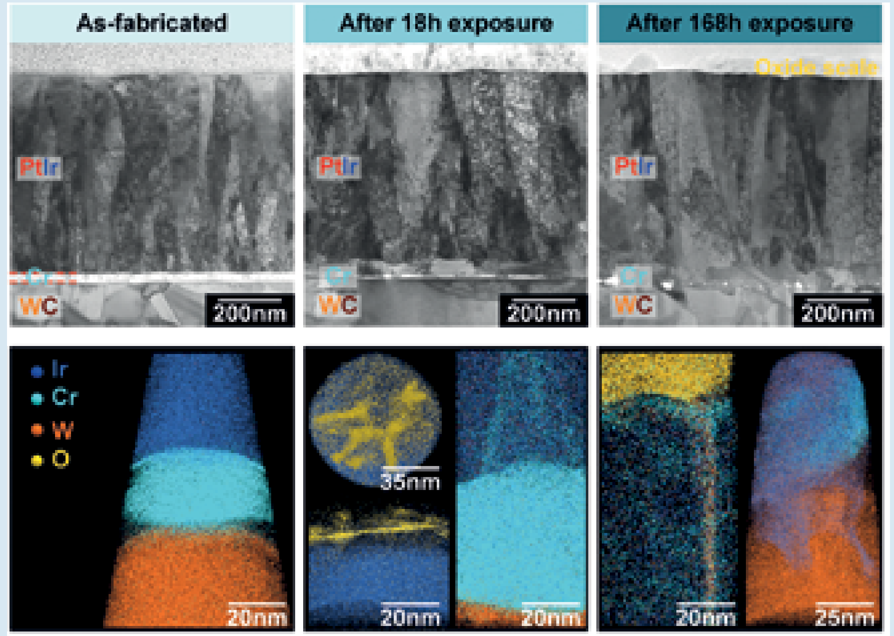


Fig. 3: *Cross-sectional STEM images and APT analysis of specimens after different periods of isothermal exposure at 630°C under an oxidizing atmosphere (PO2≈1.12×10-23 bar).*

mechanisms leading to its failure. To be more specific, we investigate the degradation mechanisms of a mould material made of cemented tungsten carbide protected by a PtIr coating deposited on an intermediate layer of Cr (PtIr/Cr/WC). This Cr layer serves at interlayer between the PtIr coating and the hard metal to ensure good adhesion of the former on the latter. However, during operation, the Cr layer degrades and Cr diffuses to the surface of the PtIr layer where its oxides cause the glass to stick to the surface, thus leading to quick degradation of the surface, rendering the tool unsuitable for the production of high quality lenses.

In order to investigate the degradation mechanisms and thereby find ways to limit or suppress them, a fundamental investigation of the underlying diffusion and oxidation mechanisms was initiated. To better control the oxidation conditions, we used an in-house designed furnace to expose the specimens to an extremely low pressure of oxygen (below 10-22 mbar). The nanometre-scale, three-dimensional, elemental and microstructural information were obtained using a combination of advanced microscopy techniques: atom probe tomography (APT) and scanning transmission electron microscopy (STEM).

Fig. 3 shows a series of cross-sectional STEM images and corresponding APT analyses of samples after different exposure times. In the as-fabricated state, the PtIr coating, the Cr interlayer and the WC substrate can be clearly identified. Both interfaces, PtIr/Cr and Cr/WC, are sharp and flat, with no visible voids or cracks. After 18h of exposure at 630°C, although the Cr layer can still be distinguished, it has started mixing with the PtIr coating. Cr is seen to segregate to grain boundaries in the PtIr, and Cr-oxides islands are seen at the surface. After exposure for 168h at the same temperature, the original Cr layer has completely disappeared and was replaced by a series of voids. The local dissolution of the WC substrate has caused a roughening of the Cr/WC interface. A complete intermixing of the layers is also observed, with PtIr migrating downwards, while W penetrated into the PtIr layer. The interactions between PtIr, Cr and W within the interfacial region give rise to the nucleation of various intermetallic particles. The continuous supply of Cr to the surface through the grain boundaries allows for the growth of a 30–90 nm-thick surface oxide scale.

Based on our experimental observations, we schematised the evolution of the degradation process in Fig. 4. The nano-sized columnar grain structure of the PtIr coating

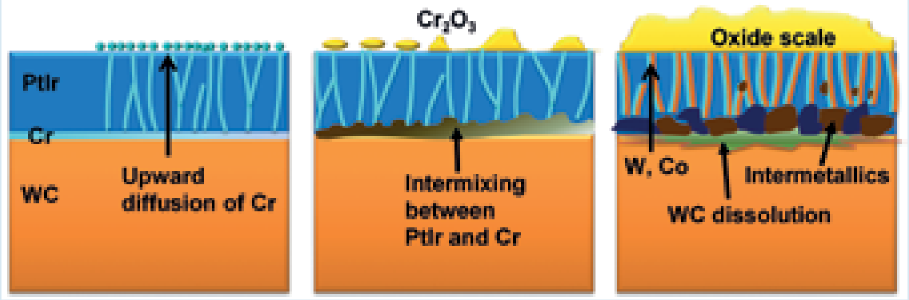


Fig. 4: *Schematic illustration of the evolution of degradation.*

provides numerous fast diffusion channels for Cr, accelerating the degradation progress. The newly formed Cr oxide scale on the one hand influences the morphology of the mould's surface, and hence the surface quality of the final glass product; on the other hand, this oxide hampers the non-sticking property of the mould. Finally, the dissolution of the Cr layer and the formation of voids and intermetallic particles at the interface strongly impact the cohesion of the protective coating. Coating spallation frequently appears in practice, terminating the service lifetime of the mould. According to the above-mentioned findings, measures to retarding the degradation process are being tested now, including using different types of interlayer and reducing the oxygen partial pressure in the chamber.

This work has been performed in a collaboration with Fraunhofer IPT.

This article shows a joint work of the MPIE departments "Computational Materials Design" (CM), "Interface Chemistry and Surface Engineering" (GO), and "Microstructure Physics and Alloy Design" (MA).

CM authors: Dr. Dmitry A. Aksyonov, Dr. Poulumi Dey, Dr. Tilmann Hickel, Dr. Jörg Neugebauer

GO authors: Dr. Michael Rohwerder

MA authors: Zirong Peng, Dr. Baptiste Gault

References:

[1] D.A. Aksyonov, T. Hickel, J. Neugebauer, A.G. Lipnitskii, J. Phys.: Condens. Matter 28 (2016) 385001.

Awards and Achievements

Julian Rechmann, doctoral student in the group "Interface Spectroscopy", won the Best Poster Award at the 16th International Conference on Organized Molecular Films in Helsinki, Finland.

Dr. Michael Rohwerder, head of the group "Corrosion", Dr. Asif Bashir and Dr. Motomichi Koyama, former postdoctoral researchers at the MPIE, received the "Japan Institute of Metals and Materials Metallography Award".

Dr. Hauke Springer, head of the group "Combinatorial Metallurgy and Processing", received the "Werner Köster Award" being the first author of the paper "A novel roll bonding methodology for the cross-scale analysis of phase properties and interactions in multiphase structural materials", together with Prof. Dr. Dierk Raabe and Prof. Dr. Cem Tasan.

Dr. Frank Stein, head of the group "Intermetallic Materials", was awarded with the "APDIC Best Paper Award 2015".

Dr. Xiankang Zhong, postdoctoral researcher from China, was awarded a research fellowship of the Alexander von Humboldt Foundation and is now working in the group "Corrosion".