MAX-PLANCK-GESELLSCHAFT

Annual Report 2000

Max-Planck-Institut
für Eisenforschung GmbH

MAX-PLANCK-INSTITUT
FÜR EISENFORSCHUNG GMBH
DÜSSELDORF

ANNUAL REPORT 2000

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December 2000

Preface

In the year 2000, the institute has seen substantial changes. After Professor Raabe had joined the institute on 1.7.1999 as scientific member of and director at the institute, Professor Stratmann accepted a corresponding position as of 1.1.2000, five months prior to Professor Grabkes retirement on 29.5.2000. Both established new scientific directions in their departments, which are reflected by the new department names "Microstructure Physics and Metal Forming" and "Interface Chemistry and Surface Engineering". Furthermore, they engaged a number of excellent young scientists as group leaders who will help to tackle the new scientific challenges.

On 1.11.2000, Dr. Tacke, head of the department "Metallurgy", left the institute in order to accept new tasks in industry. Since metallurgy is considered an important field of interest for the institute, it is planned to appoint a new scientific member for this area.

The reconstruction of all of the institute buildings is progressing well. A large fraction of the institute is working now in a container village, whereas almost all of the experimental equipment has been transferred to the workshop areas. In this way, certain continuity can be maintained also as far as the experimental work is concerned.

To summarize, all of these new developments have been very fruitful for an extension and widening of the scientific perspectives of the institute. In spite of that, there are certain limitations in working conditions due to the continuing reconstruction work. Therefore, everybody is looking forward now to the time when the main building with its wealth of modern technical facilities will be available for embarking upon exiting new scientific questions.

Peter Neumann

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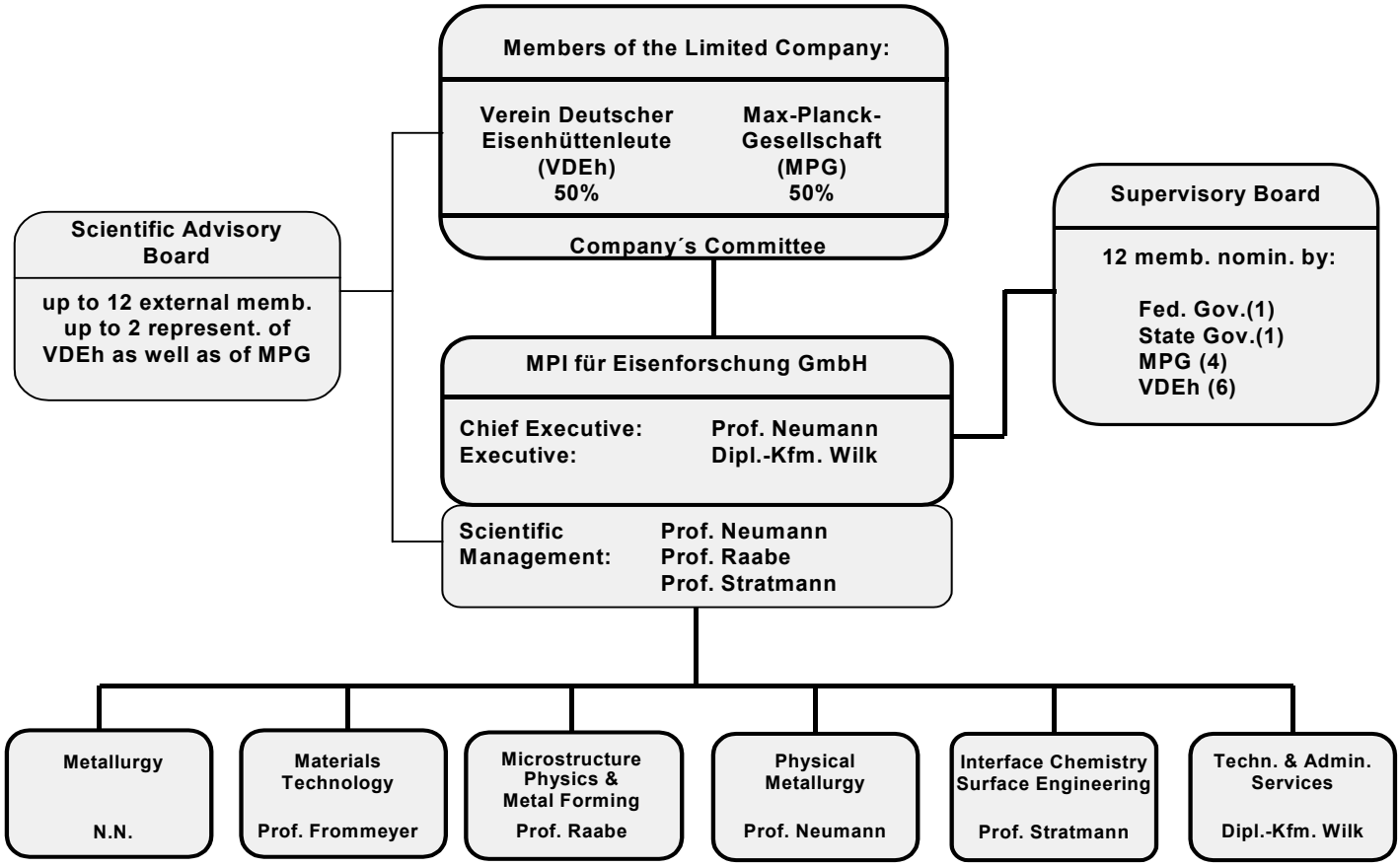

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Members of the Limited Company

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NIX, William, Prof. Dr., Stanfort
DE WIT, J.H.W., Prof. Dr., IJmuiden

Management

NEUMANN, Peter, Prof. Dr. rer. nat.
WILK, Herbert, Dipl.-Kfm.

Scientific Members

Scientific Members:	NEUMANN, Peter, Prof. Dr. rer. nat.
	RAABE, Dierk, Prof. Dr.-Ing. habil.
	STRATMANN, Martin, Prof. Dr. rer. nat.
Scientific Members em.:	ENGELL, Hans-Jürgen, Prof. Dr. rer. nat. Dr.Ing. E.h. Dr.-Ing. E.h.
	PAWELSKI, Oskar, Prof. Dr.-Ing.
	PITSCH, Wolfgang, Prof. Dr. rer. nat.
External Scientific Members:	HILLERT, Mats, Prof. Dr.
	LÜCKE, Kurt, Prof. Dr. rer. nat. Dr. h.c.

Scientific Staff

Metallurgy

Tacke, Karl-Hermann, Priv.-Doz. Dr.-Ing.
(head of department) until 31.10.2000
Büchner, Achim, Dr. rer. nat.
Drücker, Sascha, Dipl.-Ing. until 31.12.2000
Gnauk, Joachim, Dipl.-Phys. until 31.12.2000
Heckmann, Carl Justus, Dipl.-Ing. until 31.12.2000
König, Markus, Dipl.-Ing.
Li, Mingjun, Dr. (China)
Meißner, Steffen, Dr. rer. nat. until 31.07.2000
Messerschmidt, Rainer, Dipl.-Ing. until 31.03.2000
Reichert, Axel, Dipl.-Ing. until 31.03.2000
Thiemann, Michael, Dipl.-Phys. from 01.09.2000
Zhang, Jiaquan, Dr. (China) until 31.03.2000

Materials Technology

Frommeyer, Georg, Prof. Dr.-Ing.
(head of department)
Brüx, Udo, Dipl.-Phys.
Fischer, Rainer, Dipl.-Phys.
Knippscheer, Sven, Dipl.-Ing.
Rablbauer, Ralf, Dipl.-Phys.
Schneider, André, Dr. rer. nat.
Jiménez, José, Dr. (Spain) 25.02.-19.03. u. 30.6.-30.7.2000

Microstructure Physics and Metal Forming

Raabe, Dierk, Prof. Dr.-Ing. habil.
(head of department)
Elsner, Alexander, Dipl.-Ing. from 01.10.2000
Filatov, Dmitri, Dipl.-Ing. (RUS)
Jamet, Jean-Marcel, Dr. (F)
Juntunen, Pasi, Dipl.-Ing. (FIN) 01.01.- 30.06.2000
Kaspar, Radko, Dr.-Ing.
Klüber, Christian, Dipl.-Ing. from 01.06.2000
Kuo, Jui-Chao, (Taiwan) Dipl.-Ing. from 01.08.2000
Lücken, Hermann, Dipl.-Ing. from 01.02.2000
Park, Seong-Jun, Dr. (KOR) 01.01.-30.04.2000
Rasp, Wolfgang, Dr.-Ing.
Roters, Franz, Dr.rer.nat., from 01.04.2000
Scheele, Georg, Dipl.-Ing. from 01.05.2000
Vanik, Hans-Georg, Dipl.-Ing.
Wang, Yanwen, Dr. (China) from 01.07.2000
Wengenroth, Walter, Dipl.-Phys.
Wichern, Christan, Dr., (USA) from 01.08.2000
Zaefferer, Stefan, Dr.-Ing. from 01.05.2000
Zhao, Zisu, Dr. (China)

Physical Metallurgy

Neumann, Peter, Prof. Dr. rer. nat.
(head of department)
Balun, Jozef, Dipl.-Ing. (SK)
Eumann, Markus, Dipl.-Phys.
Huo, Guoyan, Dr. (China) until 30.06.2000
Inden, Gerhard, Prof. Dr. rer. nat.
Knezevic, Vida, Magister of Sience (YU)
Löffler, Falk, Dipl.-Ing.
Palm, Martin, Dr. rer. nat.
Prakasch, Ujjwal, Dr. (IND) until 16.06.2000
Sauthoff, Gerhard, Priv.-Doz. Dr. rer. nat.
Stein, Frank, Dr. rer. nat.
Vilk, Julius, Dipl.-Ing. (SK) from 01.07.2000
Zhang, Jianqiang, Dr. (China) from 01.11.2000
Zhang, Lichun, Dr. (China)

Physical Chemistry (until 29.5.2000)

Grabke, Hans Jürgen, Prof. Dr. rer. nat.
(head of department)

further staff s. Interface Chemistry and Surface Engineering

Interface Chemistry and Surface Engineering

Stratmann, Martin, Prof. Dr. rer.nat.
(head of department)
Baumert, Birgit, Dipl.-Phys.
Bonk, Stephan, Dipl.-Phys. from 01.11.2000
Chumak, Alexander, Dr. (Ukraine) 01.08.-30.09.2000
Hassel, Armin, Dr.rer.nat.
Hausbrand, René, Dipl.-Phys.
Hornung,Elke, Dipl.-Ing.
Hüning, Boris, Dipl.-Phys.
Michalik, Adam, Dipl.-Ing. (PL) from 01.10.2000
Moszynski, Dariusz, Dr. (PL) from 01.01.2000
Nieto-Quintas, Felix, Dr. (ARG) 01.08.–30.09.2000
Ogura, Yuzuru, Dr. (J) (guest)
Parezanovic, Ivana, Ms.Sc. (YU) from 16.10.2000
Piehl, Carmen, Dipl.-Chem.
Rohwerder, Michael, Dr. rer. nat.
Sämann, Nicole, Dipl.-Chem.
Schlüter, Thorsten, Dipl.-Chem.
Schmidt, Wolfgang, Dipl.-Ing. until 31.08.2000
Shirtcliffe, Neil, Dr. phil. (GB)
Spiegel, Michael, Dr. rer. nat.
Tarasenko, Alexander, Dr. (Ukraine) 01.08.-30.09.2000
Tareelap, Napachat, Dipl.-Ing. (THA)
Tsuri, Shiro, Dipl.-Chem. (J) guest
Uebing, Christian, Dr. rer. nat. (guest) until 30.09.2000
Vander Kloet, Jana, Dipl.-Phys. (NL) from 15.08.2000
Viefhaus, Helmut, Dr. rer. nat.
Wicinski, Mariusz, Dipl.-Chem. (PL)
Zahs, Armin, Dr. rer. nat. until 15.05.2000

Kemnitz, Hans-Dieter, Dr.-Ing.,
Head of Electronics and Computer Services
Gahn, Ulrich, Dr. rer. nat.

RESEARCH IN PROGRESS
(January 1, 2001)

Metallurgy: A.R. Büchner (provis.)

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Büchner: Considerations in construction of thin strip casting units

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Frommeyer: Investigations on structural superplasticity and superplastic forming at high-strain-rates of high aluminum content UHC-steels and duplex stainless steels

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Brüx, Frommeyer: Investigations on plastic anisotropy and deformation mechanisms of lightweight steels based on iron-aluminum

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Frommeyer, Rablbauer: Investigations on structural superplasticity and deformation mechanism in NiAl(Cr) based alloys

Fischer, Frommeyer, Schneider: Characterization of the defect structure in nickel aluminides using atom probe field ion microscopy (APFIM)

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Schneider, Frommeyer: Investigations on the effects of Cr, Mo, W, V, Nb on microstructure and mechanical properties of Fe_3Al-X-alloys

Schneider, Fischer, Frommeyer: Characterization of the defect structure and determination of the site preference of ternary alloying elements in Fe_3Al-X-alloys using APFIM and ALCHEMI.

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Frommeyer, Büchner: Microstructural characterization of high silicon content transformer steels produced by strip casting

Rablbauer, Frommeyer: Alloy design and characterization of high temperature properties of dispersion strengthened NiAl based alloys

Frommeyer, Brüx: Alloy development and investigations on microstructures and mechanical properties of high strength and supraductile (Fe-Mn-Al-Si) lightweight TRIP and TWIP steels

Schneider, Frommeyer, Sauthoff: Fe-Al-Nb/Ta/Ti-C/B- alloys for applications in the chemical industry

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Roters, Raabe, Zhao: Development and application of crystal plasticity finite element methods

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Rasp, Wengenroth: Flexible control of cross-section in the dieless drawing process

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Vilk, Inden: Ferritic steels with maximum creep resistance: thermodynamics and kinetics of precipitation reactions

Inden: Diffusion in multicomponent systems and complex phases

Schön, Inden: Atomic ordering in multicomponent alloy systems

Balun, Inden: Phase equilibria in the systems Fe-Ni-Si and Fe-Rh-X (=Co, Ti)

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Bernst, Inden: Development of the Cluster-Site-Approximation for body centred cubic structures

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Sauthoff: Creep of multiphase alloys

Sauthoff: Deformation behaviour of Fe-Al-Ta alloys

Sauthoff: Ferritic Fe-NiAl superalloys

Sauthoff, Palm: Deformation behaviour of intermetallic NiAl-Ta-Cr alloys with strengthening phases

Sauthoff, Palm, Stein: Screening of Al-rich intermetallics

Sauthoff, Palm, Löffler: Constitution and mechanical behaviour of intermetallic phases in the Mg-Fe-Si and Fe-Si-Ti systems

Palm, Sauthoff, Stein: Phase equilibria and mechanical behaviour of intermetallic phases in the Fe-Al-Zr system

Sauthoff, Palm, Stein, Messerschmidt (MPI für Mikrostrukturphysik, Halle): Microprocesses of deformation of Fe-Al-Zr alloys with strengthening intermetallic phases

Palm, Stein: Phase equilibria in the Al-rich part of the Al-Ti system

Sauthoff, Knežević: Ferritic steels with maximum creep resistance: alloy development and long-term behaviour

Sauthoff, Palm, Jiang: Mechanical behaviour of ordered Fe-Al-Nb alloys with Laves phase

Sauthoff, Palm, Stein, Jiang: Structure and mechanical behaviour of Al-Ti(-Fe) alloys

Stein, Sauthoff: DTA studies of phase transitions in intermetallic systems

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Zhang, Bernst, Schneider, Inden: Decomposition of cementite during metal dusting

Viefhaus, Schneider, Inden: Analysis of carbon composition profiles in cementite and ferrite

Zhang, Schneider, Inden: Thermodynamics of diffusion controlled reactions during gas carburisation

Sauthoff, Palm, Spiegel, Viefhaus: Oxidation of intermetallic alloys

Sauthoff, Schneider, Frommeyer: Fe-Al-Nb/Ta/Ti-C/B alloys for applications in chemical processing
Spiegel, Sauthoff: Fe-Cr-Si alloys as coatings for superheaters

Interface Chemistry and Surface Engineering: M. StratmannMolecular Structure and Surface Modification

Hornung, Rohwerder: Nanoscopic mechanisms of cathodic delamination

Baumert, Rohwerder: Investigation of defect formation and behaviour in plasma polymer films under tensile loading

Michalik, Rohwerder: Potential of conducting polymers for corrosion protection

Frenznick, Rohwerder: Self-organization of phosphonates on iron and steel

Hausbrand, Rohwerder: Structure of corrosion protective coatings: the Mg-effect in Mg/Zn-alloys

Shirtcliffe: Optimization of the metal/polymer interface by plasma polymer films

Thiemann: Structure/properties correlation for ultrathin plasma polymer films

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Sanchez, Spiegel: High temperature corrosion beneath molten chlorides

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Parezanovic, Strauch, Spiegel, Grabke: stainless steels for molten carbonate fuel cells

Sämann, Spiegel, Grabke: Improvement of stainless steels for the use at elevated temperatures in aggressive environments

Ogura, Spiegel, Grabke: The influence of Si and Al on the chlorine induced high temperature corrosion of ferritic steels

Piehl, Grabke: Chromium diffusion and oxide formation in dependence on the microstructure and the surface state of high alloy steels

Müller-Lorenz, Moszynski, Schneider, Zhang, Grabke: Metal dusting of Fe, Ni, steels and high temperature alloys- role of sulfur

Müller-Lorenz, Zhang, Grabke: Reoxidation of direct reduced iron

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Viefhaus, Uebing, Hüning, Grabke: Surface analytical and tunnel-microscopic investigations on the oxide nucleation and growth on steels, high temperature alloys and intermetallic phases

Viefhaus, Lucas, Grabke: Surface analytical investigations (AES, ESCA) on iron and steel surfaces, zinc and tin coated steels, passive films and oxide layers

Sevc, Janovec, Lucas, Grabke: Interfacial segregation of tramp elements in 9-12 Cr steels - effects on materials properties

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Vander Kloet: Mechanism of Al Alloy Corrosion and the Role of Chromate Inhibitors

Hassel, Diesing: Anodic Breakdown of ultrathin Valve Metal Oxide Films

Diesing, Hassel: Temperature Dependance of Steady State Tunnel Currents and Non Steady State Relaxation Currents in Aluminium/Aluminium-Oxide Systems

Hassel, Okawa, Fushimi, Seo: Reactivity Imaging of Microstructured Polycrystalline Titanium

Hassel, Aihara, Seo: Engineering of watersplitting Photoanodes

Hassel, Aihara, Seo: Preparation and Properties of Porous Indium Phosphide

Hassel, Mingers: Microstructuring of polycrystalline Titanium for Use in Bioimplants

Mingers, Hassel: Etching and Passivation Kinetics in Invar for Use in Shadowmasks

Hassel: Investigation of Elementary Processes of Tribocorrosion in the Micrometer Range

Hassel, Mozalev: Alternative Anodising Procedures for the Formation of Oxide Films on Aluminium

SCIENTIFIC WORK OF DEPARTMENT

Department of Metallurgy

A.R. Büchner (provis.)

The department of metallurgy focuses on the fundamentals of steelmaking. The targets are both to optimise conventional process technologies as well as to support new lines of development. Among the classical processes, many of the activities refer to continuous casting. An important new technology investigated is twin roll strip casting. This process currently reaches industrial application, today mainly for stainless steels, but in the future also for carbon steels. The department also studies new processes of iron ore reduction such as smelting reduction, the use of hydrogen and the reduction of carbon composite iron ore pellets. Although the blast furnace will dominate iron ore reduction in the future, innovative reduction processes may provide interesting alternatives when the supply of energy and raw material is appropriate. All new technologies studied at MPI can contribute to save process steps, cost and energy and may be part of future concepts for new steel production lines.

Among the methods applied at the department of metallurgy, numerical modelling is a central tool. At the same time, various experimental studies are carried out using laboratory measurements and empirical plant data.

Parts of the activities of the department were terminated during the period of report because the head of the department left the institute. As he lead simultaneously the group of Metallurgical Process Models most of the corrresponding activities ended during the year 2000. The group of Near Net Shape Casting was not touched by that and is in continuous action.

Metallurgical process models

The capabilities of numerical modelling are continuously enhanced such that more complex problems can be analysed in several areas than previously. The first action of all model development is the formulation and abstraction of the problem and the establishment of a set of equations, usually differential equations. These equations reflect the underlying physical and chemical processes such as transport phenomena (diffusion and convection of heat, momentum and matter, turbulence), chemical reactions and equilibria, phase change (solidification in particular), but also mechanical questions, mostly relating to high temperatures as encountered in continuous casting.

For processing by a computer, the equation systems are discretised using numerical methods, for example finite differences or finite elements. Workstations and personal computers are available for the solution. To evaluate the large quantity of output values, graphical representation is needed as an important part of modelling work. Data sets are condensed and interpreted using simplifying approaches to provide conclusions and optimisation approaches for engineering requirements.

MPI participates in an ECSC project "Determination of **high temperature surface crack formation** criteria in continuous casting and thin slab casting". The partners are IRSID, TKS, Dillinger Hüttenwerke and Rautaruukki Steel; the project is coordinated by IRSID. MPI has adapted a previously developed numerical model for the computation of thermally induced stresses and cracking risk for application to the new casting machine no. 5 at Dillinger Hüttenwerke and the casting machine no. 6 at Rautaruukki Steel. Stress fields, stress-ductility maps and indices for the cracking intensity are obtained using thermal fields as determined at DH in high resolution and the corresponding ductility curves for a microalloyed steel. TKS carries out cyclic tests under different conditions. MPI uses the results of TKS to develop a new creep law and will apply it to the current model. Plant data from the partners, laboratory tests by IRSID and dilatometric tests at MPI will be used to calculate CCT-diagrams (continuous-cooling-transformation-diagrams) by a formalism given by [1]. The thermal fields mentioned above and the calculated CCT-diagrams will be used to produce a phase field in high resolution which will cover the gamma-alpha transformation with more precision than has been previously possible. The phase field will be considered in the already mentioned mechanical model. The aim is to obtain more reliable crack prediction for the benefit of surface quality in continuous slab casting.

The process of **strand reduction in continuous casting** and its effect on centreline segregation are examined in an ECSC project. Partners are British Steel Teesside Technology Centre, Dillinger Hüttenwerke, Institut für Allgemeine Metallurgie (Clausthal Technical University) and MPI [2]. The aim is to obtain an understanding of the processes occurring during soft reduction, to determine critical parameters of soft reduction and the influence of strand reduction on internal quality. Investigations on solidification shrinkage, fluid flow and macrosegregation are used together with strand reduction trials to assess the influence of soft reduction on the product.

MPI develops a three dimensional finite element model for soft reduction in continuous casting. It can be applied both to strands compressed with liquid and with solid core. The computations provide several important parameters such as stress

and strain fields, and the roller and withdrawal forces. Numerically calculated roll forces due to soft reduction, which are of particular interest for that the model predictions using standard high temperature data produce far too high roll forces. This could be drastically improved by adopting formulations of material behaviour as developed in the project on strand unbending such that computed roll forces are now in the order of the values measured in Dillingen. The model can be used to quantify the effect of transition from reduction with liquid core to reduction with solid core, which can be an important event during casting. The work was finished successfully.

Numerical models are developed for the reduction of carbon composite iron ore pellets in the **ITmk3 process**, a new technology currently developed by Kobe Steel. MPI works within a multinational collaboration of researchers at Kobe Steel and universities in Japan and UK. The aim of the joint project is to investigate the fundamentals of this process. The model developed at MPI describes the sequence of reduction and melting steps including the evolution of temperatures, composition and reduction degree and melting within the pellet (RCM = Reduction, Carburization, Melting). This involves transport equations, phase change phenomena and chemical reactions. It also includes a description of the slag components as another module. Thermodynamic data as well as kinetic factors for various reactions are necessary. Access to empirical data from collaborators within this project provides the required unknown model parameters and a chance to correct model assumptions. In the reporting period, the model has evolved a level of quantitative description through various enhancements and by contrasting model results to measurement carried out at Surrey University. The final report was submitted [3].

Near Net Shape Casting

Two twin roll laboratory casters are operated in this group for producing steel strip in the thickness range of 1 to 3 mm. A smaller machine casts up to 15 kg of steel at a width of 65 mm from a 40 kW induction furnace. Steel rolls and copper rolls (with and without nickel coating) are available. The rolls on this machine have no water cooling. This caster permits inexpensive trials in short intervals and is used extensively for various kinds of test within projects and also for orders from industry.

The larger machine casts 120 mm wide strip using water cooled copper rolls, also with or without Ni coating. This caster is used for all tests which require thermal steady state. The capacity of this machine has been increased recently. A modern 150 kW furnace is able to deliver heats of up to 250 kg. The furnace can now be teemed directly into a gas protected tundish which can prevent reoxidation more efficiently.

plant operation, depend strongly on the assumption about the material behaviour. Plant data from the project partners have shown

In line rolling is of large interest for strip casting. One purpose is to eliminate possibly occurring shrink holes in the strip. Other aims still to be studied are influences on the strip structure. The cooling effect by rolling can also be of use to reduce scale formation. To be equipped for corresponding investigations in the future a rolling mill was fit out with a rapid hydraulic system. During one casting experiment of, say 20 seconds, it is possible now to apply three or more reduction degrees and intermediate open roll gages to obtain the original strip thickness. The roll gap can be changed by 2mm/s; the rolling force can be measured now very exactly from the hydraulic pressure. The important problem to balance the velocities in twin roll caster and rolling mill is solved by manual speed control.

For the purpose of storing longer strip or also for a quick in line cutting, e.g. of furnace compatible portions, a pneumatic shear was constructed and is now available.

The department of metallurgy is supporting the development by performing series of casting tests on stainless steel grades for fundamental questions concerning the new twin roll machine at KTN, Krefeld.

A new ECSC-project in cooperation with Corus, CSM, Sidenor, TKS treats the problem of **surface quality of continuously cast semis**. The objective is the basic understanding of shell development and growth especially for the very critical peritectic steel type. The former intention had been that model calculations as well as suitable solidification experiments should contribute to the project. After the retirement of the modelling group the project was reconstructed and the experimental part was redefined. It will now be treated by the Near Net Shape Casting group; this is appropriate, as the solidification process in the early state takes place in similar way in both techniques, continuous and thin strip casting. In preparation to this project a model mould was constructed where metallic walls of different type come in contact to a rising melt. Thermocouples in the walls will give information on heat contact and heat flow, and this will be analysed in connection with microscopic studies of the cross section of the strip.

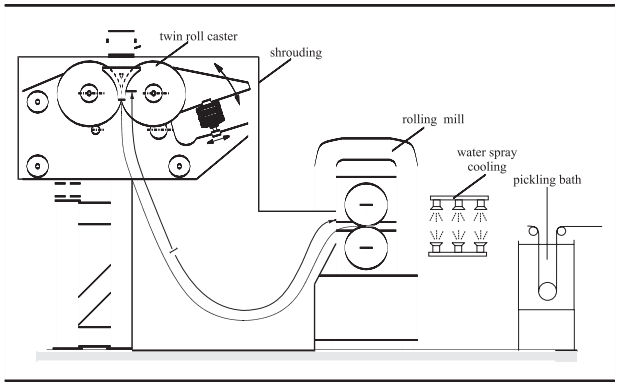
The **contact and heat transfer between melt and roll in twin roll casting** is a theme of prime importance. The length of pool contact during casting can be observed and gives important information. From the experience that this contact depends strongly on the kind of melt and kind of rolls it is deduced that microscopic physical effects should be studied. The model mould mentioned above will be employed to investigate contact angles, wetting behaviour and heat transfer. Large efforts had been necessary to establish a reliable temperature measurement by

thermocouples in the walls. The real temperature changes are faster than the reaction of the thermocouples, and therefore a calculation procedure for a corresponding correction was established. This problem is also connected with the heat contact of the thermocouple, and understanding and improvement of this contact had to be developed. An electronic device for storing data from up to sixteen thermocouples with sufficient velocity was constructed.

The investigation of **feeding systems** was continued using both water model tests and trials on the twin roll machine. Several types of nozzles were applied, such as slit nozzles, rows of round orifices and submerged entry nozzles with two round outlets. The slit and round hole nozzles are applied just above the liquid pool or slightly immersed. The type of nozzle has a drastic effect on the stability of the meniscus. Turbulent conditions with strongly fluctuating meniscus levels are analysed, but also more stable cases. After the experiences with the water model corresponding trials were carried out by casting LC-steel in the small twin roller with Cu-rolls. Roll velocity and roll force were varied; the influence of the nozzle type and of all above quantities on the surface quality of the strip was investigated; especially grooves and bleeds were used as a measure of quality. An important effect consists in different patterns of turbulence in the pool, depending on the type of nozzle, which can result in resmelting of the already solidified shells thus disturbing the strip surface. Melt velocitiy in the nozzle seems to be an important quantity; the interpretation of the observations is going on.

The **formation and prevention of scale during twin roll strip casting** is a multipartner, multinational project including IRSID, TKS and Teesside Technology Centre as partners, coordinated by MPI [4]. In strip casting, surface scale can result both in yield loss and in product quality problems. Twin roll casting must reach at least the standards of conventional continuous casting, which is more difficult due to the larger surface area. The project focuses on the mechanisms of scale formation and the determination of process parameters required to reduce scale formation and growth.

From the use of special quenching tests and experiments in the shrouding equipment of the small caster a full knowledge was established on scale formation in dependence on temperature, time and oxygen content, outside and inside the housing. As an example of application and using furthermore knowledge from the literature on water cooling and pickling, it was possible to discuss a roller - in line equipment for a total scale removal. This plant consists in an inert gas box, separated from outside by a pair of rolls (which also remove heat), a range of water cooling and finally a pickling tank, see **fig. 1**. Due to leakage in the shrouding the rest oxygen content is connected with the inert gas rinsing effort. The consumption of inert gas, cooling water and pickling acid versus the expense of equipment size could be optimized by this study.



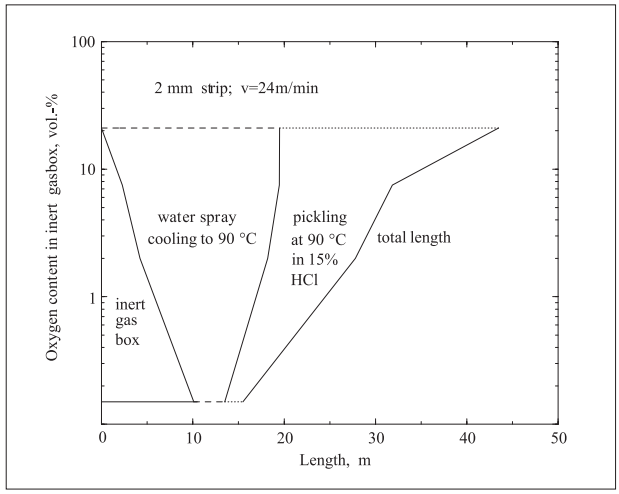


Figure 1: (top) *A possible arrangement in line of a twin roll caster to produce a scale free strip; a shrouding with a reduced oxygen content, terminated by a rolling mill; water spray cooling; pickling tank*

(bottom) *The optimisation between equipment length and the efforts of inert gas rinsing is shown; from the calculations developed here, the scale formation is estimated in dependence on time and rest oxygen in the gas box*

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4. Drücker, S.; et al: The formation and prevention of scale during twin roller strip casting, Final Report ECSC-Project 7210-PR/014.

Publications and Abstracts

DiDonato*, A.; Malgarini*, G.; Knoop**, W. van der; Beiter, K.; Kuang, C.; Tacke, K.-H.; Oeters, F.; Zhang***, L.***
Development of a combined post-combustion model (CPM) for smelting reduction process
Final Report: ECSC Project No. 7210-AA/419/607/136/137 European Commission, ISBN 92-828-9236-0, Luxemburg 2000

A new combined post-combustion model (CPM) for smelting reduction processes, including two components, a 'kinetic section' for the region in the presence of foaming slab and a 'CFD (computation fluid dynamic) section' in the free space, was developed.

This research work was especially devoted to the *C*lean*SM*elt® process (formerly cyclone converter furnace, CCF) in which post-combustion is carried out both in a foamy slag (smelter) and in a free space (smelter and cyclone). A new detailed mathematical description of flame behaviour and of heat transfer from the post-combustion gas to the foamy slag in different zones was written. Such a new detailed description allowed simultations of smelting reduction processes; calculations for a 170 tonne reactor and the *C*lean*SM*elt process on *C*lean*SM*elt -PDU (pilot demonstration unit) were made.

Major components of this detailed description were assumed as the basis of the kinetic section of the CPM. This is able to predict the amount, composition and temperature of the metal, slag and gas phase. By using the model, at any given reactor configuration and operating condition, the post combustion ratio (PCR) can be calculated. The kinetic section of the CPM can run on a fast PC for an on-line application.

In the CFD section, three-dimensional mathematical modelling of post-combustion in free space was established. The simulations describe both the cyclone and the smelter. All computations are carried out for cylindrical vessels. They cover the gas space in both domains and include the solid and liquid iron oxide layers on the cyclone wall. Resulting quantities are fluid flow and combustion fields, the thickness of the solid crust and heat losses to the cooling water.

The new CPM (both kinetic and CDF sections) was validated in a joint way by all the partners, using both data collected during experimental trials realised on *C*lean*SM*elt-PDU and data coming from other smelting reduction experiences.

*CSM Italy, **Corus Netherlands, ***TU Berlin

Girgensohn*, A.; Büchner, A.R.; Tacke**, K.-H.
Twin roll strip casting of low carbon steels
Ironmaking and Steelmaking 27, No. 4 (2000), p. 317 – 323

Strip casting of low carbon steels has been investigated using a laboratory twin roll machine with copper rolls. The following grades have been studied: a deep drawing low carbon (LC), a LC steel with titanium addition, and a high strength low alloy (HSLA) grade. The casting behaviour of these steels has been examined, and the observed surface defects classified. Defects are most pronounced for the LC grade and significantly less for the HSLA steel and the LC steel with titanium addition. The as cast structure has been analysed. It can be modified by post-cast treatment, e.g. by normalisation or in line rolling. The mechanical properties of cold rolled and annealed strip materials and their textures are presented. Satisfactory sheet properties can be achieved both as hot band and as cold rolled sheet when adequate treatment steps are applied. Consequences for strip casting applications and future research are discussed.

*SMS-Demag, Düsseldorf; ** KTN, Krefeld

Grimm, G.; Andrzejewski*, P.; Müller*, K.; Tacke, K.-H.
Inclusions in continuous cast steel slabs – numerical model and validation
steel research 70 (1999), No. 10, 420- 429

A numerical model for liquid flow and inclusion transport and separation in continuous casting moulds is presented, which covers several features simultaneously. The free surface at the meniscus is computed; the submerged entry nozzle is discretised in detail to resolve the outlet geometry; gas injection through the SEN and its effect on liquid steel flow are considered; capture of inclusions within gas bubbles is covered in a simplified approach; the solidifying shell and the process of inclusion entrapment by the growing shell are simulated. Computed flow profiles are compared to experimental results on water and to measurements on liquid steel in a slab caster. Predicted inclusion profiles in solid slabs are compared to empirical findings from literature. Results of the model for various cases will be presented in a subsequent publication.

*TKS Dortmund

Steinert*, I.
Mathematische Modelle zur Spannungs- und Rißentstehung beim Stranggießen
Dissertation, RWTH Aachen 1999

The present work is focused on mechanical modelling to investigate the effect of the secondary cooling on the crack formation in continuous casting. A finite element model is developed that tracks a section of the strand through the machine. The mechanical calculations are based on high resolution thermal modelling of the strand surface and internal temperature profiles provided by different steel producers. Finite element modelling was established which accounts for non-linear high-temperature mechanical properties of steel, plastic deformations modelled by creep laws, ferrostatic pressure and the effects of phase transformations (solid/liquid and γ-α). Contact boundary conditions are introduced to model the strand support in the mould and at roller positions.

The model is applied to billet and slab casting. The formation of stresses at the strand surface is investigated in detail. Typical stress patterns could be observed in the nozzle sprayed area and at roller contact. The results are interpreted with the aim of identifying regions of high stresses and, simultaneously, low cracking resistance. The ductility is a suitable measure for the material specific reasons of surface crack formation. The high resolution of the computations permits to detect those zones of the secondary cooling system or even individual nozzles which cause the largest cracking problems. A special crack index is introduced to evaluate the local cracking hazard both by the magnitude of tensile stress and brittleness of the steel.

Internal cracking occurs in a region near the phase front where the steel is not fully solidified and not able to sustain plastic deformations. A special procedure is established to calculate tensile strains accumulated in the low ductility range near solidus temperature. To determine critical regions for internal cracking the calculated tensile strains are compared with experimental data of critical strains that are a measure of maximum allowed deformation without cracking. The model is applied to billet strands and slabs in the mould region. Empirical results from steel producers are used for verification of all numerical models.

*Soft-Wert, Düsseldorf-Meerbusch

Tacke, K.-H.
Zweirollengießen – Entwicklung einer neuen Technologie der Stahlherstellung
Jahrbuch 1999 der Max-Planck-Gesellschaft, 490-494 (1999)

In this report a survey is given on the characteristics, advantages and economic attractivity of thin strip casting of steel. Furthermore the activities of MPI in this field are outlined. Especially the projects referring to strip surface, its defects and their understanding and avoidance are discussed. Furthermore results are given on the casting of LC-steel and an improving effect of adding small amount of Titanium.

Zimmermann*, H.; Büchner, A.R.; Tacke, K.-H.
Cracking of phenomena in twin roll strip casting of steel
EUROMAT'99, Volume 7, Wiley-VCH, Weinheim 2000, 29-32

The twin roll process, producing strip in the thickness range of 1 to 3 mm, can save energy, investment and operational costs and it is on its way into industrial realisation. The surface quality of twin roll cast strip can be affected by various flaws, among which cracking is one of the most serious defects. This paper reports observations on surface cracking and measures for crack prevention.

The tests were performed on a commercial 0.6% C steel, which also contained 0.7% Mn, 0,3% Si, 0.007% P, 0.015% S and 0.3% Cu. The strip has been cooled on air.

*TKS, Duisburg

Zimmermann*, H.
Oberflächenrisse beim Dünnbandgießen von Stahl
Dissertation, RWTH Aachen 1999

In this doctoral thesis the phenomenon of surface cracks is studied during thin strip casting of carbon steel C60. The surface cracks are observed and classified by statistical treatment referring to their distribution of length, of direction and over the strip surface. It was observed that crack formation has to be studied separately in hot spots and colder areas of the strip. Process parameters as roll material, roll roughness, roll force, roll coating are effective in crack formation. In total all experimental observations lead to the evaluation of the basic crack formation reasons, such as inhomogenious rolling and cooling. Measures for crack provention were deduced.

*TKS Duisburg

Oral and Poster Presentations

***Büchner**, A.R.; Messerschmidt, R.; Tacke, K.-H.:* Surface Quality of Twin Roll Cast Steel Strip, Materials Week. München, 25.09.-28.09.2000.

***Harste**, K.; **Tacke**, K.-H.:* Mikrostruktur- und Morphologieentstehung bei der Stranggießerstarrung, Ausschuß für metallurgische Grundlagen. TKS, Duisburg, 03.05.2000.

Department of Materials Technology

G. Frommeyer

Innovative Steel Research (ISR)

Light-weight steels based on Iron-Aluminium – Influence of microalloying elements (B, Ti, Nb) on the microstructure and mechanical properties

Due to their low density and higher specific strength light-weight steels based on iron-aluminium provide an outstanding potential for industrial applications in the automotive industry, particularly for car body components, [1].

The specific weight reduction by alloying aluminum to iron is associated with solid solution strengthening (about 50 MPa per 1 wt% Al) but likewise with a commencing embrittlement at certain Al contents, which restricts the application of iron aluminum alloys as deep drawing quality steels to about 6.5 wt% Al. According to this Al content a reduction in density of approximately 8 % can be obtained. At 6.5 wt% Al and more the complex K phase occurs in the solid solution at temperatures below 400 °C with short range order and preordering phenomena; at about 9 wt% Al the composition meets the$D0_3$ ordering phase field . The appearance $D0_3$ ordering domains causes a noticeable decrease in tensile ductility and impact toughness.

Depending on thermal treatment procedure a carbon content of 20 ppm (wt.) generates precipitations of very fine κ carbides due to the low solubility in the ferritic microstructure. These κ-carbides ($Fe_{4-y}Al_yC_x$; $0.8 \le y \le 1.2$, $0 \le x \le 1$) possess a perovskite structure $L1_2'$ at temperatures between 800 °C and 1200 °C. and primarily precipitate at grain boundaries.

The tensile ductility of carbon containing Fe-Al alloys markedly decreases with increasing C content caused by the carbide precipitates. The strain to fracture is very low ($\varepsilon_{fr} < 2\%$ at 350 ppm C). In the same manner the brittle ductile transition temperature (BDTT) of iron aluminium samples with charpy V notch tested substantially increases (ΔBDTT > 100 K).

In order to avoid the ductility reducing influence of carbon on the one hand the C content must be adjust as low as possible (< 100 ppm). On the other hand the undissolved carbon is fixed by an adequate addition of microalloying elements. In boron doped Fe-Al alloys (boron content ~30 ppm) carbo-borides are formed in the microstructure accompanied by iron-borides and boron-nitrides. By fixing undissolved carbon the ductility slightly increases compared to low carbon binary Fe-Al alloys. The tensile strength is raised of about 40 MPa due to grain refinement (Hall-Petch-relation). By increasing boron content up to 200 ppm coarser precipitates will be formed in the microstructure. These precipitates, which consist of iron-borides (Fe_2B) detected by EDX-analysis, are revealing in the optical microscope with an average size of about 3 µm. The increasing boron content causes a lack in ductility, the tensile strength in tension test is reduced of about 20%.

According to the amount of dissolved carbon in the ferritic matrix Fe-Al alloys with varying boron contents and different temperatures show a more or less distinct dynamic strain aging effect at elevated temperatures (100 °C ≤ T ≤ 400 °C) due to the Portevin-le Chatelier effect. Because of the interaction between carbon atoms in solution and dislocations associated with the resulting blockade of these dislocations the dynamic strain aging causes an increase in the tensile strength of a Fe-6Al (wt%) alloy without boron to a maximum of about 500 MPa at T = 250 °C. But the strain aging effect even occurs in Fe-Al alloys doped with higher boron content of 200 ppm at elevated temperatures. From this fact it is concluded that not the total carbon content is fixed to carbo-borides and a relevant portion is still interstitially solved.

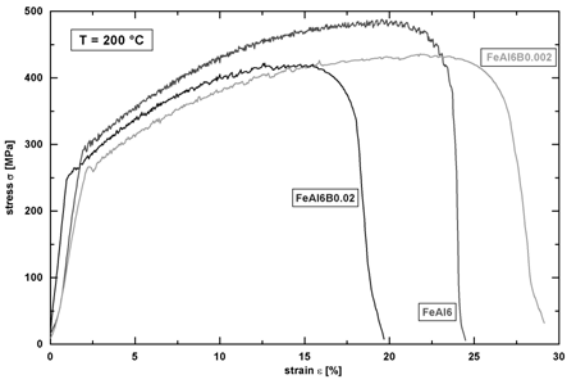

Figure 1: *Engineering stress-strain-curves of FeAl6 alloys with varying boron contents showing serrations referred to dynamic strain aging effects. Test temperature T = 200 °C.*

An enhanced fixing of carbon by carbide formation can be obtained by the addition of the microalloying elements such as titanium and niobium. These elements have a higher affinity to carbon, which results in a more negative free enthalpy (Gibbs energy) (Ti: $\Delta G^0_{carbide}$ = -72.3 kJ/mol; Nb: $\Delta G^0_{carbide}$ = - 74.1 kJ/mol). Titanium and niobium form carbides and nitrides in C and N containing steels. Therefore the ductility is improved, even though a certain C-content is still dissolved in spite of a hyper stoichiometric addition of Ti and Nb. The existence of interstitial carbon is verified by the appearance of the dynamic strain aging effect in the iron aluminium steel doped with Ti and Nb at higher temperatures. Otherwise the dynamic strain aging effect is not as pronounced as in

binary or boron doped Fe-Al alloys due to the reduced content of interstitial carbon.

In addition to the fixing of interstitially dissolved carbon titanium or niobium carbides act as inhibitors during the formation of the recrystallization texture. They will stimulate the development of the {111}-texture which effects an enhanced normal anisotropy and thereby an improved deep drawability. A further accentuation of a sharp {111}-texture is made possible by an increasing degree of deformation (η) after cold rolling ($\eta > 80$ %), because the recrystallization during the annealing process is accelerated and the formation of {111}-oriented grains is supported.

Investigations on the strain rate dependent mechanical properties of high manganese TRIP/TWIP steels

The strain rate dependent mechanical properties of high manganese (15 – 25 wt%) steels with additions of silicon (3 wt%) and aluminium (3 wt%) have been investigated, particularly at high strain rates up to about 10^3 s^{-1}, [2]. Mechanical twinning (TWIP-effect) or multiple martensitic phase transformation (TRIP-effect) under mechanical load causes extraordinary mechanical properties even at high strain rates.

The TRIP steel X 5 MnAlSi 20 3 3 exhibits a total elongation of about 82 % and an ultimate tensile strength of about 830 MPa at room temperature. The transformation of γ_{fcc} to ε_{hcp} and α_{bcc} martensite enhances the tensile elongation due to retardation of local necking. A too low or high value of the phase transformation rate results in preliminary fracture. In order to achieve large tensile elongations a gradual formation of the phase transformation is necessary. In the strain rate range of $1\ s^{-1} \leq \dot{\varepsilon} \leq 10^3\ s^{-1}$ the failure strain as well as the reduction in area are independent of the strain rate. Even at the highest strain rate of about 2500 s^{-1} strain hardening is dominating the deformation process up to about 40 % plastic deformation. In the range of low and medium strain rates of $10^{-4}\ s^{-1} \leq \dot{\varepsilon} \leq 1\ s^{-1}$ almost no strain-rate-sensitivity of the flow stress in compression tests was observed.

The TWIP-steel X 5 MnAlSi 25 3 3 exhibits a total elongation of about 92 % in tension and an ultimate tensile strength of 650 MPa at room temperature. These properties are due to extensive twinning formation in the austenitic matrix during deformation.

With increasing strain rate the total elongation decreases to a minimum of about 45 % ($\dot{\varepsilon} = 10^{-1} s^{-1}$).

The high tensile ductility and strength of these light-weight TRIP/TWIP steels improve e.g. the crash resistance of structural car body parts. The excellent formability enables deep and stretch forming of parts with complex shape. The reduced specific weight ($\rho \approx 7.3\ gcm^{-3}$) leads to an overall weight reduction of components.

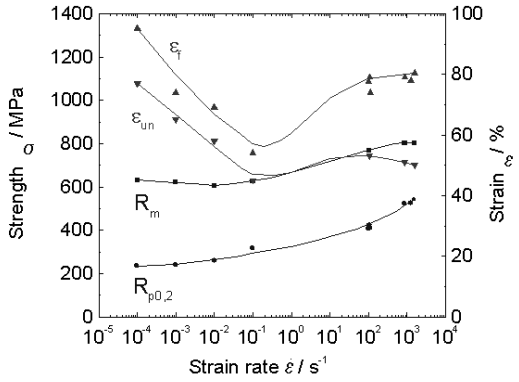

Figure 2*: Yield stress $R_{p0.2}$, tensile strength R_m, uniform elongation ε_{un} and total elongation ε_f in dependence on strain rate at T = 20 °C of the* high *manganese TWIP steel X 5 Mn Al Si 25 3 3*

Development and characterization of high strength steels

The physical and mechanical properties of the ultra high-strength maraging steel X1 Ni Co Ti16 10 have been studied in correlation with the martensitic and age-hardened microstructure.

In order to achieve the ultra high-strength state via transformation to martensite with subsequent age hardening the steel was heat treated – solution annealed and austenitized at 830°C for 180 min and quenched in ice water below the Ms temperature. The transformed martensite is of massive morphology possessing high dislocation densities of $>10^{14}$ dislocations/cm^2. The orientation relationship is: $(111)\gamma \parallel (011)\alpha$ and $[\bar{1}\,\bar{1}\,0]\gamma \parallel [\bar{1}\bar{1}1]\alpha$.

The observed platelet interfaces are rather wavy and the habit plane was indexed to [0.46; 0.53; 0.708]γ tilted about 10° away from (111) γ.

The age-hardening treatment was performed at 525°C/120 min in order to achieve the hardness of 49 to 50 HRc by precipitation reaction of η-Ni_3Ti. However. in lower nickel content maraging steels γ'-Ni_3Ti precipitates have been detected by X-ray analysis and by electron diffraction in the TEM.

The elastic modulus of the investigated steel is in the age-hardened state of about 195 GPa. The internal stresses cause an increase of about $\Delta E/E \approx 0{,}04$ compared with the soft annealed and stress relieved state.

The linear thermal expansive coefficient behaves in a similar way and is of the order of $\alpha_{RT} = 10.5 \times 10^{-6}\ grd^{-1}$. The achieved high yield stress of $R_{P0,2} = 1575$ MPa and ultimate tensile strength of about $1650 \leq R_m \leq 1850$ MPa is accompanied by an exceptional good fracture toughness – stress intensity factor of about $85 \leq K_{IC} \leq 110$ MPa$\sqrt{m}$ were recorded at room temperature.

At higher temperature the strength properties are quite remarkable. Yield stresses of $R_{P0,2}$=975 MPa and tensile strength of Rm=1080 MPa have been recorded at 500ºC. The elongation to failure reaches about ε_{tot}=20%. The high warm strength is due to dislocation pinning mechanisms caused by the small precipitates and the superior ductility is due to thermal activated dislocation climb.

The creep experiments of the nickel-cobalt-maraging steel type alloyed with small amounts of titanium showed in the temperature regime of 650 to 750ºC stress exponents of $4 \leq n \leq 5$ which indicates dislocation creep as the dominant deformation mechanism.

The creep strength at the strain rate of $\dot{\varepsilon}=10^{-7}s^{-1}$ is about 100 MPa (test temperature: δ=700ºC). The determined activation energies yields Q=175±5 kJ/mole which indicates grain boundary diffusion of iron and solutes (Ni, Co) controlled dislocation creep.

One interesting feature is that this ultra high strength maraging steel exhibits severe shear band formation under impact loading with strain rates of $\dot{\varepsilon}=10^{3}s^{-1}$, represented in the TEM image.

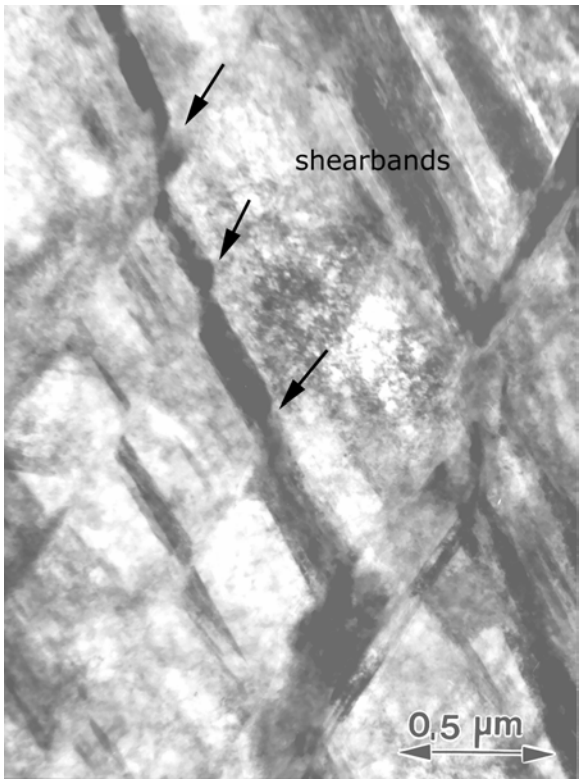

Figure 3: *TEM bright field image showing extensive shear band formation in the microstructure of the deformed maraging steel (strain rate: $\dot{\varepsilon}=10^{3}s^{-1}$, T=20ºC, plastic strain: ε_p=8 %*

Development and investigations on the strengthening mechanisms of ultra-high-strength pearlitic steel wires based on iron-aluminum-carbon

Eutectoid and Hypereutectoid plain carbon steels can achieve very high strengths in wire or rod form. These high strengths result from the mechanical work introduced during wire and rod processing and have been observed to increase with carbon content. In wire form, tensile strengths approaching 6000 MPa are predicted for ultrahigh carbon steels containing about 1.6 to 1.8 wt.% C. For pearlitic steels, yield and ultimate strength are functions of colony size, carbide size, plate spacing and orientation. Alloying additions such as C, Cr, Si and Al can influence the effect of processing on the microstructural features. For spheroidized steels, strength and ductility are influenced by the size of coarse carbides and of composition.

Amounts of aluminium up to 3 wt.% will increase the strength properties and the resistance against corrosion. Another important effect is the reduction in density or specific weight. These advantages will not be achieved by conventionally patented and heavily drawn pearlitic steel wires.

Expected effects of the aluminium addition are increasing strength by reducing the pearlite interlamellar spacing, an additional strengthening by solid solution, the reduction of specific weight and a better corrosion resistance.

With increasing aluminium content the pearlite point is shifted to higher carbon concentrations and therefore the proeutecoid cementite on grain boundaries can be avoided.

Rapid Solidification Technology

Martensitic Phase Transformation in High-Purity Iron due to Rapid Quenching

Martensitic phase transformation in thin high-purity iron foils of 25µm in thickness produced by rapid quenching either from the liquid or from the solid state (γ-phase regime) have been demonstrated for the first time. The contents of the interstitials, such as carbon was determined to C_C=22±4ppm and that of nitrogen to C_N=12±3ppm.

The thin foils experienced cooling rates during splat quenching-liquid to solid transformation-of the order of $>10^6$ K/s and during the solid state γ→α' transformation by quenching in ice brine of about $5x10^4$ K/s.

As the cooling rate is increased, the transformation temperature of 911ºC is reduced to about 550ºC when lath martensite appears.

There are three strong evidences for the martensitic transformation in high-purity iron: the martensite relief will appear on the surface and the shape of primary austenite grains including annealing twins will remain. This is shown in the micrograph of **fig. 4**.

The morphology of the martensite is either of lath type with high dislocation density or of twin type with almost no dislocations depending upon the cooling rate.

The Bain strain of $\varepsilon_{[110]}$=0.124 (dilatation in the [110] direction) and $\varepsilon_{[001]}$=-0.205 (contraction in the [001] direction is completely released by shear or twinning formations. The diffraction patterns do not show any evidences for a tetragonally distored b.c.c. lattice and some peak broadening is indicated accompanied with a suppression of the intensity of the (200) reflex. The orientation relation between γ and α' is different from the Kurdumow-Sachs relation and was determined to $(111)_\gamma \parallel (110)_\alpha$ and $[211]_\gamma \parallel [121]_\alpha$.

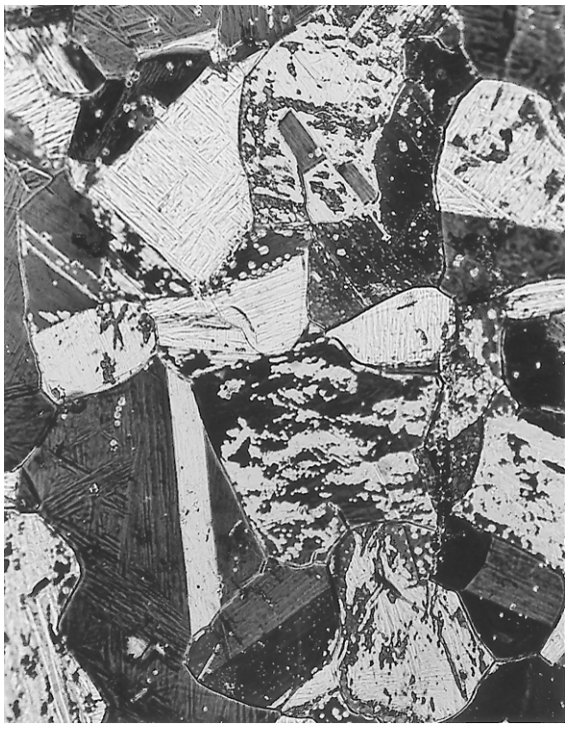

Figure 4: *Martensite relief and primary γ-annealing twins in an rapidly quenched high-purity iron foil; quenching rate: > 5x10^{4}K/s*

Development and Characterization of New Materials (DCNM)

Superplasticity of the Iron Aluminide $Fe_3Al(Cr)$

High temperature deformation properties like superplasticity and creep of iron aluminides are of gaining interest. One important reason for that is the fact that iron aluminides show great potential applications because of their lower specific weight, excellent oxidation resistance and high strength at elevated temperatures.

Another aspect is the technological relevance of superplasticity for near net shape forming processes, such as die forging of precission parts and blow forming of sheets.

Superplastic properties of a large variety of intermetallics, such as Ni_3Al and Ni_3Si with $L1_2$ structure, body centered cubic B2 and DO_3 ordered iron aluminides, tetragonal face centered γ-TiAl with $L1_0$ structure, and α_2-Ti_3Al with the complex hexagonal DO_{19} structure, have been demonstrated. The superplastic behavior of intermetallics is quite similar to that of non-ordered alloys. An interesting observation is the fact that some intermetallics, such as nickel silicides and iron aluminides exhibiting superplasticity with coarser-grained microstructures of 15 to 20 μm in size, respectively.

Coarse-structure superplasticity of an Fe_3Al based intermetallic alloy with 3 at.% chromium has been investigated in the strain-rate range from 10^{-5} to 10^{-2} s^{-1} at test temperatures between 700 and 900°C. The overall composition of the iron aluminide was Fe-28at%Al-3at%Cr with small amounts of titanium and carbon. In the thermomechanically processed state the material possessed a coarse-grained microstructure with an average grain size of 55 ± 10 μm. Superplasticity occurred at strain-rate exponents of $0.33 \leq to \leq 0.42$ and at strain rates of the order of 10^{-4} s^{-1}. Maximum elongations to failure of 300 % and more were achieved.

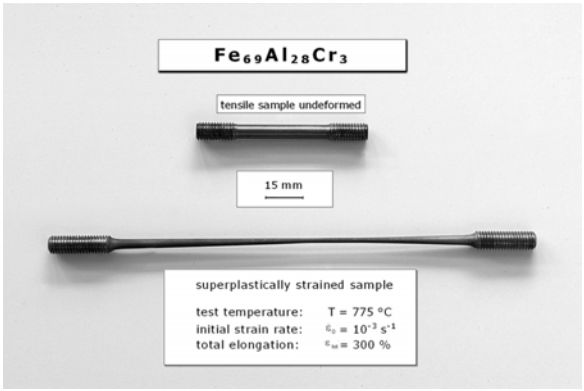

Figure 5 *shows a superplastically strained Fe_3AlCr tensile sample.*

From thermal activation analysis of superplastic flow an activation energy of 185 ± 10 kJmol^{-1} was derived. This value is comparable with activation energies of superplastic flow in $Fe_3Al(Ti)$ alloys. However, in unalloyed Fe_3Al the activation energy is higher, about 263 kJmol^{-1}.

Optical microscopy showed grain refinement to about 30 ± 5 μm in size in superplastically strained tensile samples. Transmission electron microscopy gave evidences for the formation of subgrains of the order of 0.3 to 0.5 μm in size. Superplasticity in this iron aluminide is mainly due to viscous dislocation glide,

controlled by solute drag in the transformed B2 lattice at the actual deformation temperatures.

Limited dislocation glide is also expected in solid-solution class I alloys in which the acting lattice friction is strongly influencing the dislocation mobility. Similar mechanism occurs in B2 or DO_3 superlattices, where dislocation glide is disturbing the short range ordering and chemical diffusion is reinstating the ordering behind the gliding dislocations.

From site preference studies on $Fe_3Al(Cr,Ti)$ aluminides that transformed from DO_3 into the B2 superlattice at the given deformation temperatures (750 to 850ºC) it is deduced that preferential formation of Fe-Cr (or Fe-Ti) pairs occur. These interatomic changes lead to a decrease in the dissociation energy of the substituting Fe-Cr (Ti) pairs compared with Fe-Al pairs in the B2 lattice. As a consequence the activation energy for diffusional processes controlling superplastic flow in Fe_3Al (Cr, Ti) is decreasing compared with stoichiometric Fe_3Al aluminides. The weaker bond of Fe-Cr pairs favors also an increase in the vacancy concentration in the B2 lattice at the given deformation temperatures. This may also accelerate the chemical diffusivity of the iron and aluminum species in this ordered aluminide of solid-solution class I type of alloy.

After a certain amount of superplastic deformations subgrain formation and grain refinement in the strained gauge sections is revealed. This leads to the conclusion that dynamic recrystallization is an important contribution to the deformation mechanism of superplastic flow in this material, [3].

TiAl based alloys

Titanium aluminides have attracted attention as lightweight structural materials since the early seventies. Hence, industrial application of single-phase TiAl and Ti_3Al alloys was not feasible at this time because of their brittleness and poor workability. In the meantime TiAl-based alloys are one of the most promising alternative high temperature materials to conventional heat-resistant steels and superalloys in high-performance automotive and aircraft engines. Extensive fundamental studies on these promising Titanium Aluminides as well as engineering oriented alloy development yielded quite ductile two-phase γ/α_2-alloys with improved properties. The alloy Ti-46.8Al-1Mo-0.2Si (at%) and recent developments at the Max-Planck-Institute für Eisenforschung, i.e. alloying modification with Cu, exhibit a well-balanced combination of physical and mechanical properties – e.g. low specific weight of about $\rho \approx 3.8 – 4.1$ g/cm^3, good oxidation and burn resistance, sufficient low temperature ductility, high elastic stiffness and enhanced high temperature strength. Yield strength and plasticity of thermomechanically processed material have been considerably increased by the addition of molybdenum which is also quite effective to improve high temperature oxidation resistance. Silicon additions lead to higher creep resistance and improve the castability.

Ingots of the alloy Ti-46.8Al-1Mo-0.2Si were extruded to rods at 1250˚C with the reduction in cross section of $A_0/A = 7$ and at 1300˚C with the reduction ratio of about 12.5:1. The axisymmetrically deformed sample at 1250˚C exhibits a dynamically recrystallized fine grained microstructure with equiaxed α_2 and γ grains of about $\leq 3\mu m$ in size and larger primary γ grains of 10 to 40 μm in size, respectively. The investigated aluminide shows in this processed state an excellent balance of high strength –yield strength of 730 MPa- and sufficient ductility-elongation to failure of about 3% in tension due to enhanced mechanical twinning in the larger γ grains of lower complex stacking fault energy. With increasing test temperature up to 700˚C the yield and ultimate tensile strength remain constant and the plastic elongations are increasing. Beyond 700˚C the strength properties are decreasing –flow stress of 350 MPa at 800˚C- and the tensile samples achieve more than 200% plastic elongations in tension test. The stress exponent decreases from n=5 at RT and 550˚C to n≈2 and indicates superplastic behaviour. The tensile samples show uniform elongations to failure of about 280% via grain boundary sliding. The axisymmetrically deformed rod like samples extruded at 1300˚C with a reduction ratio of A_0/A= 12.5:1 possesses an equiaxed microstructure with lamellar grains in the centre of the axisymmetrically deformed rods. The yield strength is about 800 MPa and the elongation to failure is slightly reduced to ε_{pl}=2.5%. TEM observations gave evidence that the amount of deformation twins is not so pronounced as in the samples described above. However, at higher temperatures the heavily deformed rod like samples exhibit a higher strength compared with the rods deformed with a reduction in area of A_0/A =7:1 , [4,5].

Alloying modifications with additions of about 1at% Cu possess improved castability due to lower melt viscosity. A significant decrease of the melting temperature of TiAl based alloys due to Cu additions has been detected by DSC measurements. TiAl(Cu) alloys exhibit extremely fine-grained solidification microstructures. The sustained grain refinement effect by Cu has also been detected in fully lamellar samples heat treated above the α-transus temperature and in samples having near-γ microstructure produced by near-α extrusion. However, the γ phase and small precipitates of a ternary phase, probably TiAlCu, are stabilized by Cu additions. Larger amounts of single phase γ regions in near-net-shape cast components could be detrimental to ductility at low temperatures. Adaptation of alloy composition is necessary to obtain suitable phase morphologies in diverse treatment conditions, especially in the as-cast state.

An improved combination of strength and ductility of various TiAl based alloys modified Cu additions alloys at low temperatures has been determined in series of compression tests (see **fig. 6)**. Due to en-

hanced plasticity of TiAl(Cu,Mo,Si) alloys at temperatures above 900°C processing by quasi-isothermal forging and superplastic near-net-shape die forming is particularly suitable. Thermomechanical treatments can be carried out at lower temperatures and/or with lower deformation forces.

Tensile tests of newly developed TiAl(Cu,Mo,Si) alloys in the hot-extruded condition (A_0/A=14:1) show superior strength and sufficient ductility ($\varepsilon_{p(20°C)} \geq 1.5\%$) at temperatures from 20°C up to 900°C. Brittle behavior of some samples is attributed to excessive oxygen contents and significant deviations from the proper alloy composition. Comprehensive investigations on these alloys in various treatment conditions, i.e. as-cast, heat treated and hot extruded, exhibit excellent physical and mechanical properties for potential light-weight applications in combustion engines like valves, turbine wheels of exhaust gas turbochargers, connecting rods and pistons.

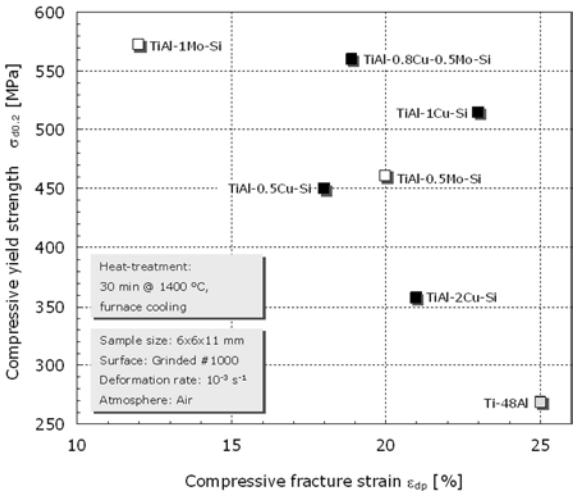

Figure 6: *Compressive yield strength versus fracture strain of various TiAl(Mo,Cu,Si) alloys at 20°C.*

NiAlCr-alloys

Inert gas atomized hypoeutectic $NiAlCr_{27}$-powders were consolidated by hot isostatic pressing at temperatures between 1100° and 1250°C to bars of 70mm in diameter. Maximum plastic deformation in compression test and fine microstructures with average grain sizes of d=2µm were achieved with samples which have been processed at the consolidation temperature of T=1150°C. The ultimate tensile strength of these samples at room temperature achieved in comparison to other NiAl-base alloys a relatively high value of UTS = 350MPa.

For optimizing the oxidation resistance and ductility at room temperature $NiAlCr_{27}$-alloys in the as cast condition were microalloyed with 0.1 and 0.4 wt% of the reactive elements Hf or Y. Alloying with Hf or Y below the limit of solubility of the elements increased the plasticity in compression tests. Only $NiAlCr_{27}Y_{0.2}$ (0.4 wt%) showed embrittlement due to the formation of an additional phase. Quantitative EDX spectroscopy evidenced these as a Y rich NiAlY(Cr,Si) phase, not yet indicated in the ternary Al-Ni-Y phase diagram, [6].

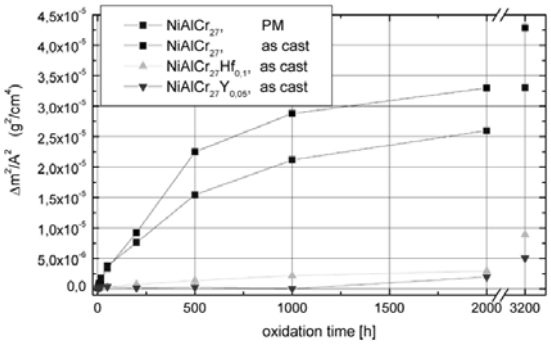

Figure 7: *Parabolic mass gain per surface unit at 1200°C in air of powder metallurgically processed and with Y or Hf modified as cast $NiAlCr_{27}$ alloys.*

The high temperature oxidation properties of microalloyed $NiAlCr_{27}$(Y,Hf) in the as cast condition and of powder metallurgically processed $NiAlCr_{27}$ alloys were characterized in long-term constant and cyclic oxidation tests at 1200°C.

The parabolic growth constants k_p (linear regression from 50h to 500h) of the as cast and of the powder metallurgically processed $NiAlCr_{27}$ base alloy show nearly the same values, despite the different microstructures, and are comparable to k_p values of pure NiAl for the formation of not stable Al_2O_3-modifikations. The parabolic growth constant of $k_p=5{,}6\cdot10^{-13}$ $g^2cm^{-4}s^{-1}$ of $NiAlCr_{27}Hf_{0.1}$ at 1200°C is lower than the k_p value of pure NiAl forming stable α-Al_2O_3-layer, [7].

$NiAlCr_{27}Y_{0.05}$ showed after the early stages of oxidation particularly weigh loss. Gravimetric oxidation tests by accurate scales revealed continuous mass loss due to sublimation of Cr.

Two cyclic oxidation tests with fast and slower (300°C/h) heating temperature rates up to 1200°C showed relatively high mass gains of the $NiAlCr_{27}$ base alloy and nearly complete cracking of the oxide layers due to thermal stresses at the cooling stage. The mass gains are not reduced at slower cooling rates and are commensurate to the cycle numbers.

The mass gain of $NiAlCr_{27}Y_{0.05}$ is sensitively dependent on the test parameters. $NiAlCr_{27}Hf_{0.1}$ showed in all oxidation tests the lowest mass gains. The adhesion of the thin oxide layer to the matrix material is significantly increased.

This investigations is part of the BMBF project 03N2009: Intermetallic NiAl components for nonpolluting energy conversion systems, [8].

Nanostructural Characterization using Atom Probe Field Ion Microscopy (APFIM)

Cr rich precipitation in NiAl(Cr) alloys of the compositions: $Ni_{50}Al_{48}Cr_2$, $Ni_{49}Al_{49}Cr_2$, and $Ni_{48}Al_{50}Cr_2$ were investigated after thermal treatment at 1200°C/100h and 550°C/500h and subsequent furnace cooling.

The Cr concentration in the NiAl matrix measured by APFIM increases with increasing heat treatment temperature and with increasing Ni content: e.g. for the 1200°C thermal treatment it amounts to 1.1 at% (50 at% Ni), and to 0.2 at% (48 at% Ni); for the 550°C treatment the Cr content ranges between 0.1 and 0.2 at%. In the B2 ordered NiAl matrix precipitates of Cr-rich phases were observed in the field ion microscope. Their lateral sizes ranged from about 3 to 100 nm in the FIM images (see **fig. 8**). The particle sizes were confirmed by TEM investigations.

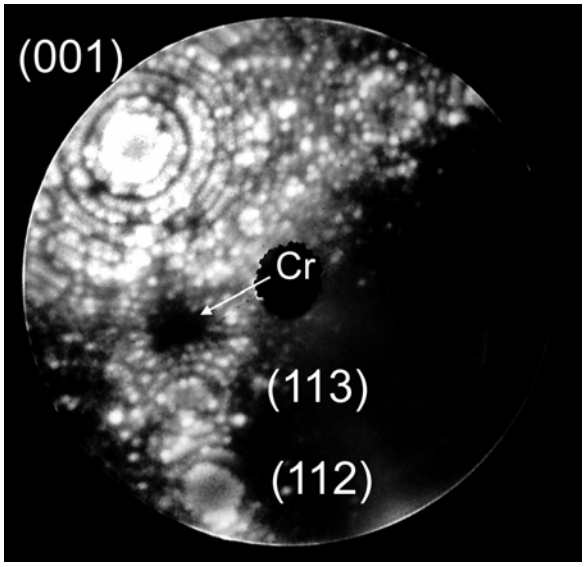

Figure 8: *FIM image of an α-Cr precipitate in the vicinity of the (001) pole of the NiAl matrix. Particle diameter d=3 nm.*

Whereas α-Cr precipitations with some amounts of dissolved Al (c_{Al} = 3.0 at%) and Ni (c_{Ni} = 1.5 at%) were observed to be present in the investigated compositional range for ratios of Ni/Al ≥ 1, another phase containing about 77 at% Cr and 23 at% Al was detected in $Ni_{48}Al_{50}Cr_2$ after thermal treatments. Referring to the literature data concerning the binary Al-Cr system this phase (composition) is termed 'X-phase'. The X-phase has not yet been indicated in the ternary Ni-Al-Cr system.

Because of the relatively low desorption field strength of Cr both α-Cr and the X-phase appear darkly in FI micrographs using Ne as an imaging gas. The different precipitates can be distinguished by the enhanced imaging properties of the X-phase due to the higher Al content. The preferential Cr evaporation of large precipitates causes an irregular tip shape leading to trajectory aberrations of image gas ions and desorbing substrate ions. Therefore FIM images and atom probe surveys have to be carefully interpreted. A steep concentration gradients between the Cr-rich phases and the surrounding NiAl matrix were detected by APFIM and the interfaces are well defined on the atomic scale (see **fig. 9**).

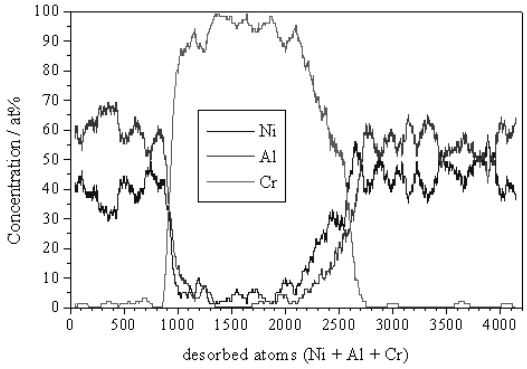

Figure 9: *Concentration profiles of an α-Cr precipitate in NiAl showing a sharp phase transition from NiAl to α-Cr.*

In the $Ni_{50}Al_{48}Cr_2$ alloy an antiphase domain boundary (APB) of the a/2<111>{123} orientation was imaged in the FIM. Atom probe measurement revealed a strong Cr segregation on the APB with the Cr atoms occupying Al sites. This is in good agreement with literature data of calculated APB energies of plain and Cr alloyed NiAl with Cr substituting either for Al or for Ni sites, [9].

APFIM studies on the Atomic Distribution of the Alloying Elements V, Nb and Cr and on the composition of the γ-TiAl phase

The atomic distribution of the transition metals V, Nb and Cr and their influence on the composition ratio $(C_{Al}/C_{Ti})_{\gamma}$ of the γ-phase of TiAl base alloys were investigated by atom-probe field ion microscopy (APFIM).

Niobium atoms are preferentially located in the titanium sublattice and require higher evaporation field strength than Ti and Al atoms for field ion imaging. Nb atoms tend to form clusters in Ti layers and show

also a strong tendency to continuous ordering by the formation of a tetragonal superlattice (γ' phase).

In contrast no superstructure evolution was detected for chromium and vanadium atoms. These species are more homogenously distributed troughout the γ-phase than Nb atoms.

The concentration ratio $(C_{Al}/C_{Ti})_\gamma$ of the γ-phase is about 1.02 for $Ti_{50}Al_{46}Cr_3$. $(C_{Al}/C_{Ti})_\gamma$ = 0.98 were detected for $Ti_{51}Al_{46}V_3$, respectively. Alloying TiAl with Nb, however cause a strong deviation from the ratio $C_{Al}/C_{Ti} \approx 1{,}00$ to 1,02 for plain γ-$Ti_{50}Al_{50}$. Random area analysis of the $Ti_{48}Al_{47}NB_5$ alloy showed a C_{Al}/C_{Ti} ratio of 1.33. These results are consistent with site preference studies performed with ALCHEMI, [10].

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Publications and Abstracts

Blum, M.; Choudhury, A.; Jarczyk, G.; Scholz, H.; Busse, P.; Frommeyer, G.; Knippscheer, S.; Laudenberg, H.J.; Segtrop, K.
Properties of Low Cost TiAl Automotive Valves Produced by Cold Wall Induction Melting and Permanent Mold Centrifugal Casting
In: Proc. 9th World Conference on Titanium in St. Petersburg, Volume 3, Symp. 8. Central Research Institute of Structural Materials, St. Petersburg 2000, 1433-1441.

Due to its much lower density and higher tensile properties at elevated temperatures TiAl is most suitable as valve material than austenitic steel grades for new generation automobiles. But the present-day production technology for Ti-based alloys, which is developed mainly for the aerospace industry, is not economically suitable for automobile valves. A new manufacturing process for an economical mass production of TiAl valves has been developed by a joint research project, which is financially supported by the Federal Ministry for Education and Research of Germany.

The new process enables the production of TiAl valves in high annual volumes and at cost comparable to conventional steel exhaust valves. The expected price is feasible through the very high level of process integration. Melting, alloying, purification and casting are integrated in single step. The two main features of the manufacturing process are the use of a modified induction cold crucible and a heatable metallic permanent mold in an evacuable centrifugal casting unit.

Based on the results of numerical process simulation as well as casting experiments a pilot plant has been built. In order to minimize the effort for the optimization of melting and casting parameters, regarding, the mechanical properties of the valve, an experimental program based on modern DoE-technique was performed. The development of the process and the results of this program will be presented.

Choudhury, A.; Blum, M.; Jarczyk, G.; Scholz, H.; Busse, P.; Frommeyer, G.; Knippscheer, S.; Laudenberg, H.J.; Segtrop, K.
Massenherstellung von TiAl-Automobilventilen durch Schmelzen und Schleudergießen in einem Arbeitsgang
In: DVM-Tag 1999 - BAUTEIL '99 - Werkstoffe und Verfahren im Wettbewerb, DVM, Berlin (1999) 125-133.

Combustion engines of new generation automobiles exhibit higher exhaust gas temperatures due to optimized combustion at stoichometric conditions. TiAl-based alloys possessing lower density and higher tensile properties at elevated temperatures are most suitable as valve material than austenitic steel grades. However, the present-day production technology for Ti-based alloys is not economically suitable for automobile valves. Melting by conventional vacuum induction technique using ceramic crucibles is not applicable due to the high reactivity of TiAl-based alloys. In order to attend to the world market with a potential annual production of about 300 million automotive valves the development of a technologically optimized manufacturing process for the economical mass production of TiAl valves is required.

Frommeyer, G.; Drewes*, E.J.; Engl*, B.
Physical and mechanical properties of iron-aluminium-(Mn, Si) lightweight steels
Journal de Physique 10, 1245-1253 (2000)

Ferritic iron-aluminium and austenitic iron-manganese-aluminium-silicon alloys are showing promising physical, mechanical and technological properties, which are suitable for the development and design of new types of high strength lightweight steels.

The relatively high aluminium contents up to C_{Al} = 8.5 wt-% (~ 16 at-% Al) lead to a reduction in specific weight of 10 % and more combined with an improvement of elastic stiffness and strength by effective solid solution hardening mechanisms.

The multiple TRIP effect [$\gamma_{fcc} \rightarrow \varepsilon_{hcp(MS)} \rightarrow \alpha'_{bcc(MS)}$] in the X 5 Mn Si Al 15 3 3 steel causes high work-hardening rates and tensile strength with improved tensile ductility.

With increasing manganese content up to about 22 wt-% Mn the stacking fault energy will be decreased and extensive mechanical twinning occurs and causes extraordinary high plasticity (Twinning Induced Plasticity: TWIP effect).

*Thyssen Krupp Stahl AG, Duisburg

Frommeyer, G.; Kreuss, M.; Rosenkranz, R.
Microstructures and Properties of Newly Developed Alpha Titanium Ti_5Si_3 Alloys
In: Proc. 9th World Conference on Titanium in Saint Petersburg, Russia, Central Research Institute of Structural Materials (CRISM), Volume 3, Symp. 12, 1896-1905

The high melting point titanium silicides, such as Ti_5Si_3 and $TiSi_2$ have been investigated in recent years. Alpha titanium forms with the complex hexagonal Ti_5Si_3 compound (D_8^8-type of crystal structure) an eutectic system with large volume fractions of about 30 vol.% Ti_5Si_3 embeded in the hexagonal α-Ti(Si) solid solution. For the development of high temperature oxidation resistant Ti-based alloys two different processing routes have been considered: One is directional solidification in

order to achieve a fibre reinforcement of α-Ti matrices due to the presence of high strenght and elastically stiff discontinuous Ti_5Si_3 fibres which are aligned parallel to the road axes. The other route is to produce a fine grained eutectic or hypoeutectic microstructure consisting of α-Ti with a fine dispersion of Ti_5Si_3 particles of several microns in size.

The present paper describes and discusses the physical and mechanical properties of newly developed α-Ti/T_5Si_3 materials under consideration of their excellent high temperature properties of the refractory intermetallic Ti_5Si_3 compound.

Grässel*, O.; Krüger**, L.; Frommeyer, G.; Meyer, L.W.***

High strength Fe-Mn-(Al, Si) TRIP/TWIP steels development –properties–application

International Journal of Plasticity 16 (2000) 1391-1409

Deforming twinning, martensitic phase transformation and mechanical properties of austenitic Fe-(15-30) wt.% Mn steels with additions of aluminium and silicon have been investigated. It is known that additions of aluminium increase the stacking fault energy γ_{fcc} and therefore strongly suppress the γ→ε transformation while silicon decrease γ_{fcc} and sustains the γ→ε transformation. The γ→ε phase transformation takes place in steels with $\gamma_{fcc} \leq 20 mJ/m^2$. For steels with higher stacking fault energy twinning is the main deformation mechanism. Tensile tests were carried out at different strain rates and temperatures. The formation of twins, α- and ε-martensite during plastic deformation was analysed by optical microscopy, X-ray diffraction, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The developed light weight high manganese TRIP ("transformation induced plasticity") and TWIP ("twinning induced plasticity") steels exhibit high flow stress (600-1100 Mpa) and extremely large elongation (60-95%) even at extremely high strain rates of about $10^{-3}s^{-1}$. Recent trends in the automotive industry towards improved safety standards and a reduced weight as well as a more rational and cost effective manufacturing have led to great interests in these high strength and "super tough" steels.

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Jiménez*, J.A.; Carsi*, M.; Frommeyer, G.; Ruano*, O.A.

Characterization and Mechanical Properties of a δ/γ Duplex Stainless Steel

Key Engineering Materials 171-174, 389-394, 2000

The mechanical behavior at high temperature of a duplex stainless steel was investigated by means of strain-rate-change tests in tension. Analysis of the stress-strain rate data revealed a change in the behavior of the material at about 950˚C, which is attributed to the presence of the σ phase. However, stress exponents of about 5 and 2 were observed at strain rates above and below $10^{-3}s^{-1}$ respectively, at all testing temperatures. These results suggest a change in the mechanism controlling deformation from slip creep to grain boundary sliding, GBS, as the strain rate decreases. Contribution of GBS to deformation was associated with the fine microstructure developed by recrystallization before testing. This microstructure consisted of colonies of austenite grains of 10 to 15 μm in size surrounded by a ferrite matrix at testing temperatures above 1000˚C or by a lamellar microstructure below 950˚C. Superplastic behavior of the material at low stresses, where n≈2, was checked by monotonic strain rate tests at 900 and 1050˚C at $10^{-4}s^{-1}$. The importance of GBS in this case was corroborated by analysis of the microstructure and the texture in the gage region. The grains of the present phases are intermixed after testing in the superplastic regime. This is due to grain rearrangement occurred during deformation by grain boundary sliding. On the other hand, only minor changes in the texture along the most important fibers (Θ-fiber and α-fiber for the ferrite and the ζ-fiber for the austenite) were observed between the undeformed grip region and the gage region.

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Knippscheer, S.; Frommeyer, G.

Structure and properties of intermetallic TiAl(Cr,Mo,Si) alloys for lightweight engine parts

In: Titanium'99 Science and Technology (ed.: Gorynin, I.V.; Ushkov, S.S.) CRISM "Prometey", St. Petersburg, Russia (2000) 320-327.

The economical exploitation of fuel as well as the reduction of exhaust gas and noise emission cause an increase in the demand of lightweight materials for rotating or oscillating components in power converting systems – internal combustion engines and jet engines. Two-phase intermetallic TiAl/Ti_3Al-alloys with additions of molybdenum or chromium are well suited for lightweight engine parts under high thermal and mechanical load, because of their low density ($\rho \approx 3{,}8\ g/cm^3$), relatively high thermal conductivity ($\lambda_{(RT)} \approx 22\ W/mK$), high elastic stiffness and enhanced high-temperature strength ($R_{m(800°C)} > 500\ MPa$). Examples for the application in combustion engines are

valves, connecting rods, piston bolts and exhaust gas turbocharger rotors. Due to the considerably high specific Young's modulus ($E/\rho \approx 46$ GPa cm^3 g^{-1}) and high yield strength of about $R_{p0,2} \approx 800$ MPa of the TiAl(Cr,Mo,Si)-alloys in the as-extruded state applications for lower temperatures have also been taken into consideration (e.g. rotors of centrifuges).

Variation in the processing parameters for the manufacturing of semifinished products or components leads to modification of the microstructure in order to optimize the mechanical properties with regard to different applications. In the as-cast state the alloys exhibit lamellar microstructures of high creep resistance and fracture toughness ($K_{IC(RT)} \approx 30$ MPa m^{0,5}). Dynamic recrystallization during axisymmetrical deformation by hot extrusion leads to a fine-grained equiaxed microstructure consisting of near-γ and/or lamellar phase morphologies. The extruded material possesses improved strength as well as sufficient ductility ($\varepsilon_{p(RT)} \approx 3$ %). Due to the enhanced plasticity of the microcrystalline near-γmicrostructure blanks and components can be manufactured by quasi-isothermal forging or superplastic deformation. The present paper describes and discusses the microstructural related properties of advanced TiAl(Cr,Mo,Si)-alloys with regard to structural applications at high temperatures.

Knippscheer, S.; Frommeyer, G.
Intermetallic TiAl(Cr,Mo,Si) Alloys for Lightweight Engine Parts - Structure and Properties
In: Proc. EUROMAT 99 in München, Symposium B1, Materials for Transportation Technology, (Ed.) Winkler, P.J., Wiley-VCH, Weinheim (2000) 12-18.

The reduction of exhaust gas and noise emission cause an increase in the demand of lightweight materials for rotating or oscillating components in power converting systems – internal combustion engines and jet engines. Two-phase intermetallic TiAl/Ti_3Al-alloys with additions of molybdenum or chromium are well suited for lightweight engine parts under high thermal and mechanical load, because of their low density ($\rho \approx 3{,}8$ g/cm^3), relatively high thermal conductivity ($\lambda_{(RT)} \approx 22$ W/mK), high elastic stiffness and enhanced high-temperature strength ($R_{m(800°C)} > 500$ MPa). Applications in combustion engines are valves, connecting rods, piston bolts and exhaust gas turbocharger rotors. Due to the considerably high specific Young's modulus ($E/\rho \approx 46$ GPa cm^3 g^{-1}) and high yield strength of about 800 MPa of the TiAl(Cr,Mo,Si)-alloys in the as-extruded state parts for lower temperature applications have also been taken into consideration (e.g. rotors of centrifuges).

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Knippscheer, S.; Frommeyer, G.; Baur, H.; Joos, R.; Lohmann, M.; Berg, O.; Kestler, H.; Eberhardt, N.; Güther, V.; Otto, A.
TiAl Automotive Valves - Fabrication and Properties
In: Materials for Transportation Technology (ed.: Winkler, P.J.) Wiley-VCH, Weinheim (2000) 110-115.

In a joint research project a fabrication process based on thermomechanical processing for lightweight valves made out of a γ-TiAl base alloy with additions of molybdenum and silicon has been developed. In the first step of the fabrication process as-cast TiAl(Mo,Si) ingots were hot extruded. Near-net shape valve blanks have been produced by bulging and subsequent quasi-isothermal die forging of segments of the as-extruded rods. The thermomechanical processing – extruding, bulging and die forging – was carried out at fairly high temperatures between 1100 °C and 1300 °C. The deformation rate of TiAl alloys is considerably lower compared to that of conventional valve materials – valve steels or Ni-based alloys. However, the TiAl valve blanks successfully produced at industrial production devices exhibit a very homogeneous microstructure without any cavities or other internal defects. Application of coatings made out of high temperature brazing alloys will improve the bearing properties and the resistance against high temperature corrosion. The production process and the properties of thermomechanically processed TiAl valves are presented and discussed. This research project is financially supported by the German Federal Ministry of Education and Research (BMBF).

Pérez*, P.; Jiménez*, J.A.; Frommeyer, G.; Adeva*, P.
The Influence of the Alloy Microstructure on the Oxidation Behavior of Ti-46Al-1Cr-0.2Si Alloy
Oxidation of Metals Vol. 53, Nos.1/2, 99-124 (2000)

The influence of microstructure of the two-phase alloy Ti-46Al-1Cr-0.2Si on the oxidation behavior in

air between 600 and 900˚C was studied. The oxidation rate, type of scale, and scale spallation resistance were strongly affected by the type of microstructure, i.e., lamellar in as-cast material and duplex after extrusion at 1300˚C. The oxidation rate was affected by the size and distribution of the α_2-Ti_3Al phase, being faster for the extruded material with coarse α_2-Ti_3Al. The type of oxide scale determines the spalling resistance. Cast material developed a uniform scale that spalled off after short exposure times at 800 and 900˚C when a critical thickness was reached. The extruded material presented a heterogeneous scale with predominant thick regions formed on γ-TiAl-α_2-Ti_3Al grains and thin scale regions formed on γ-TiAl grains. This type of scale could permit an easier relaxation in the matrix of stresses generated by both thermal-expansion mismatch between scale and alloy and oxide growth, resulting in a higher spallation resistance.

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Wesemann, J.; Falecki, W.; Frommeyer, G.
Distribution of the Transition Metals V, Nb, Cr and Their Influence on the Composition of the γ-Phase of TiAl Base Alloys
Physica Status Solidi (a) 177, 319-329, 2000

Two phase α_2/γ TiAl alloys without and with additions of the transition metals Cr, Nb and V were investigated by atom probe field ion microscopy (APFIM). Cr and V atoms are more homogeneously distributed in the γ phase than Nb atoms. These preferentially occupy the Ti sublattice and tend to form a superlattice structure. No similar lattice formation was observed in gamma titanium aluminides with Cr and V additions. In comparison to a binary TiAl alloy the concentration ratio $c_{(Al)}/c_{(Ti)}$ in the γ phase is only slightly changed by V and Cr additions, but remarkably increased by Nb additions. The γ phase of the TiAlNb alloy revealed more britte than those of the conventional binary alloy and TiAl based alloys with addition of Cr and V.

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Denizci, M.: Charakterisierung von γ-TiAl Basislegierungen für Triebswerk- und Motor-komponenten. FH Düsseldorf 2000.

Marinkovič, A.: Mikrostrukturen und mechanische Eigenschaften von NiAl-HfB_2-Gusslegierungen. FH Düsseldorf 2000.

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***Fischer**, R.; Frommeyer, G.; Schneider, A.:* Chromium Precipation in B2 -Ordered NiAl-2 at% Cr Investigated by Atom Probe Field Ion Microscopy, 46th International Field Emission Symposium, Pittsburgh, Session 7 "APFIM Applications 3- Physical Metallurgy: Phase Transformations". Pennsylvania, USA, 23.07.-28.07.2000.

***Fischer**, R.; Frommeyer, G.; Schneider, A.:* Investigations on Cr Precipitations in B2 ordered NiAl -2 at% Cr alloys using Atom Probe Field Ion Microscopy (APFIM), Materials Week 2000, Symposium H" "Intermetallics and Superalloys". München, 25.09.-28.09.2000.

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***Frommeyer**, G.:* Innovative Leichtbaustähle mit höherer Tiefziehfähigkeit, Werkstoffkolloquim der Salzgitter Stahl AG. Salzgitter, 03.08.2000.

***Frommeyer**, G.:* Innovative Leichtbauwerkstoffe für den Hochtemperatureinsatz, Institut für Werkstofftechnik, TU Hamburg. Hamburg, 18.04.2000.

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***Frommeyer**, G.:* Potential hoch aluminiumhaltiger Leichtbaustähle, Saarstahl AG. Völklingen, 02.11.-03.11.2000.

***Frommeyer**, G.:* Spannungsanalyse und Festigkeitsnachweis an hochfesten perlitischen Stählen, Forschungs- und Entwicklungs- GmbH. Essen, 01.03.2000.

***Frommeyer**, G.:* Superplastizität geordneter Legierungen, Universität Duisburg, Institut für Werkstofftechnik, FB Maschinenbau. Duisburg, 20.09.2000.

***Frommeyer**, G.:* Warmfeste Werkstoffe für die Zukunft, Werkstoffkolloquium, Internationale Raumstation ISS. Freiburg, 04.07.2000.

***Frommeyer**, G.; Fischer, R.; Schneider, A.:* Untersuchung der Strukturgradienten an Phasen- und Antiphasengrenzen in B2 geordneten NiAl(Cr, Fe, Mo)-Mischkristallen mit der Atomsonden Feldionenmikroskopie, Kolloquium DFG Schwerpunktprogramm "Strukturgradienten in Kristallen". Fulda/Hünfeld, 04.10.-06.10.2000.

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***Schneider**, A.; Inden, G.; Viefhaus, H.; Grabke, H.J.:* Phase Transformation in the Fe-C System during Gas Carburization, CALPHAD XXIX, Massachusetts Institute of Technology, Cambridge. Massachusetts, USA, 18.06.-23.06.2000.

Department of Microstructure Physics and Metal Forming

D. Raabe

The development of new steels with tailored and reproduceable properties demands a closer and closer integration of forming technology and physical metallurgy. Reduction of final grain size by optimised ferritic hot rolling, influence of strip-scale formation on hot rolling, properties of cold rolled and annealed ferriticly hot rolled specimens, properties of thin slabs and their final products and texture optimisation of soft magnetic Si-steels are examples of this integration in current projects in the Microstructure and Metal Forming department.

The concept of linking together metal forming and physical metallurgy is the basis of the department work. The new department covers a broad spectrum of topics, reaching from practical questions of industrial casting, forming and thermomechanics to topics of physical metallurgy like microstructure evolution. The department is divided into four scientific groups, namely Theory and Simulation (Dr. Roters), Diffraction and Microscopy (Dr. Zaefferer), Thermomechanical Treatment (Dr. Kaspar), and Metal Forming (Dr. Rasp). The four scientific groups are assisted by the Computation, Metallography, Metal Forming, and Mechanical Testing service groups. The idea of this concept is to build up an interdisciplinary research centre where forming technology and microstructural research as well as theory and experiment are treated simultaneously and in close collaboration.

Theory and Simulation

F. Roters

The activities of the research group Theory and Simulations were focused on the two topics **crystal plasticity finite element method** (CPFEM) and **dislocation density based constitutive laws** for the plastic deformation of metals and alloys.

In the field of CPFEM some work was done to improve the method itself. Different UMAT-Subroutines for fcc and bcc metals were joined into one general routine which than was extended to also treat simple cubic and hexagonal materials. The originally used empiric hardening law was replaced by the phenomenological Voce equation. Also the formulation for the elastic behaviour was changed from isotropic to anisotropic. This is especially important for the prediction of spring back in forming simulations. Another focus was the improvement of macro texture representation for the simulation of technical forming processes.

Secondly the method was applied to fundamental research topics as well as to technical forming processes. A simple analytic model was developed to predict the tendency for **grain fragmentation** during plastic deformation. It is based on the long known flow field theory by Bunge [1] and uses the divergence of the flow field as measure for the fragmentation tendency. Single crystal CPFEM calculations were successfully used to prove the predictions of the model [2]. To study the influence of grain interaction also bicrystal simulations were carried out, where one crystal was completely surrounded by another crystal [2]. This calculations showed only a weak influence of the surrounding crystal on the embedded one. Moreover simulations of the channel die deformation of polycrystalline Al-samples were carried out. As the real samples consisted of through-thickness columnar grains a 2D geometry was used for the simulation. The original grain orientations were measured by EBSD and than assigned to the finite elements. The results showed good qualitative accordance with the experimental results. Different calculations were carried out to study the influence of friction on the deformation process (**fig. 1)**.

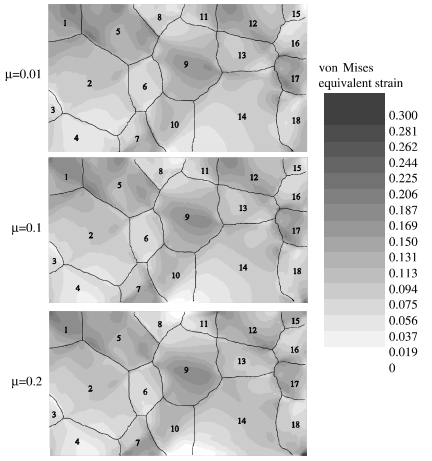


Figure 1: *CPFEM calculations of plain strain compression test of polycrystal Al, results for different friction coefficients μ*

The fact that both CPFEM as well as continuum FEM calculations were performed allowed to distinguish the effects of continuum and crystal mechanics [3]. Proper evaluation of the numerical data obtained showed very nicely that grain interaction was confined to the region in the direct vicinity of the grain boundaries, while most of the grain volume showed homogeneous behaviour. It is important though to notice that this statement is not generally valid but only applies to the special case studied.

While every integration point has one distinct orientation for all the calculations mentioned so far the situation is completely different for the simulation of technical forming processes. In this case every integration point has to represent the materials macroscopic texture since it is not possible to use FE meshes with sub grain resolution for macroscopic work pieces. The work done in this field concentrated on the deep drawing process and the prediction of earing behaviour as an important measure for the anisotropy of a material.

The **constitutive law** plays a key role in every forming simulation. Therefore the group works on the development of **dislocation density based** models for the plastic deformation of metals and alloys [4, 5]. Within these models the dislocation density (or more precisely a couple of different dislocation densities) serves as a physical variable of state that reflects the complete history of the material concerning forming and heat treatment. These models can be used for the simulation of all kinds of forming operations ranging from rolling to creep. For the simulation of multi stand rolling it is a special advantage of the model that it can not only describe the dynamic behaviour of the material but that it treats static recovery as well. It was therefore possible to markedly improve the simulation of Al hot rolling [5]. In the field of steady state creep it could be shown, that the model developed is capable of explaining the so called **power law breakdown** [6]. Within the framework of the model the effect is attributed to the increasing importance of spontaneous annihilation of mobile dislocations with increasing external load.

Microscopy and Diffraction

S. Zaefferer

Task of the microscopy and diffraction group is the investigation of the evolution of microstructure and texture of various materials during different processes by means of modern experimental methods. The investigations are especially focused on the micro mechanisms of these processes. Thus, experimental methods with a high spatial resolution are used with preference. These methods include transmission and scanning electron microscopy (TEM and SEM) and the appropriate electron diffraction techniques (transmission Kikuchi patterns (TKP) and spot patterns in the TEM, electron backscatter patterns (EBSD) in the SEM) as well as micro x-ray diffraction.

An important field of research is the investigation of mechanisms that lead to the evolution of textures during deformation and recrystallization processes of "classic" materials such as iron, aluminum and copper and their alloys. During the deformation of poly- or monocrystals of these metals the crystals rotate depending on their orientation along certain rotation paths into stable orientations thereby forming deformation textures. The global mechanisms of these rotations are well understood. However, the local mechanisms which are also responsible for the development of the microstructure still remain unclear: in which way occurs the adaptation of different deforming crystals close to the grain boundaries? Which crystals rotate as a whole, which split up into different orientations? How does the microstructural evolution depend on the start orientation of a crystal? How do deformation heterogeneities like transition bands, shear bands or lamella bands develop during deformation and how does this depend on the orientation and the neighborhood of the crystal as well as on the deformation process?

The structure and orientation distribution of deformation heterogeneities are of fundamental importance for the recrystallization mechanisms. The nucleation rate depends strongly on the misorientation and lattice curvature as well as on the exact dislocation structure and may thus be very different for different microstructures. This is one important reason, in some cases maybe the most important for the development of recrystallization textures.

An example for the strong influence of the local deformation on the recrystallization texture is the development of the cube recrystallization texture in heavily cold rolled Fe-36% Ni [7, 8]. During cold rolling this face centered cubic alloy develops a strong copper-type deformation texture. During recrystallization a sharp cube texture is formed. In order to determine the recrystallization mechanisms the deformation structures and local textures of the deformed material were studied in detail. Since the spatial resolution of EBSD in the SEM was not sufficient for this particular material the study was carried out in the TEM. Already after small deformations (40 to 60%) the microstructures of differently oriented crystals can be distinguished. Cube-oriented crystals develop dislocation cells while other orientations develop dense dislocation walls. With increasing deformation the microstructures of differently oriented crystals differ more and more.

Fig. 2 displays the TEM microstructure of a sample after 94 % of cold rolling in form of an orientation map. The color coding of the map is done by relating every crystal direction to a specific color in the standard orientation triangle. Since two crystal directions are necessary to define a crystal orientation the microstructure is shown twice, once color-coded for the rolling direction and once for the normal direction. From the maps it becomes evident that the cell structure in the center of the microstructure is cube oriented, while the lamella structures belong to the C- and S-deformation texture components. The misorientation between the subgrains or cells have been calculated along the white lines in the microstructure. While the cube-oriented cells show a strong and continuous orientation gradient almost no gradient exists in the lamella areas. The figure on the right side shows the quality of diffraction patterns of the measured crystals. The diffraction pattern quality is a (qualitative) measure for the local degree of recovery. It can be seen clearly that the cube-

oriented crystals are most highly recovered. During recrystallization the cube areas start to form new crystals significantly quicker than others due to the strong orientation gradient and due to the high degree of recovery.

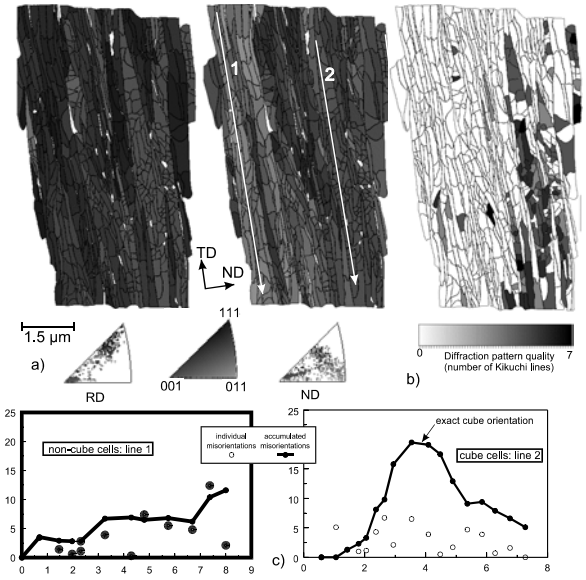
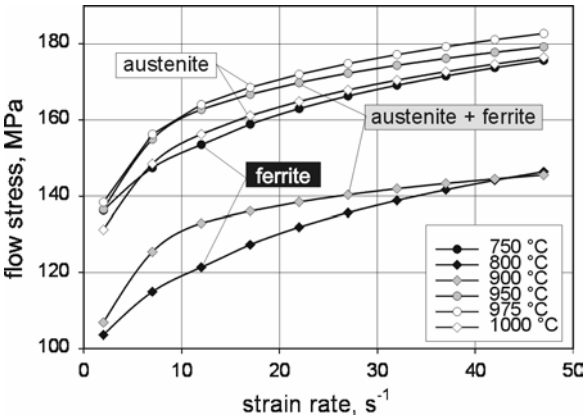


Figure 2: *Microtexture and diffraction pattern quality of an Fe 36% Ni sample after 94% of cold rolling measured in the TEM.*



The detailed investigation of the evolution of the microstructure and texture during deformation and recrystallization allowed to clarify the nucleation mechanisms and to develop a model for the cube texture formation in Fe 36% Ni. In future studies this model will be tested on aluminum and copper which also develop a cube texture. Some pre-investigations have been carried out on high-purity aluminum. Unfortunately the large grain size of the material didn't allow statistical meaningful investigation of cube nucleation mechanisms in the TEM or even the SEM. Experiments in order to produce finer grains on the material are currently carried out. Investigations on the recrystallization nucleation mechanisms are also planned for highly deformed bcc steels.

For the future it is planned to extend the deformation and recrystallization investigations to intermetallics, for example TiAl or Fe3Al. The measurement of orientations in TiAl by means of EBSD is problematic since higher order lattice reflections which are essential for the correct orientation determination can't be resolved with this technique. A way out of this problem is the usage of the TEM where self-developed software enables the unambiguous orientation determination [9].

Thermomechanical treatment

R. Kaspar

The activities of the research group of thermomechanical treatment were dedicated to several projects and diverse investigations in a direct cooperation with the industry. In the project **Thermomechanical treatment of near net shape cast and directly rolled steel strips with the cast thickness within the range of 5-20mm** the investigations were carried out to improve the microstructure and the mechanical properties of three different steel grades (austenitic stainless steel, pearlitic high carbon steel and IF steel) and three different treatments (as-cast strips, direct hot rolling, and hot rolling after cooling down and reheating). The strips were cast in a new built double-roller casting machine, designed and built in institute for as-cast thicknesses of 5-20 mm. For all three steels the direct hot rolling leads to the elimination of microdefects (closing of voids) to improved microstructure and mechanical properties. For a sufficient ductility as-cast thickness should be larger than 10 mm.

For the project **Optimization of the process parameters of ferritic rolling of deep-drawable steels** the results of the successful simulation of ferritic rolling by the plane strain compression test carried out in a previous project [10,11,12,13,14,15] give a basis for the rolling tests on specimens with real thicknesses by applying of a roll lubrication. A series of pre-tests was focused on the determination of the flow stresses of an IF steel for the relevant regions of temperature and strain rate, **fig. 3**. Four various lubricants were tested for the application at the temperatures of ferritic rolling.

Figure 3: *Flow stress of IF steel as a function of strain rate after deformation of ε = 0.6 for various phases showing lower values for the ferrite region*

In the preliminary investigations of the group it was established that phosphorus as a tramp element deteriorates the toughness and enhances the brittle fracture in high strength CrV-steels for leaf springs [16,17,18,19]. In a new project on **Limit values of tramp elements in SiCr high strength steels for spiral springs** an optimal chemistry design, application of thermomechanical treatment instead of conventional heat treatment and optimizing tempering process should allow a maximum acceptable amount of tramp elements, especially phosphorus, copper and tin in the production of high power spring steels employed in the automotive industry. The effect of sulphur on the fracture mechanics, fatigue and cutting properties has been studied on microalloyed forging steels with various type of microstructure [20].

Two research works carried out in **a close cooperation with industrial partners** should be mentioned: The first regarded the optimization of forging parameter in the manufacturing of the large shafts of alloying steels (diameter > 1000 mm) to eliminate the formation of coarse microstructure (Edelstahlwerke Buderus AG). It involved simulation tests (multiple deformation and controlled cooling) by the hot deformation simulator WUMSI and subsequent microstructure evaluation. The second work was dedicated to the possibility to induce dynamic recrystallization of low temperature austenite in Nb-microalloyed high strength low carbon steels with various level of manganese (Niobium Product Company GmbH, McMaster University Hamilton). The aim of this work is a high toughness of such steels due to an ultra fine grain structure.

Metal Forming

W. Rasp

In the last few years the legal regulations, which control air pollution, energy, and resource consumption, have considerably grown in importance. One solution to the environmental protection is the development of light-weight components, which are distinguished by their favourable combination of mechanical and weight properties. An improvement in the mechanical properties is the macroscopic structuration of the sheet surface, which leads - on the condition of equal weight - to a higher formstiffness than non-structured workpieces. The actual state of technique (e.g. hydroforming) only allows the production of single-structured sheet products. So far, a continuous production of macro-structured sheet strips (especially ribbed sheet strips) in rolling mills has not yet commercially been exploited. The aim of this research project is the fabrication of such strips by a cold-rolling process starting with a plane rectangular strip and processing in one line up to the structured sheet. By this proposed procedure much handling cost can be saved. Particularly the material flow into the rib pocket is studied in a computer model as a function of different set-up parameters like tool geometry, deformation, and friction. The theoretical investigations are carried out by the upper-bound theory. Additionally, the results are compared with an FEM-analysis. In a large series of experiments it has been tested, in which way the mechanical properties of rolled sheets can be improved. The aim was to generate rolling conditions, where the chosen geometry leads to a significant lateral flow into gaps, which were machined in the roll body. Hence, a ribbed sheet can be produced. This is the precondition of macro-structured sheets. At the end, the resulting geometry like rib height, rib form, and material flow in width direction was determined. Three-point bending tests showed that a remarkable **increase of formstiffness of sheets for light-weight constructions by cold rolling** [21,22,23] was reached.

Wire and rod drawing, well known long before the beginning of metal forming research, is combined with several disadvantages. The tool has to sustain very high pressure and therefore one has to put up with more or less wear combined with a loss of accuracy at the final dimensions of the workpiece. Here, lubrication reduces this problem, but new problems of lubricant supply and environment must be mastered. The dieless-drawing technique replaces the drawing die by an inductor, which heats up the specimen. Thus, the reduction can take place without the limitations of the conventional technique and is stopped by a cooling device immediately behind the deformation zone. In the last annual report it was reported about theoretical research into the dieless-drawing process. A simplified system of thermal and mechanical equations has been derived which yielded the temperature distribution and the shape of the deformation zone. With this model it is possible to study the influence of various process parameters very quickly. The control requirements for the production of variable cross-sections can be discussed. Besides theoretical investigations an **Experimental Verification of Dieless-Drawing Theories** [24] has been performed at a laboratory plant of the Max-Planck-Institut.

In a close co-operation between the „Thermomechanical Treatment“ group and the „Metal Forming“ group the **Application of Dieless Drawing for Getting Desired Steel Properties** [25] has been studied. As mentioned above, this method allows a thermomechanical treatment by a purposeful combination of heating, forming, and cooling. The improvement of mechanical properties with two different steel grades, a high carbon steel C78 D and a steel C15, was demonstrated, **fig. 4.**

In order to quantify the effects of friction during large-scale plastic deformation, such as that which occurs during hot or cold rolling of steel, **a newly developed test method for characterization of frictional conditions in metal forming** [26] was developed. This test methodology incorporates the high deformation levels, high strain rates, and new surface development, which are present during rolling, into a simple qualitative and quantitative frictional analysis. In this analysis a test specimen is upset with a drop hammer, using both steel and alu-

minium test specimens and a series of lubricants with a similar base and varied additives. Different frictional conditions at the upper and lower test specimen-tool interfaces are created by use of different lubricants or different surface preparations. The difference in the frictional conditions between the upper and lower interfaces can be quantified by measuring the out-of-plane-angle, which forms in the workpiece during upsetting. This angle is formed because the workpiece material at the interface with lower friction will be less constrained and thus has more freedom to deform plastically under otherwise similar conditions.

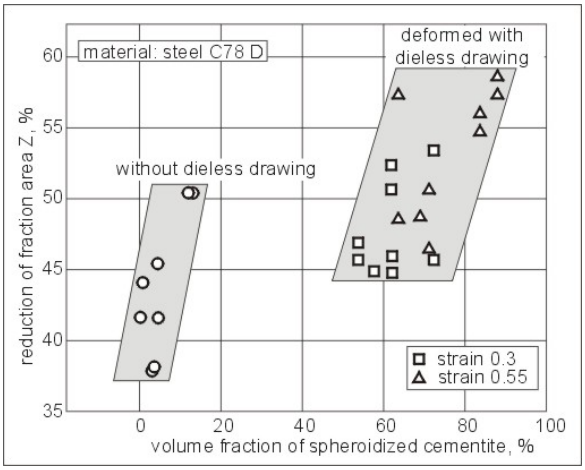


Figure 4: *Improvement of ductility by the enhanced cementite spheroidization due to dieless drawing*

A greater difference in the frictional conditions between the upper and lower interfaces will result in a greater out-of-plane deformation and a larger measurable angle. The angle measured during experimentation can be correlated to actual friction-factor values via two methods. The first method is calibration using an interface of know friction factor. A model of the deformation using either the upper-bound analysis or the finite-element method can be used to calculate the friction factor at the unknown interface via the measured angle on the deformed test specimen and the friction factor at the known interface. The second method is comparison using two interfaces with unknown friction conditions. In this method the relative effectiveness of different lubricants, for example, can be evaluated under different forming conditions – strain rate, strain level, temperature, etc. The effects of the size, orientation and arrangement of different surface-topography features on the resulting out-of-plane angles were also examined. Additionally, the effect of different deformation conditions on the resulting surface topography was examined. Variation of lubricant additives during testing resulted in significantly different frictional conditions under otherwise identical forming conditions. Large concentrations of lauric-acid additives resulted in large decreases in the friction under identical testing conditions. It was, however, observed that the effectiveness of lubricant additives is very sensitive to deformation rate. At higher speeds some lubricant additives showed poorer frictional behaviour than neat oil. It was observed that surface features with a large aspect ratio, aligned perpendicularly to the direction of plastic flow, resulted in lower frictional values. If the alignment of the surface features becomes parallel to the direction of the plastic deformation the frictional values increase parabolically. It was also observed that an increase in strain rate, and an increase in lubricant viscosity both resulted in an increase in arithmetic mean surface roughness Ra and in entrapped lubricant pockets on the tested surface.

The interaction of stress and plastic strain in technical processes is subject of **Technical Plastomechanics** [27], a discipline founded on mathematical continuum theory. In the first part of the textbook the most important fundamental equations are described for stress, strain, strain rate, equilibrium of forces, yield criterion and material laws. They are used to characterize the fields of elementary plastomechanics, load bounding, and theory of similarity. The second part gives 29 exercises, fully elaborated with the computer-algebra-system Mathematica and completely documented on a CD attached to the book for individual application. A supplement gives a short introduction into calculation with Cartesian tensors. The book is written as well for students as for engineers and physicists working in research and development.

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27. Pawelski, H.; Pawelski, O.: Technische Plastomechanik (inkl. CD mit Übungen). Düsseldorf: Verlag Stahleisen 2000.

Publications and Abstracts

Gottstein*, G.; Goerdeler*, M.; Roters, F.
Work hardening of Al-Cu-Mg alloys - a dislocation model based on three internal state variables
Proceedings of the International Symposium on Light Metals 2000, Ottawa, Canada, eds.: J. Kazadi, J. Masounave, The Canadian Institute of Mining, Metallurgy and Petrolium, 209 - 223

A new dislocation model is introduced to predict work hardening behaviour of aluminium alloys during ambient and elevated temperature deformation. The model distinguishes three different dislocation populations in cell forming alloys, mobile dislocations and dislocations stored in both cell walls and cell interiors. The different types of dislocations follow generic but coupled evolution laws which account for specific dynamic recovery processes. The model explicitly incorporates crystallographic texture. Model predictions will be compared to measured flow curves for single and two phase Al-Cu-Mg alloys. Applications in FEM simulations will be discussed.

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Kaspar, R.; Tomitz*, A.
Ferritic rolling in the thin slab direct rolling technology
Proc. of the Int. Conf. on Thermomechanical Processing of Steels, London, 24-26 May 2000, Vol. 2, IOM Communications, p. 607-614

The application of the ferritic rolling in the process of thin slab direct rolling, with the aim to produce thin deep-drawable hot strips, was investigated on an IF steel by using laboratory tests with a thin slab casting simulator linked with the hot deformation simulator WUMSI. The process parameters of two potential final products were simulated: *„soft" hot strips* (directly recrystallized in coil) and *„hard" hot strips* (produced at low finishing and coiling temperatures), the latter additionally batch annealed for recrystallization. The results were focused on the r-values computed from the texture measurements. The much slower process of ferrite recrystallization under direct rolling conditions appears to be the essential difference to the conventional cold charging. For this reason, austenite grain refinement combined with a sufficient finishing strain in ferrite is recommendable. Nevertheless, a total deformation in ferrite region (without austenitic rolling) may be a promising alternative.

*now with: HOESCH HOHENLIMBURG GmbH, Hohenlimburg, Germany

Kaspar, R.; Tomitz*, A.
Ferritic rolling to produce deep-drawable hot strips of steel
Electronic Proc. of the 9th Int. Metallurgical Conf. METAL 2000, Ed. TANGER Ltd., Ostrava, May 2000

The aspired good deep-drawability (high *r*- and *n*-values, $\Delta r \approx 0$) is basically achieved by a definite anisotropic flow mechanism. Such necessary anisotropy can be ensured in a deep-drawable steel sheet by a preferential *{111}||ND*-texture. In a conventional production, a hot rolling in austenite and a cold rolling at room temperature together with a subsequent recrystallization annealing are applied for such texture development in the final *cold strip*. As a cost saving replacement for this, a *thin-gauge hot strip* with a required deep-drawability can be employed. As a promising realization of cost saving thin-gauge deep-drawable hot strips of steel, a ferritic rolling can be implemented. In this new practice the finishing is shifted down into the temperature region of ferrite. To optimize the process parameters, extensive laboratory tests on IF steel were carried out by using the hot deformation simulator WUMSI. By the measurements of the texture development as well as by the computing of *r*-values, the texture formation could be optimized achieving a deep-drawability in hot strips comparable to that of a cold strip after a conventional austenitic rolling.

*now with: HOESCH HOHENLIMBURG GmbH, Hohenlimburg, Germany

Kaspar, R.; Tosal-Martinez*, L.; Richter**, J.; Köthe**, A.
Eigenschaftspotential von mikrolegierten Stählen für Gesenkschmieden
Stahl und Eisen 120 (2000), Nr. 10, p. 95-102

The property spectrum of the forging steel 27MnSiVS6, initially developed for a direct controlled continuous cooling from the forging temperature (so-called BY treatment) to form a precipitation-hardened ferrite-pearlite (F+P) microstructure, can significantly be extended by using other types of microstructure and additional microalloying additions. Besides F+P, the following types of microstructure have been investigated: a) directly quenched and tempered martensite (M), and b) a complex microstructure consisting of ferrite and bainite/martensite (F+B/M) produced by means of a two-step cooling and annealing. The microalloying variants tested were V, V+Ti, and V+Ti+Nb. In addition to steels having the conventional enhanced sulphur content of 0.03 - 0.05%, a low-sulphur (0.006% S) variant has been included. The investigations comprised tensile and V-notch impact tests, the determination of linear-elastic and elastic-plastic fracture toughness properties and of the push-pull fatigue limit as well

as the tests of machinability. The M and (F+B/M) microstructure exhibit properties superior to some of the conventional (F+P) microstructure, thus justifying - for some safety critical applications - the higher technological efforts to produce the M or (F+B/M) microstructure. The influence of the variations of microalloying additions caused less important property changes than the modifications of microstructure. A reduction in S content yielded positive effects with respect to ductility and upper shelf toughness.

*now with: The Research Centre of the SIDMAR Group, Zerzate, Belgium ** Institut für Festkörper- und Werkstoffforschung (IFW), Dresden

Pawelski*, H.; Pawelski, O.
Technische Plastomechanik (inkl. CD mit Übungen)
Verlag Stahleisen, Düsseldorf 2000, 214 p.

Many products used in daily life are significantly manufactured by plastic forming. Cars and beer cans are well-known examples. The capability of plastic deformation is therefore one of the most important properties of metallic materials. The interaction of stress and plastic strain in technical processes is subject of Technical Plastomechanics, a discipline founded on mathematical continuum theory.

In the first part of the textbook the most important fundamental equations are described for stress, strain, strain rate, equilibrium of forces, yield criterion and material laws. They are used to characterize the fields of elementary plastomechanics, load bounding and theory of similarity.

The second part gives 29 exercises, fully elaborated with the computer-algebra-system Mathematica and completely documented on a CD attached to the book for individual application.

A supplement gives a short introduction into calculation with Cartesian tensors.

The book is written as well for students as for engineers and physicists working in research and development.

*SMS Demag AG, Düsseldorf

Pawelski, O.; Rasp, W.; Wengenroth*, W.
Experimental Verification of Dieless-Drawing Theories
Proc. 33rd Int. MATADOR Conference, Manchester, UK. In: London: Springer-Verlag 2000

The dieless-drawing process was analysed with the disc method. A simplified system of thermal and mechanical equations was derived which yielded the temperature distribution and the shape of the deformation zone. With this model it is possible to study the influence of various process parameters very quickly. The control requirements for the production of variable cross-sections are discussed. Besides theoretical investigations measurements have been performed at a laboratory plant of the MPI which are presented briefly.

*now with: GKN Automotive AG, Lohmar

Raabe, D.
Metallurgical reasons and mechanical consequences of incomplete recrystallization
Stahl und Eisen Vol. 120, Nr. 6 (2000) 73–78

Incomplete recrystallization of cold worked steels reduces quality in terms of strength, elongation to fracture, plastic anisotropy (e.g. r–value) and appearance. It is particularly observed in low–carbon steels, in ferritic stainless steels, in the ferritic phase of duplex steels, and in iron–silicon transformer steels. The report reviews recent models and results about the major metallurgical reasons and technical consequences of incomplete recrystallization. It is shown that the reasons for incomplete recrystallization are particularly to be found in the subgrain structure of steels.

Raabe, D.
Scaling Monte Carlo kinetics of the Potts model using rate theory
Acta Materialia 48 (2000) 1617–1628

The paper introduces a method for scaling Monte Carlo kinetics of the Potts model using rate theory. The method is particularly designed for the kinetic and spatial scaling of multistate kinetic Potts models using one or more sets of non-conserved structural or orientational state variables each of which can assume a number of degenerate ground states (multistate Potts models) as commonly employed for simulating recrystallization and curvature driven grain growth phenomena. The approach is based on the equivalence of single-site state switches in the Potts model and grain boundary motion as described by Turnbull's classical rate theory mapped on a simulation lattice. According to this approach the switching probabilities can be scaled by the ratio of the local and the maximum occurring values of the grain boundary mobility and by the ratio of the local and the maximum occurring values of configurational and scalar contributions to the driving force. The real time step elapsing during one Monte Carlo time step is scaled by the maximum occurring grain boundary mobility, the maximum occurring driving force, and the lattice parameter of the simulation grid.

Raabe, D.; Becker, R. C.*

Coupling of a crystal plasticity finite element model with a probabilistic cellular automaton for simulating primary static recrystallization in aluminum

Modelling and Simulation in Materials Science and Engineering, Vol. 8, No. 4 (2000) Seiten 445 - 462

The paper presents a two dimensional approach for simulating primary static recrystallization which is based on coupling a viscoplastic crystal plasticity finite element model with a probabilistic kinetic cellular automaton. The crystal plasticity finite element model accounts for crystallographic slip and for the rotation of the crystal lattice during plastic deformation. The model uses space and time as independent variables and the crystal orientation and the accumulated slip as dependent variables. The ambiguity in the selection of the active slip systems is avoided by using a viscoplastic formulation which assumes that the slip rate on a slip system is related to the resolved shear stress through a power−law relation. The equations are cast in an updated Lagrangian framework. The model has been implemented as a user subroutine in the commercial finite element code Abaqus. The cellular automaton uses a switching rule which is formulated as a probabilistic analogue of the linearized symmetric Turnbull kinetic equation for the motion of sharp grain boundaries. The actual decision about a switching event is made using a simple sampling non–Metropolis Monte Carlo step. The automaton uses space and time as independent variables and the crystal orientation and a stored energy measure as dependent variables. The kinetics produced by the switching algorithm are scaled through the mesh size, the grain boundary mobility, and the driving force data. Coupling of the two models is realized by: translating the state variables used in the finite element plasticity model into state variables used in the cellular automaton; mapping the finite element integration point locations on the quadratic cellular automaton mesh; using the resulting cell size, maximum driving force and maximum grain boundary mobility occurring in the region for determining the length scale, time step, and local switching probabilities in the automaton; and identifying an appropriate nucleation criterion. The coupling method is applied to the two dimensional simulation of texture and microstructure evolution in a heterogeneously deformed high purity aluminum polycrystal during static primary recrystallization considering local grain boundary mobilities and driving forces.

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Raabe, D.; Miyake, K.; Takahara*, H.*

Processing, microstructure, and properties of ternary high–strength Cu–Cr–Ag in situ composites

Material Science and Engineering, A 291 (2000) S.186-197

A new class of ternary *in situ* metal matrix composites with high strength and high electrical conductivity consisting of heavily co–deformed Cu, Cr, and Ag is introduced. Three alloys are investigated in detail, namely, Cu–10 wt.% Cr–3 wt.% Ag, Cu–10 wt.% Cr–1 wt.% Ag, and Cu–4.5 wt.% Cr–3 wt.% Ag. The alloys were produced by inductive melting and chill casting. Since Cu–Cr and Cu–Cr–Ag alloys with hypereutectic Cr content are less ductile than previously investigated Cu–Nb, Cu–Ag, and Cu–Nb–Ag alloys, special attention was placed on optimizing microstructure with respect to both strength and ductility using thermal and thermo–mechanical processing schemes. These included various combinations of swaging, heavy wire deformation (using different lubricants), solution annealing at different temperatures followed by quenching, and aging at different temperatures. Optimized processing allows one to attain maximum wire strains of η=8.48 ($\eta=\ln(A_0/A)$, A: wire cross section). The wires have very high strength (for instance Cu–10 wt.% Cr–3 wt.% Ag: 1260 MPa at a strain of η=8.48) and good electrical conductivity (62% of the conductivity of pure Cu (IACS) at a strain of $\eta = 2.5$ after solution treatment). Up to wire strains of $\eta \approx 8.5$ the strength is equal to that of Cu–20 wt.% Nb. The wire strength is much higher than predicted by the linear rule of mixtures. The investigation presents the evolution of microstructure during the various thermo–mechanical treatments and relates the results to the observed mechanical and electrical properties. The strength is discussed in terms of Hall–Petch–type hardening.

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Roters, F.; Raabe, D.; Gottstein, G.*

Work hardening in heterogeneous alloys – a microstructural approach based on three internal state variables

Acta materialia 48, 4181 – 4189 (2000)

A new work-hardening model for homogeneous and heterogeneous cell-forming alloys is introduced. It distinguishes three internal state variables in terms of three categories of dislocations: mobile dislocations, immobile dislocations in the cell interiors and immobile dislocations in the cell walls. For each dislocation population an evolution law is derived taking into account dislocation generation, annihilation and

storage by dipole and lock formation. In particular, these rate equations take into account the number of active glide systems and, thus, introduce texture in the model in addition to the Taylor factor. Microstructure is represented by the dislocation cell structure as well as second-phase particles, which may undergo changes by precipitation and Ostwald ripening. Interaction of mobile dislocations with the microstructure is taken into account through an effective slip length of the mobile dislocations. For the same set of parameters, the predictions are in excellent agreement with measured stress–strain curves of both a precipitation-hardened aluminium alloy (Al–4.16 wt% Cu–1.37 wt% Mg, AlCuMg2) and a precipitation-free model alloy (Al–0.35 wt% Cu–0.25 wt% Mg), the composition of which corresponds to the matrix of the two-phase alloy.

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Schroller, F.
Increase of Formstiffness of Sheets for Light-Weight Constructions by Cold Rolling
Dr.-Ing. Diss. RWTH Aachen 2000. In: Umformtechnische Schriften, Volume 90. Aachen: Shaker Verlag 2000

In today´s increasingly competitive business environment, companies must look for innovative solutions to come up against the competition. In the metal-forming industry the engineers are turning to new technologies in order to achieve the goals. One new innovative process is the macroscopic structuration of strips by cold rolling for use in light-weight constructions. Components with a macro-structured surface demonstrate - on the condition of equal weight - a higher area moment of inertia and consequently a higher stiffness than non-structured workpieces. The subjects presented in this paper refer to ribbed sheets produced in a cold-rolling process. Particularly the material flow into the rib pocket is studied in a simplified model as a function of different set-up parameters like tool geometry, deformation, and friction. The theoretical investigations are carried out by the upper-bound theory. Additionally, the results are compared with an FEM-analysis.

Schroller, F.; Pawelski, O.; Rasp, W.
FE Model and its Verification for Increasing the Formstiffness of Sheets by an Improved Cold-Rolling Concept
Proc. ECCOMAS 2000, Barcelona, Spain, and XIX Verformungskundliches Kolloquium, Institut für Verformungskunde und Hüttenmaschinen, Montanuniversität Leoben, Austria

In the last few years the legal regulations, which control air pollution, energy, and resource consumption, have considerably grown in importance. One solution to the environmental protection is the development of light-weight components, which are distinguished by their favourable combination of mechanical and weight properties. An improvement in the mechanical properties is the macroscopic structuration of the sheet surface, which leads - on the condition of equal weight - to a higher formstiffness than to that of non-structured workpieces. The actual state of technique (e.g. hydroforming) only allows the production of single structured-sheet products. So far, a continuous production of macro-structured sheet strips (especially ribbed sheet strips) in rolling mills has not yet commercially been exploited. The aim of this research project was the fabrication of such strips by a cold-rolling process starting with a plane rectangular strip and processing in one line up to the structured sheet. By this proposed procedure much handling cost can be saved.

Tomitz*, A.; Kaspar, R.
Deep-Drawable Sheet of Steel Produced as Hot Srip by Ferritic Rolling
In: Steels and Materials for Power Plants, EUROMAT 99 - Volume 7, Edited by P. Neumann, D. Allen and E. Tenckhoff, WILEY-VCH Verlag GmbH, 2000, p. 94-99

A good deep-drawability of steel assumes a favorable final texture (after a complete recrystallization) with a large fraction of {111}oriented grains. The beneficial texture development, similar as in the case of a conventional *cold strip*, can be achieved already in a *hot strip* by finishing in a temperature region of ferrite (so-called ferritic rolling). Reducing finishing temperature of ferritic rolling more favorable initial rolling texture can be generated.

A minimum coiling temperature (670 °C for the IF-steel tested) must be met if producing deep-drawable „soft“ hot strips directly after coiling. By a further lowering of finishing and coiling temperature (to achieve thinner hot strips) „hard“ (not recrystallized) hot strips must additionally be annealed after coiling to guarantee a complete recrystallization. Lower coiling temperatures are more beneficial for these products.

*now with: HOESCH HOHENLIMBURG GmbH, Hohenlimburg, Germany

Tomitz*, A.; Kaspar, R.
Deep-drawable thin-gauge hot strip of steel as a substitution for cold strip
ISIJ International 9 (2000) p. 927-931

The aspired good deep-drawability (high *r*- and *n*-values, $\Delta r \approx 0$) is basically achieved by a definite anisotropic flow mechanism. Such necessary anisotropy can be ensured in a deep-drawable steel sheet by a preferential *{111}||ND*-texture. In a

conventional production, a hot rolling in austenite and a cold rolling at room temperature together with a subsequent recrystallization annealing are applied for such texture development in the final *cold strip*. As a cost saving replacement for this, a *thin-gauge hot strip* with a required deep-drawability can be employed. A conventionally (in austenite) hot rolled strip is hardly applicable for this because of its unsatisfactory texture as well as for the technical difficulties to produce hot strips with a thickness less than about 2 mm. As a promising realization of cost saving thin-gauge deep-drawable hot strips of steel, a ferritic rolling can be implemented. In this new practice the finishing is shifted down into the temperature region of ferrite. To optimize the process parameters, extensive laboratory tests on IF steel were carried out by using the hot deformation simulator WUMSI. By the measurements of the texture development as well as by the computing of *r*-values, the texture formation in a hot strip after ferritic rolling could be optimized achieving the deep-drawability in hot strips comparable to that of a cold strip.

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Tomitz*, A.; Kaspar, R.
Ferritic rolling to produce „soft“ deep-drawable thin hot strips
steel research 71 (2000) 6+7, p. 233-238

In a conventional production of deep-drawable sheets of steel, a hot rolling in austenite and a cold rolling at room temperature together with a subsequent recrystallization annealing are applied with a *cold strip* as a final product. As a cost saving replacement for this, a *thin-gauge hot strip* with a required deep-drawability can be employed. A conventionally (in austenite) hot rolled strip is hardly applicable for this because of its unsatisfactory texture as well as for the technical difficulties to produce hot strips with a sufficiently small thicknesses. As a promising realization of cost saving thin-gauge deep-drawable hot strips of steel, a „warm“ rolling can be applied with reduced finish rolling temperatures. In this practice the finish rolling is shifted down into the temperature region of ferrite. In the present work extensive laboratory tests on IF- and ELC- steel were carried out by using hot deformation simulator WUMSI. By the measurements of the texture development as well as by the computing of *r*-values, the process parameters of ferritic rolling and a subsequent direct recrystallization in the coil of these steels could be optimized.

*now with: HOESCH HOHENLIMBURG GmbH, Hohenlimburg, Germany

Tomitz*, A.; Kaspar, R.
Ferritic rolling with additional annealing to produce a deep-drawable ultra-thin-gauge hot strip
steel research 71 (2000) 12, p. 497-503

In order to produce ultra-thin hot strips by ferritic rolling, that exhibit a good deep-drawability, finishing temperatures must be reduced, so that an additional recrystallization annealing of hot strips after coiling becomes necessary. In the present work laboratory investigations were carried out on a commercial IF and ELC steel by using the hot deformation simulator WUMSI. By means of texture measurement and the calculation of *r*-values the process parameters of the ferritic rolling and of a subsequent annealing were optimized. Additionally to a conventional annealing of cold coils a new energy saving processing route with direct charging of „warm“ coils was tested by the laboratory simulation. Particularly good deep-drawabilty were achieved by this technology.

*now with: HOESCH HOHENLIMBURG GmbH, Hohenlimburg, Germany

Tomitz*, A.; Kaspar, R.
Deep-drawing quality of cold rolled sheet made of ferriticly rolled hot strip
steel research 71 (2000) 12, p. 504-510

In the so-called ferritic rolling the finishing is shifted down into the temperature region of ferrite, which enables a production of thinner hot strips (compared to the conventional hot rolling in austenite) with a changed texture development. The present study is focused on the effect of the process parameters of such initial “warm“ rolled hot strips on the texture formation and hence on the deep-drawing quality of the final cold strips. A special attention is given to the transmission of the hot strip texture to the cold strip. The investigation was carried out on commercial IF- and ELC-steels by the laboratory simulation with the hot deformation simulator WUMSI (rolling simulated by the plane stain compression test). By means of the measurements of the texture development during the ferritic (warm) deformation, cold rolling and subsequent annealing as well as by the calculation of *r*-values, the parameters of the processing route of such special production of cold strips could be optimized. If compared with the conventional processing route, a considerable improvement of deep-drawability with a diminished earing is achievable especially with the IF-steel.

*now with: HOESCH HOHENLIMBURG GmbH, Hohenlimburg, Germany

Weidig*, U.

Application of Dieless Drawing in order to Reach Desired Steel Properties
Dr.-Ing. Diss. RWTH Aachen 2000. In: Umformtechnische Schriften, Volume 97. Aachen: Shaker Verlag 2000

Wire and rod drawing, well known long before the beginning of metal-forming research, is combined with several disadvantages. The tool has to sustain very high pressure and therefore one has to put up with more or less wear combined with a loss of accuracy with respect to the final dimensions of the workpiece. Here, lubrication reduces this problem, but new problems of lubricant supply and environment must be mastered. The dieless-drawing technique replaces the drawing die by an inductor, which heats up the specimen. Thus, the reduction can take place without the limitations of the conventional technique and is stopped by a cooling device immediately behind the deformation zone. This method allows a thermomechanical treatment by a purposeful combination of heating, forming, and cooling. The improvement of mechanical properties with two different steel grades, a high carbon steel C78 D and a steel C15, were proved.

*now with: SM Schweiz. Munitionsges., Attinghausen, Switzerland

Wettlaufer*, M.
Einflussmöglichkeiten auf die Wirkung von Begleitelementen in hochfesten Federstählen
Umformtechnische Schriften, Band 93, Shaker Verlag, Aachen 2000, 151 p.

Modern spring components require high strength steels with excellent fatigue properties. But conventional producing schedules do not exploit the maximum resources existing steel grades offer. But as inevitable trace elements can deteriorate the material properties seriously. In this context especially phosphorus gains particularly attention because even very low bulk concentrations can severely deteriorate the material properties. Three approaches were chosen to reduce the detrimental effect of phosphorus in quenched and tempered high strength CrV-steels for high power leaf springs: Change in the chemistry (addition of boron for repelling phosphorus from the grain boundaries), application of thermomechanical treatment (TMT) (producing lattice defects as intragranular traps for phosphorus atoms) instead of conventional heat treatment (CHT) and optimizing tempering process (balancing grain boundary segregation and lattice restoration). Thermomechnical treatment leads to better ductility, especially for the highest strength R_m > 2000 MPa. The best strength - ductility combination was found for the range of tempering temperatures ϑ_{temp} = 280-330 °C even for phosphorus contaminated steels. Outside of this range of ϑ_{temp}, there is a significant deterioration of ductility for P ≥ 0.02. This study reveals that the advantageous effects of TMT can be reproduced even with impurity contaminated industrial grades. Consequently TMT is a promising concept for progressive spring production.

*now with: BLANCO GmbH + Co. KG in Oberderdingen

Wettlaufer*, M.; Kaspar, R.
Thermomechanical treatment to improve the fatigue behaviour of phosphorus containing high strength spring steels
steel research 71 (2000) 9, p. 362-365

Modern spring components require high strength steels with excellent fatigue properties. But conventional producing schedules do not exploit the maximum resources existing steel grades offer. It is well known that thermomechanical treatment (TMT) in addition with metallurgical microalloying facilitates superior strength–fatigue combinations. But as inevitable trace elements can deteriorate the material properties seriously the objection originates that these disadvantageous effects dominate over the TMT induced improvements. In this context especially phosphorus gains particularly attention because even very low bulk concentrations can severely deteriorate the material properties. This study reveals that the advantageous effects of TMT can be reproduced even with impurity contaminated industrial grades. Consequently TMT is a promising concept for progressive spring production.

*now with: BLANCO GmbH + Co. KG in Oberderdingen

Wettlaufer*, M.; Kaspar, R.
The notched tensile test: a novel method for the prediction of cyclical fatigue properties
Materialprüfung 42 (2000) 3, p. 74-78

The determination of the fatigue properties of steel is of concern to design components that endure cyclical load. Such measurements involve a large experimental effort. For this reason the (more simple) tensile test on notched specimens was employed as an alternative method to predict the fatigue strength from easier attainable (static) data. A good correlation was obtained.

*now with: BLANCO GmbH + Co. KG in Oberderdingen

Wettlaufer*, M.; Kaspar, R.
Effect of phosphorus on the ductility of high strength spring steels
steel research 71 (2000) 9, p. 357-361

Phosphorus as a tramp element deteriorates the toughness and enhances the brittle fracture in high strength steels. Even a very low bulk concentrations can cause severe enrichment on the prior austenite grain boundaries. This seriously restricts the applicability of highly demanded components. Three approaches were chosen to reduce the detrimental effect of phosphorus in quenched and tempered high strength CrV-steels for high power leaf springs: Change in the chemistry (addition of boron for repelling phosphorus from the grain boundaries), application of thermomechanical treatment (TMT) (producing lattice defects as intragranular traps for phosphorus atoms) instead of conventional heat treatment (CHT) and optimizing tempering process (balancing grain boundary segregation and lattice restoration). Whereas no effect of boron was determined, a thermomechnical treatment leads to better ductility, especially for the highest strength R_m > 2000 MPa. The best strength - ductility combination was found for the range of tempering temperatures ϑ_{temp} = 280-330 °C even for phosphorus contaminated steels. Outside of this range of ϑ_{temp}, there is a significant deterioration of ductility for P ≥ 0.02. Independent of P-content, there is a dramatic decrease in 0.2% proof strength for ϑ_{temp} decreasing below 280 °C due to residual internal stresses.

*now with: BLANCO GmbH + Co. KG in Oberderdingen

Wolff*, C.; Pawelski, O.; Rasp, W.
A Newly Developed Test Method for Characterization of Frictional Conditions in Metal Forming
Proc. 8th Intern. Conference on Metal Forming, Krakow, Poland. In: Rotterdam: Verlag A. A. Balkema 2000, 91-97

The frictional conditions in the experiment must be similar to metal-forming operations of industrial scale. With the tribologically asymmetric flat-compression test it is possible to apply extreme conditions like high strains and strain rates in an easy and cost-effective way. By compressing a flat specimen between two punches, which overlap the specimen in its width, the different kinds of lubrication on the upper and lower punch initiates bending of the plate. Here, the different friction conditions are characterized by the friction factor. Friction can directly be measured using the angle at a final height, or by comparing lubricants qualitatively by watching the bending direction of the specimen. Even slightest lubrication differences cause a measurable angle. When using gravity-drop hammers strain rates over 2000 s^{-1} are within easy reach. In case of strain rates and flow stresses in that range the inertia does not influence the angle. Friction conditions in cold strip rolling or foil rolling can therefore be simulated. Furthermore, it is possible to optimize mineral-oil emulsions by varying the concentration of the additives. Typical additives for cold rolling of aluminium are alcohol or fatty acid esters. These boundary additives of long-chain molecules help the base oil to form films which are adsorbed on the surface. Experiments with lauric acid, methyl laureate, and fatty alcohol were carried out with concentrations up to 15 %. In addition, the effect of boundary additives depends on the forming speed. The tribologically asymmetric flat-compression test can be used for hot forming as well. By preheating the punches friction conditions for extrusion, die forging, or hot rolling can be simulated without large equipment.

*now with: Ford-Werke, Saarlouis

Zaefferer, S.
New developments of computer-aided crystallographic analysis in transmission electron microscopy
J. Appl. Cryst. 33, 10-25 (2000)

A new computer program for on-line crystallographic analysis in the TEM is presented. The program is based on the fast on-line determination of single crystal orientations from Kikuchi and spot patterns. Spot patterns which are particularly useful in the case of highly deformed metals are analyzed by a new digital image processing procedure. This procedure improves the precision and ease of the orientation measurement.

The program permits the on-line measurement of glide systems characterized by the Burgers vector and the crystallographic line direction of dislocations and their glide planes. The determination of twin systems, based on the misorientation calculation for any crystal structure is included as well. The possibility of determining the foil thickness permits the complete crystallographic characterization of interfaces. Finally, the program facilitates the discrimination of phases and includes the fit of the lattice parameters a, b, c from diffraction patterns. The new procedures are described in detail. Application examples are given for all functions.

Diploma Works

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Since the mechanical behaviour of materials is controlled by microstructure, a most detailed physical understanding of the microstructure evolution during processing and service is a prerequisite for materials optimisation and prediction of materials behaviour. For this, **phase equilibria** and **phase transformations** in multinary alloy systems are studied both experimentally by x-ray diffraction and electron microscopy and theoretically by thermodynamic computer simulations of equilibria and reactions including simulations of the atom and spin configurations. The **mechanical behaviour** of multinary multi-phase alloys is studied with respect to strength and toughness at low and high temperatures with particular emphasis on the long-term materials behaviour at high temperatures under creep conditions with mutual interaction of microstructure changes and deformation processes. The work is centred on Fe-base alloy systems including alloys on the base of intermetallic phases.

Phase Equilibria and Phase Transformations

The main themes of research embrace the experimental and theoretical analysis of phase equilibria and phase transformations in multicomponent systems, particularly in steels. The theoretical work on phase equilibria focused on the thermodynamic stability of atomic and/or spin configurations using statistical mechanics methods (Monte Carlo Simulation (MC), Cluster Variation Method (CVM)). The experimental work concentrated on the determination of phase diagrams of multicomponent systems. In order to arrive at a maximum information with a least number of specimens the composition gradient technique and the diffusion couple technique were applied. The analysis was performed with microprobe, scanning (SEM) and transmission electron microscopy (TEM). Further techniques applied are x-ray diffraction (including in situ high temperatures up to 1600°C) and differential thermal analysis.

The work on phase transformations in steels and other multicomponent systems focused on diffusion controlled reactions. This includes growth or dissolution under very general conditions (isothermal or continuous heating/cooling) and gas atmospheres (carburising). The experimental work covers the study of phase transformations as a function of heat treatments by metallography, SEM and TEM observations, and the in situ observation of reactions under carburising gas atmospheres using thermal balance measurements.

The experimental study of the **ternary systems Fe-Rh-Ti** and **Fe-Rh-Co** has been continued in cooperation with Tohoku University in Sendai/Japan. These materials are promising functional materials exhibiting a first order antiferro- to ferromagnetic transition associated with strong magnetostriction effects. The phase equilibria in two isothermal sections at 800°C and 1000°C were determined by diffusion couple technique as well as with selected bulk alloys. After the bonding treatment the long term diffusion annealing at 1000°C or 800°C was done under vacuum (10^{-5} mbar) for 1 and 2 weeks, respectively. The composition profile was afterwards analysed by electron probe microanalysis (EPMA WDX). Due to a strong interaction between (Fe, Rh) and Ti, the ordered B2-phase is observed in a large domain of the phase diagram. A difficulty arose from the observation of "**pseudo interfaces**", see **fig. 1**, which look just like phase boundaries defining a miscibility gap. But in fact, the chemical potential at both sides of the "pseudo boundary" is not the same (as required for a true phase boundary). The strong long range ordering in the B2 phase leads to a very strong variation of the chemical potential within a very small composition range around the stoichiometric composition.

This effect could be explained by means of theoretical calculations. In systems with strong interactions between unlike atoms complex short and long range ordering effects occur leading to first and second order transitions, multicritical points, and ternary miscibility gaps even in systems where all limitrophe binary systems are of pure ordering type. Such complicated phenomena have to be treated by statistical thermodynamics methods. A very important quantity for treating kinetic problems is the **thermodynamic factor Φ for diffusion**. The **CVM** and **MC calculations** provide this information. It has been shown for the systems Fe-Al [1] and Ni-Al that Φ varies by orders of magnitude at compositions close to stoichiometric compositions. This behaviour of Φ produces abrupt changes in composition in diffusion couples ("pseudo interfaces") which may be mistaken for phase boundaries (see **fig. 1**).

Experimental work on **phase transformations under controlled gas atmospheres** (e.g. carburising) was conducted to determine the relation between temperature, carbon activity in carburising atmospheres and the **kinetics of carbide formation**, here **cementite** Fe_3C and **Haegg carbide** Fe_5C_2 [2,3,4]. Starting from results previously obtained in the Department of Physical Chemistry in the context of the metal dusting problem, the effect of H_2S on the formation and decomposition of Fe_3C and Fe_5C_2 was studied. These results allowed to define conditions such that the carbide formation could be observed over periods sufficiently long to derive parabolic growth constants and that the carbides grew to sizes allowing to determine C-composition profiles within the carbides by microprobe analysis. From these results the **diffusivity of C** in cementite and Haegg carbide and the range of off-stoichiometry of cementite was determined. The comparison of the experimental data with diffusion calculations allowed not only to determine C transfer coefficients, but also to derive new information on the phase diagram (e.g. **C-solubility range**

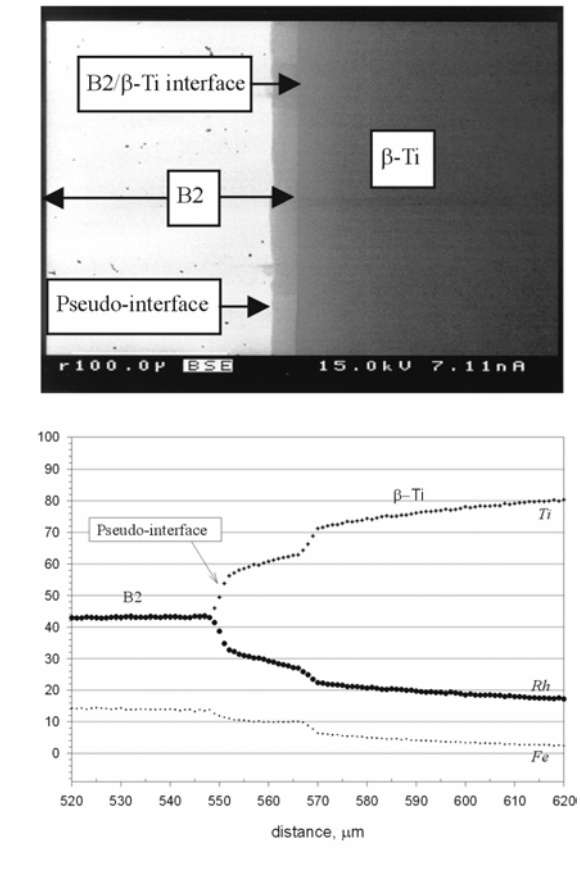

Figure 1: *Diffusion couple $Fe_{14}Rh_{43}Ti_{43}$/Ti annealed at 1000°C. Microstructure and composition profile obtained from EPMA.*

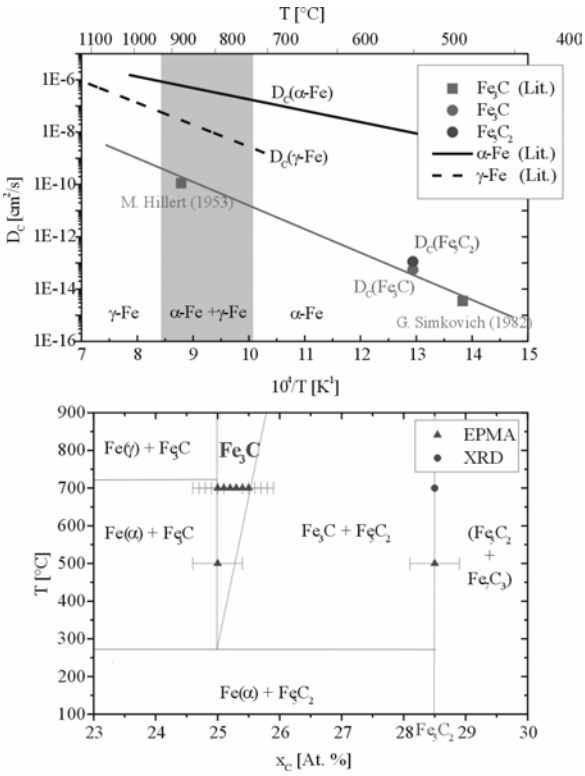

Figure 2: *Carbon diffusion constant in cementite and Haegg carbide and Fe-C phase diagram obtained from carburisation experiments.*

of cementite M_3C, Haegg carbide M_5C_2 formation) and new data on C-diffusivity in cementite and Haegg carbide, **fig. 2.**

The decomposition of the carbides due to graphite precipitation at the surface was also analysed by surface analytical methods [3].

The treatment of **surface effects during nucleation and coarsening** has been revised. It was shown that the traditional way of treating this effect suffers from inconsistencies. In particular, the equilibrium condition cannot be obtained from a parallel tangent construction. A more general treatment including compressible phases like bubbles in a liquid was derived [5].

In **co-operation with IRSID** an analysis was undertaken of the kinetics of austenite to ferrite transformation in Fe-Mn-C steels during continuous cooling [6]. IRSID provided dilatometric data for continuous cooling and phase fraction data obtained from quantitative metallography after interrupted cooling experiments. The main questions to be answered were: (a) are the reactions controlled by **para-equilibrium** or by **local equilibrium** conditions, (b) do the calculations reproduce the phase fractions formed as a function of time (or temperature) for various cooling rates, (c) is it possible to derive phase fraction data from dilatometer curves.

The results clearly showed that the reactions do not occur according to para-equilibrium conditions. At moderate cooling rates (<5°C/s) local equilibrium with negligible partitioning yielded good agreement between experiment and calculation. At higher cooling rates (>5°C/s) the reaction started at lower temperatures than calculated, obviously because of nucleation problems. Assuming forced nucleation in the calculations yielded again good agreement. The dilatation calculated from the phase fractions did not reproduce the measured dilation curves. This clearly shows that the common practice in industry to derive phase fraction data from dilatometer measurements is to be put in question.

High Temperature Materials

There is an unchanged high interest in new structural materials on the basis of intermetallic phases. Accordingly, the progress in research and development is fast, and various developments are on the brink of commercialisation [7]. The physical understanding of the manifold processes of mechanical deformation of intermetallic materials is far from complete, and (re)assessments of the current state of knowledge are

still in order [8,9]. Multiphase intermetallic alloys offer advantageous possibilities for balancing strength and ductility [10]. In view of the need for data for estimating the application potential, basic data for the intermetallic phases and alloys of practical interest have been collected with special emphasis on powder-metallurgically processed materials [11].

The **screening of intermetallic phases for materials developments** has been continued with emphasis on ternary Fe-base systems with Al or Si and various transition metals. An exploratory study was directed at the **mechanical behaviour of ordered Fe-Al-Ti alloys with Laves phases** [12]. Significant increases in strength and hardness with varying ratios of strength and ductility may be achieved in such alloys with two or more phases.

The alloy system Fe-Al-C allows the strengthening of various Fe-Al phases – disordered Fe-Al, $D0_3$-ordered Fe_3Al and B2-ordered FeAl – by precipitating the perovskite-type carbide phase Fe_3AlC_x. The exploratory study of the **mechanical behaviour of ordered Fe-Al-C alloys with perovskite-type carbide**, i.e. with various Al and C contents and various quaternary additions to produce various types of carbides in various types of matrices revealed only small differences in the low room-temperature ductility in spite of a marked variation of the yield stress [13].

The ongoing work on the **constitution and mechanical behaviour of intermetallic phases in the Mg-Fe-Si and Fe-Si-Ti systems** has resulted in a re-evaluation of the Fe-Si-Ti system [14]. The only available isothermal section of the ternary Fe-Si-Ti phase diagram at 800 °C has been up-dated and the new isothermal sections at 1000 °C and 1150 °C have been established. The variation of the mechanical behaviour has been studied in detail for two-phase Fe-Si-Ti alloys on 4 common tie lines with the C14 Laves phase $TiFe_2$ as strengthening second phase. As expected, the compressive yield stress increases with increasing volume fraction of Laves phase – e.g. up to 1350 MPa at 400 °C with corresponding increase of the brittle-to-ductile transition temperature. Increasing the Si content at constant volume fraction of Laves phase increases the yield stress only at temperatures below 800 °C.

The work on the constitution and mechanical behaviour of intermetallic phases in the Al-Fe-Mo system has been continued [15]. The mechanical behaviour has been studied in detail for two types of two-phase alloys on common tie lines, i.e. disordered Fe-Al alloys with precipitated μ phase and B2-ordered FeAl alloys with precipitated Mo_3Al. The brittle-to-ductile transition temperature as characterised by 4-point-bending tests was found to vary between 200 °C and 900 °C depending on amount and character of second phase and on heat treatment.

The study on the **phase equilibria and mechanical behaviour of intermetallic phases in the Fe-Al-Zr system** with emphasis on the Zr-poor part of the system has been continued. The isothermal sections at 800, 1000 and 1150 °C of the ternary phase diagram have been up-dated. The Laves phase in this system is of special interest since it forms with both Fe and Al, i.e. Fe and Al substitute each other more or less completely in $Zr(Fe,Al)_2$ which is accompanied by transitions from the hexagonal C14 structure to the cubic C15 structure and vice versa. The study of the mechanical behaviour is complemented by a joint project on the **microprocesses of deformation of Fe-Al-Zr alloys with strengthening intermetallic phases** (cooperation with Prof. Messerschmidt of the MPI for Microstructure Physics in Halle).

The **screening of Al-rich intermetallics** [14] has been centred on the **phase equilibria in the Al-rich part of the Al-Ti system** which have been studied by TEM and which have been strongly supported by accompanying **DTA studies of phase transitions in intermetallic systems** [16,17,18]. Lamellar microstructures can be produced in Al-rich TiAl-containing alloys by annealing between about 900°C and 1200°C. In the equilibrium state the lamellar structure consists of the two phases TiAl and r-Al_2Ti. The formation mechanism of the lamellar structure could be clarified by TEM investigations. The h-Al_2Ti plates, that had formed from the supersaturated TiAl matrix, transform into r-Al_2Ti by two alternative very slow mechanisms, a continuous and a discontinuous one. The latter mechanism leads to the formation of the fine lamellar microstructure which gradually coarsens with time. The strength of such lamellar TiAl+r-Al_2Ti alloys at high temperatures as characterised by compressive proof stress and creep resistance is of the order of that of the familiar Ti-48Al alloys. This work had been accompanied by microstructure analysis work on twinning in an Al-poor TiAl-base alloy [19,20].

The work on the **deformation behaviour of intermetallic NiAl-Ta-Cr with strengthening phases**, which is part of a large joint project on the development of **intermetallic NiAl components for non-polluting power conversion** has been concentrated on both the **creep of multiphase alloys** and the long-term oxidation behaviour at constant temperature and with temperature cycling and has been accompanied by the optimisation of processing with investment casting and powder metallurgy [21,22]. As such alloys have a considerably high brittle-to-ductile transition temperature, the behaviour under thermal fatigue conditions was evaluated. A cylindric specimen of 18 mm height and 12 mm diameter was cyclically heated at 1250°C in air for 6 to 16 h and cooled to room temperature by an Ar jet. The cooling rates were 3 K/s between 1250°C and 1000°C and 2K/s below 1000°C. No cracks could be detected on the surface of the sample and on a cross section after 720 h with 60 cooling cycles. Another specimen without any notches at the surface showed no cracks after oxidation at 1200°C for 17904 h during which the sample was cooled fifty times to room temperature by removing the sample from the furnace and cooling it outside. Model combustor liner panels have been pro-

duced successfully by investment casting and powder metallurgy. After the German and US patents the patent of the Russian Federation has been filed [23].

The new project on **ferritic steels with maximum creep resistance: alloy development and long-term behaviour**, which is part of a cooperative development project together with a theoretical project of the Phase Equilibria and Transformations Group, aims at further increasing the creep resistance and by this the service temperature possibly up to 650 °C. The work is centred on martensitic 12 % Cr steels with various additions of Ti, V, Nb, Ta as well as W to precipitate fine MX-type carbides or carbonitrides on the one hand and coarse Laves phase on the other hand which both are advantageous for increasing the long-term creep resistance. The high Cr content, which is needed for ensuring the necessary corrosion resistance, is balanced by Co additions for ensuring the required martensitic structure. **Fig. 3** shows first representative data for the observed creep behaviour of such model steels with various Laves phase precipitates.

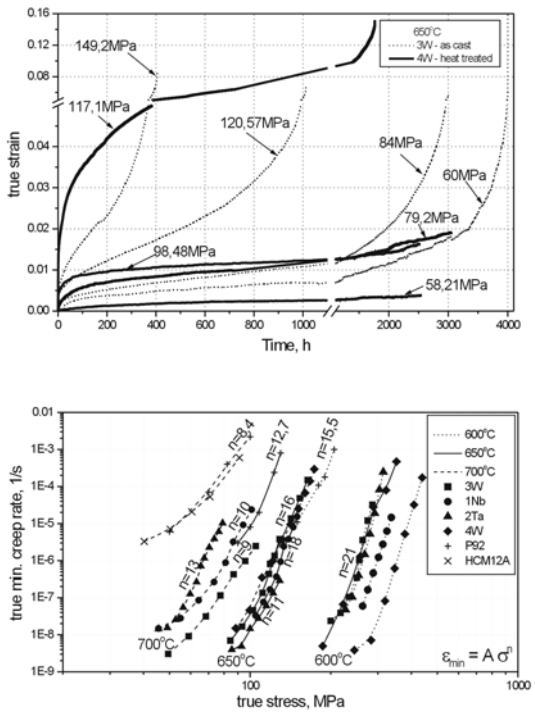

Figure 3: *Characteristic creep data for various experimental 12%Cr steels with strengthening Laves phase in comparison to the ferritic heat resistant steel HCM 12A.*

Finally the effects of steel making on the distortion of steel components have been reviewed as part of a joint topical action on the control of heating processes during production of components [24,25].

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Publications and Abstracts

Agren*, A.; Clavaguera-Mora**, M.T.; Golcheski, J.; Inden, G.; Kumar****, H.; Sigli*****, Chr.***
Application of Computational Thermodynamics to Phase Transformation Nucleation and Coarsening
CALPHAD 24, 41-54 (2000)

Computational thermodynamics is applied to two important and closely related phenomena in phase transformations, namely nucleation and coarsening. In both phenomena the surface energy plays a key role. The effect of surface energy on a two-phase equilibrium as well as the activation energy for forming a critical nucleus are both derived for the general multicomponent case. A simplified coarsening equation is derived for the general multicomponent case.

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Eumann, M.; Palm, M.; Sauthoff, G.
Constitution, Microstructure and Mechanical Properties of Ternary Fe-Al-Mo Alloys
In: EUROMAT'99, Vol. 10: Intermetallics and Superalloys, (Eds.) D.G. Morris, S. Naka and P. Caron. Wiley-VCH, Weinheim, 2000, 146-153

Both disordered and ordered Fe-Al alloys show comparatively high solubilities for Mo at 1000 °C. The obtained constitution data were used to establish the isothermal phase diagram section of the Fe-Al-Mo system. The observed phase equilibria allow the preparation of disordered and ordered Fe-Al alloys with the strengthening μ-phase (Fe_7Mo_6) precipitate and the Mo_3Al precipitate phase, respectively, with controlled variation of the Al-content of the constituent phases and the volume fraction of precipitate.

The yield stress of the studied two-phase disordered and ordered Fe-Al alloys increases with increasing volume fraction of precipitate. Marked alloy softening occurs at temperatures above about 700 °C, which may be related to the brittle-to-ductile transition. In addition, indications of an anomalous temperature dependence of the yield stress have been observed at such intermediate temperatures. Both effects are not yet clear and are subject of further study.

Herrmann, J.
Analysis of structure and mechanical properties of Fe-rich Fe-Al alloys
Fortschritt-Ber. VDI, Reihe 5, Grund und Werkstoffe/Kunststoffe, Nr. 595, VD-Verlag, Düsseldorf, 2000, 1-167

Short range ordering and mechanical properties of Fe-Alloys with up to 18at%Al was analysed. The structural characterisation was obtained by x-ray and neutron diffuse scattering on single crystals. In the range between 13-18at%Al strong sro was observed with kinetics controlled by a low activation energy of 0.3eV. The mechanical properties like BDTT and fracture strain were impaired strongly with increasing Al content, but no correlation with the degree of sro was observed. Instead, variations of dislocation structures and the effect of quenched-in vacancies seem to be responsible for the observations. The effect of traces of C was also studied.

Panin*, S.V.; Neumann, P.; Baibulatov**, Sh.A.
Investigation on mesoscale deformation of intermetalic $Ni_{63}Al_{37}$ alloy under compression
Physical Mesomechanics 3, No. 1, 75-82 (2000)

The paper presents the results of investigations into deformation of a high-strength intermetallic $Ni_{63}Al_{37}$ alloy at meso- and macrolevels. The studies have been performed using the television-optical measuring technique "TOMSC", scanning tunneling microscopy (STM), and scanning electron microscopy (SEM). It was shown that a high degree of the long-range order of the alloy under study causes an involvement of the mechanisms of meso- and macroscale deformation from the onset of loading. The deformation was revealed to evolve more intensively in a surface layer rather than in the bulk of a loaded specimen. Early in the loading, reversible relief therewith appears in the form of longitudinal folds extended up to hundreds of microns at the surface. The emergence of the inelastic reversible relief in a surface layer is attributed to the martensite transformations of the NiAl phase from the B2 structure into the $L1_o$ one.

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Sauthoff, G.
Plastic Deformation - Addendum
In: Basic Mechanical Properties and Lattice Defects of Intermetallic Compounds, (Eds). J.H. Westbrook and R.L. Fleischer. John Wiley & Sons, Chichester, UK, 2000, 64-66

The progressing developments of new intermetallic materials have promoted intensive research on the plasticity of the constituent intermetallic phases in the recent past. Important sources of information are the scientific journal INTERMETALLICS and the proceedings volumes of the international intermetallics conferences, e.g. the MRS proceedings

series “High Temperature Ordered Intermetallic Alloys” (High-Temperature Ordered Intermetallic Alloys VII,1997) and the international symposia on structural intermetallics (Structural Intermetallics 1997 (Proc. ISSI-2),1997). A brief overview with few recent references on the progress of research is given in the present addendum. A more extensive bibliography is available from the author on request.

Sauthoff, G.
Plastic Deformation
In: Basic Mechanical Properties and Lattice Defects of Intermetallic Compounds, (Eds.) J.H. Westbrook and R.L. Fleischer. John Wiley & Sons, Chichester, UK, 2000, 41-64

An overview is given on the plastic deformation behaviour of intermetallic phases. In the first part the possible deformation mechanisms are discussed with emphasis on dislocation glide, twinning and creep in view of the various temperature and stress dependencies. The second part is centred on the effects of atomic bonding, crystal structure symmetry, composition, stoichiometry, microstructure, second phases and environment on strength and ductility. This includes the discussion of possibilities for alloy design and optimisation.

Sauthoff, G.
Multiphase Intermetallic Alloys for Structural Applications, Intermetallics 8, 1101-1109 (2000)
Current more or less progressed developments on the base of intermetallic phases usually aim at new materials with highest possible strength, creep resistance and oxidation resistance at highest possible temperature and tolerable brittleness at lower temperatures for structural applications at high temperatures. Intermetallic alloys offer advantageous possibilities for reaching these aims by appropriate combination of phases and optimisation of phase distribution. This is exemplified with respect to strength and creep resistance by recent studies on NiAl alloys with strengthening Laves phase and multiphase TiAl alloys. The benefical effects of additional softening phases on deformability and toughness are demonstrated by the results of recent studies on Laves Phase alloys with disordered Fe-Al phase, NiAl alloys with disordered Ni-Fe phase and partially transformed martensitic NiAl alloys. Mechanisms and problems are discussed and perspectives are outlined.

Schneider, A.; Inden, G.; Grabke, H.J.; Wei, Q.; Pippel, E.; Woltersdorf*, J.
Effect of H_2S on formation and decomposition of Fe_3C and Fe_5C_2 under metal dusting conditions
steel research 71, No.5, 179-184 (2000)

The high temperature corrosion process metal dusting leads to the formation and decomposition of metastable iron carbides at the surface of iron samples. A small amount of H_2S in the carburising atmosphere causes the adsorption of sulphur onto the sample surface which decreases the carbon transfer rate and retards or suppresses the start of metal dusting. The extent of retardation of metal dusting depends on temperature, carbon activity and H_2S content. The higher the carbon activity the higher the H_2S content required for suppression of metal dusting. At very high carbon activities a second iron carbide, Fe_5C_2 (Hägg carbide), forms on the cementite surface. The carburisation experiments were conducted at 5000°C using CO-H_2-H_2O-H_2S gas mixtures. The microstructural investigations show that both metastable carbides decompose during metal dusting.

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Schneider, A.; Inden, G.; Grabke, H.J.
Growth kinetics of iron carbide layers during gas carburization
In: EUROMAT'99-Vol.9, Interface Controlled Materials, (Eds.) M. Rühle and H. Gleiter. Wiley-VCH, Weinheim, 2000, 30-37

The growth kinetics of carbide layers on iron surfaces has been studied by gas carburization in CO-H_2-H_2-H_2O-H_2S gas mixtures at 500°C. Small additions of H_2S have been added to the atmosphere to prevent graphite formation and carbide decomposition (metals dusting). The carburization was performed with CO-H_2-H_2O-H_2S mixtures at carbon activities in the range $12 < a_c < 4600$. At $a_c \leq 100$ only cementite (Fe_3C) is formed, at higher carbon activities an outer layer of Hägg carbide (Fe_5C_2) grows on the inner layer of cementite.

Parabolic rate constants have been determined for the growth of cementite and of Hägg carbide. From the dependence of the rate constant on carbon activity the self diffusion coefficient D_c^* for carbon in both carbides has been derived.

Schneider, A.; Viefhaus, H.; Inden, G.
Surface analytical studies of metal dusting of iron in CH_4-H_2-H_2S mixtures
Materials and Corrosion 51, 338-343 (2000)

The metastable iron carbide, cementite (Fe_3C), occurs as an intermediate phase during the high temperature corrosion process called "metal dusting". The kinetics and thermodynamics of metal dusting of iron have been studied by Grabke et al. using CO-H_2-H_2O and CH_4-H_2 gas mixtures. H_2S additions to carburising atmospheres impede the carbon transfer and retard the onset metal dusting, thus allowing to study the early stages of the process. In this work the metal dusting process was studied in CH_4-H_2-H_2S atmospheres at 700°C. Segregation experiments and surface analyses showed that S segregates on iron surfaces as well as on cementite surfaces. By means

of Auger electron spectroscopy (AES), scanning Auger electron microscopy (SAM) and energy dispersive X-ray-analysis (EDX) it was shown that coke contains graphite, cementite and iron particles with adsorbed sulphur.

Stein, F.; Palm, M.
DTA-Investigation of Phase Transformations in Al-Rich Ti-Al Alloys
In: EUROMAT'99, Vol. 10: Intermetallics and Superalloys, (Eds.) D.G. Morris, S. Naka and P. Caron. Wiley-VCH, Weinheim, 2000, 336-344

In the current search for new lightweight structural materials Al-rich Ti-Al alloys have come more into focus. These alloys have a lower density and a higher oxidation resistance than the familiar γ-TiAl alloys, and in addition it was reported recently that lamellar microstructures can be generated in the respective composition range which are advantageous for high creep resistance. A generation of specific microstructures in Al-rich Al-Ti-alloys is still difficult as phase equilibria in the range between γ-TiAl and $TiAl_3$ are not well established. The occurrence of up to six intermetallic phases has been proposed in the respective composition range and published phase diagrams differ significantly from each other. The homogeneity ranges of the different intermetallic phases in this part of the Al-Ti system up to 1200 °C have been established recently on the basis of a detailed electron-probe microanalysis investigation. A detailed DTA investigation has been performed to clarify phase relations at temperatures above 1200 °C and to determine transformation temperatures in the temperature range where compositions of coexisting phases were already determined. The results of DTA experiments are presented which contribute to an improved understanding of the phase relations in Al-rich Al-Ti alloys. The significance for the preparation of specific microstructures is discussed.

Oral and Poster Presentations

***Balun**, J.; Inden, G.:* Phase Equilibria in the Fe-Rh-Ti and Fe-Rh-Co Ternary Systems, Thermodynamics of Alloys (TOFA 2000). Stockholm, Sweden, 08.05.-11.05.2000.

Balun, J.; ***Inden**, G.:* Phase Equilibria in the Fe-Rh-Ti System, CALPHAD. Boston, USA, 18.06.-23.06.2000.

***Cugy**, P.; Inden, G.:* Microstructural evolution by diffusional reactions, Journees d'Automne 2000, SF2M. Paris, France, 17.10.-19.10.2000.

***Inden**, G.:* Diffusion et Transformation de Phases dans des Systemes Polyconstitues, Summer School THERMO'2000. Montpellier, France, 03.09.-08.09.2000.

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***Neumann**, P.:* Analytical Solutions at 180° Twist Boundaries in Cubic Crystals, 129th Annual Meeting and Exhibition of TMS, Symposion in Honour of Prof. Campbell Laird. Nashville, Tenneessee, USA, 13.03.2000.

***Neumann**, P.:* Fatigue Crack Initiation at Grain Boundaries due to Elastic Incompatibility Stresses, 10th Iketani Conference on Material Research towards the 21st century. Karuizawa, Japan, 27.06.-29.06.2000.

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***Palm**, M.:* Intermetallics for High-Temperature Structural Applications - Problems and Opportunities, European Thematic Network "Microstructural Engineering by Solidification Processing, Annual Meeting. Stockholm, 05.09.-08.09.2000.

***Palm**, M.; Sauthoff, G.:* Evaluation of Alloy Systems for Developing New Intermetallic Lightweight Materials, THERMEC 2000 - Processing and Manufacturing of Advanced Materials. Las Vegas, USA, 03.12.-09.12.2000.

***Palm**, M.; Sauthoff, G.:* Long-Term Creep and Oxidation Behavior of a Laves Phase-Strengthened NiAl-Ta-Cr Alloy for Gas Turbine Applications, High-Temperature Ordered Intermetallic Alloys IX. Boston, USA, 27.11.-29.11.2000.

***Palm**, M.; Sauthoff, G.:* Screening of Iron Aluminide-Based Alloys with Strengthening Second Phases, Materials Week 2000. München, 25.09.-28.09.2000.

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***Stein**, F.; Kaspar, R.; Sauthoff, G.:* Einfluss der Stahlerzeugung auf Verzugserscheinungen in Werkstücken aus Stahl - Eine kritische Übersicht, Unterausschuss für legierte Baustähle, VDEh. Düsseldorf, 28.11.2000.

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Department of Physical Chemistry

H.J. Grabke

The department, founded 1971 by H.J. Engell came to an end of its official existence end of May 2000 and was transferred to the new department 'Interface Chemistry and Surface Engineering'. Much valuable and successful work had been done in the nearly 30 years of its existence, in the main fields, corrosion and interfaces, but also on various other topics: hydrogen in steels, gas-metal interactions, diffusion in iron and its alloys, thermodynamics and electrochemistry.

In the more recent years the emphasis was in the research area 'high temperature corrosion', where the department has earned international reputation, especially concerning the work on corrosion in aggressive environments, carburizing, sulfidizing, chloridizing and/or nitriding atmospheres and deposits. Mechanisms of corrosion in these environments were elucidated, and ways and means were developed for protection. The studies are of high scientific level, but also of great importance for application of steels in chemical and petrochemical industry and in power plants. This kind of work will partially be continued in the new department by M. Spiegel as a groupleader (see that department report).

High Temperature Corrosion

Two main high temperature corrosion problems, arising in the **use of high alloy steels in aggressive environments** have been studied in depth in the recent years, ‚metal dusting' in carbonaceous gases [1, 2, 3, 4, 5], and the 'active oxidation' in oxidizing and chloridizing environments [6]. Protection is generally possible by Cr-rich oxide scales, which may be formed on ferritic steels with > 11 % Cr and austenitic steels with > 17 % Cr, and should consist of an outer layer of spinel $(Mn,Fe)Cr_2O_4$ and an inner layer of chromia Cr_2O_3. At temperatures < 700 °C such scales are not obtained for sure, since Cr-diffusion in the steels is too slow. To favor the Cr-diffusion and rapid scale formation, fast diffusion paths must be provided, i.e. grain boundaries and dislocations, which can be achieved with a fine-grain microstructure and / or surface-near deformation by grinding, sandblasting, shot peening etc [7]. The positive effects of grinding compared to pickling have been shown by studies on metal dusting of several 9-20%Cr steels in the temperature range 500–600 °C (Müller-Lorenz, Grabke). The most recent study was on stainless steels with 17-18%Cr [8, 9], in the frame of an ECSC multiproject on the 'Use of Stainless Steels in Aggressive Environments at Elevated Temperatures' [10]. In parallel fundamental studies Cr-diffusivities in the bulk, in grain boundaries and in deformed steels were determined using ^{51}Cr as a radioactive tracer [11, 12, 13]. The data allow calculations of the amount of Cr in the oxide formed on different steels, in dependence on ferritic or austenitic lattice, grain size and degree of deformation, which were confirmed by surface analytical or thermogravimetric studies. The topic **Cr-diffusion and initial oxide formation on Cr-steels** was also studied by taking SNMS- depth profiles on oxidized steels (Piehl, Grabke). Secondary neutrals mass spectrometry (SNMS) is a relatively new surface analytical method which renders quantitative analyses in the depth range 0.1 – 10 µm. Three ferritic 9%Cr, 11%Cr- and 16%Cr-steels and two austenitic 18%Cr-9%Ni- and 20%Cr-32%Ni-steels with different surface finishes were oxidized at 600 °C in different gas mixtures: H_2-2.5%H_2O, N_2-20%H_2-0.5% H_2O and synthetic air, for periods of 1-100 hours [14, 15, 16]. The oxidation in H_2-2.5%H_2O leads only to the Cr-rich oxides: spinel and Cr_2O_3, and the amount of these oxides formed increases with the degree of surface deformation: electropolished < polished < ground < sandblasted (fine sand) < sandblasted (coarse sand), see **fig. 1**.

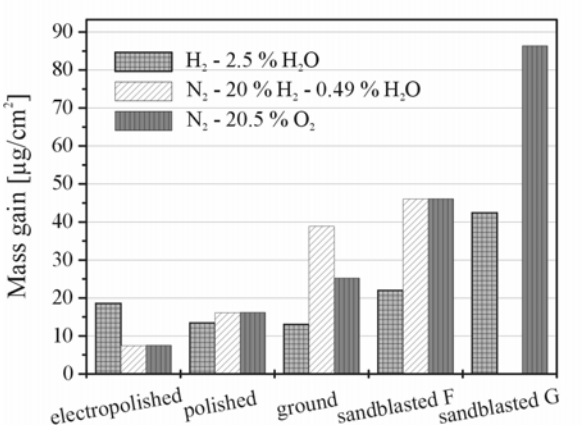

Figure 1: *Mass gain of a 20Cr-32Ni-steel (Alloy 800) after 100 h oxidation at 600 °C in different atmospheres, generally the amount of protective oxide increases with increasing degree of surface deformation caused by transport of Cr in fast-diffusion paths.*

The SNMS profiles show that Cr, Mn and Si are enriched in the scale, whereas the Fe-content is low – this trend is increased by surface working, see **fig. 2**. In the oxidation by air also the iron-rich oxides $(Fe,Cr)_2O_3$ and $(Fe,Cr)_3O_4$ can be formed and are growing on the undeformed samples, whereas surface deformation and fast diffusion paths favor the growth of the Cr-rich oxides. The SNMS depth profiles also yield information on the diffusion in the steel, depletion profiles are obtained for Cr, Si and Mn

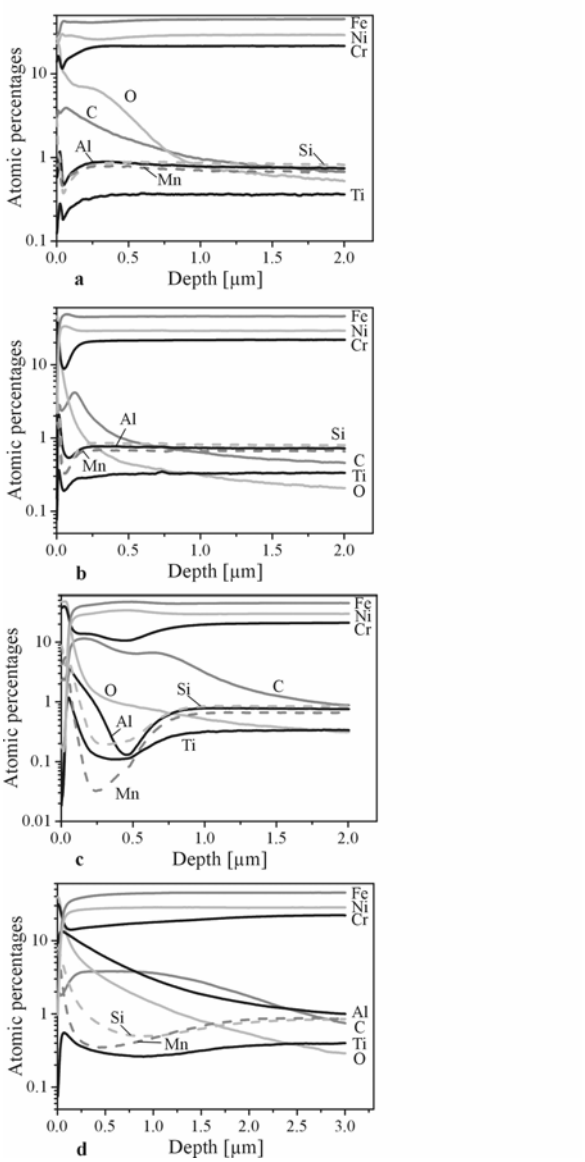

Figure 2: *Concentration profiles taken by SNMS (secondary neutrals mass spectrometry) after oxidation of a 20Cr-32Ni steel (Alloy 800) in H_2-2.5%H_2O at 600 °C, with increasing surface deformation, a) electropolished, b) polished, c) ground, d) sandblasted, the oxide layers become thicker and richer in Cr, Si and Mn, and the depletion of these elements extends into greater depths of the alloy, because of the effect of fast-diffusion paths.*

which allow calculation of diffusivities. The depletion extends to larger depths, the higher the deformation and the higher the diffusivities due to many fast diffusion paths. Bulk and grain boundary diffusivities of Cr were derived from the depletion profiles, measured in the different steels and polished and ground samples. For strongly deformed samples (sandblasted) bulk and grain boundary diffusion cannot be differentiated but an effective diffusivity is obtained. Generally all diffusivities are higher in the ferritic steels than in the austenitic steels and their values are increasing with the degree of deformation, by cold rolling or surface working.

A joint project is conducted with the Institut für Füge- und Strahltechnik, Univ. Magdeburg; on the **metal dusting behaviour of welded specimens,** made of high alloy steels and Ni-base alloys (Müller-Lorenz, Grabke). The samples are exposed in flowing H_2-24%CO-2%H_2O mixtures at 600 °C and 650 °C for several thousand hours, of special interest is the behaviour of the welds and of the heat affected zones. The ranking of alloys known from earlier research [2] was confirmed, the attack is diminishing in the sequence Alloy 800 » Alloy 600H > Alloy 601H > Alloy 602 CA, i.e. with increasing Cr- and Ni-content. The welds are generally attacked stronger, due to their dendritic structure even the weld material with the composition of Alloy 602 CA which is not attacked in the rolled state. The heat affected zone is a susceptible region, especially the border line of base metal and weld. In this line some pits have started to grow from the beginning of the exposures, their depth is in good agreement with the metal wastage rates obtained in earlier research. Alloy 600H was exposed in different surface states, the grinded specimen behaved best, clearly better than brushed, sandblasted and pickled material, but the alloy cannot be made resistant due to its low Cr content (16%), obviously 25% Cr are necessary as in Alloy 602 CA. The research on the **mechanism of metal dusting** [17, 18, 19] is continued in cooperation with other departments of the MPI (G. Inden, A. Schneider, Jianqiang Zhang). The mechanism obviously changes at temperatures > 700 °C and the metal dusting rate passes through a minimum. Probably carbon diffusion through a compact iron layer resulting from Fe_3C decomposition becomes rate determining. The **effect of sulfur**, inhibiting the cementite decomposition is studied using Auger electron spectroscopy and low energy electron diffraction (Moszynski, Grabke). Cementite in the iron surface decomposes at a notable rate at 300 °C under formation of graphitic carbon. Partial coverage with sulfur leads to a substantial decrease of the decomposition rate, and when the cementite surface is saturated with sulfur the decomposition is almost stopped but still a slow graphite growth was observed. Also the effect of sulfur on the carbon segregation was studied on the surface of highly carburized iron at 400 °C. Graphite growth in islands was detected if the saturation with sulfur was about 40 %. If the iron surface is saturated with sulfur, the graphite growth starts only at a higher temperature about 550 °C, then the graphite layer is formed above the sulfur atoms. The results confirm that the presence of sulfur largely suppresses graphite nucleation and in this way the start of metal dusting is retarded, - and this effect most probably plays an important role in the production of **iron carbide from the direct reduction of iron ores** [19].

Iron sponge or pellets from the direct reduction of iron ores tend to reoxidation and ignition during exposure to air or water. An ECSC-multiproject

(VDEh, MPI, RWTH, CRM) is conducted on this problem, at the MPI the kinetics of the **reoxidation of direct reduced iron** (DRI) is studied (Müller-Lorenz, Grabke) and the pellets are characterized by analyses before and after the trials. Thermogravimetric studies at 350 ^{o}C showed that the oxidation by O_2 is much faster than in CO_2 or water vapor. The reaction appears to be independent on the partial pressures, i.e. the oxidation reactions are zero order, due to surface saturation with the oxidizing species. Microscopic and surface analyses (SNMS) showed that the pellets (from MIDREX process, HSW) are very different concerning O- and C-distribution. Since C plays an important role retarding the oxidation, investigations are conducted on how to distinguish the different states of carbon in the pellets, as graphite, cementite or amorphous and dissolved carbon, by applying analytical methods (XRD, burning in O_2 in dependence on time and temperature) on well defined reference samples (Kurz).

Interfaces

Two review articles have been elaborated, on the **role of the interface oxide/metal** [20] in the oxidation of metals and alloys. The **nucleation and initial growth of oxides,** had been studied in several systems, one of these was the 9%CrMoV-steel (P91), where surface segregation of P and Si strongly affect the nucleation [21]. In current studies (Hüning, Viefhaus) the oxide formation is observed on intermetallic alloys NiAl-M (M = Cr, Fe) with rather heterogeneous surfaces. In a review paper the interactions of surface and interfacial reaction and diffusion in the scale and the alloy were considered [22], the theoretical treatment by C. Wagner shortly summarized and examples of surface and interface reaction control described.

In earlier studies the important role of the **grain boundary segregation of phosphorus** had been demonstrated, for turbine steels such as 3.5 NiCrMoV- and CrMoV-steels [23]. In cooperation with scientists from Slowakia (Janovec, Sevc, Výrostková) now new 9-12Cr-steels are studied, concerning the development of microstructure. Samples obtained from industrial partners, which had been in long-term creep- or relaxation tests are analyzed by transmission electron microscopy and by Auger electron spectroscopy at fracture surfaces. For these steels grain boundary segregation appears to be of minor influence, but formation of a Laves phase $(Fe,Cr)_2(Mo,W)$ deteriorates the creep resistance after 20-30 thousand hours [24, 25].

Hydrogen and Nitrogen in Steels

The **absorption**, **diffusion and solubility of hydrogen** in iron and steels had been a topic of research in the department for many years, a review paper [26] on the results was published now, and also a study on **hydrogen in austenitic stainless steel** [27], presenting results on the effects of carbon content, grain size and cold work on hydrogen diffusion in an 18Cr-8Ni steel. **Hydrogen solubility and diffusivity in hot rolled iron strip** was of interest in an ECSC-multiproject (with CRM, Thyssen Krupp Stahl and British Steel). After galvanizing hot strip, blisters had been observed below the zinc layer. In our studies the H-uptake during pickling and during annealing was determined and the H-diffusion in the steels studied [28]. In a recently proposed new technology for power plants the use of NH_3-H_2O mixtures was planned instead of only steam, this 'Kalina cycle' should yield a better heat transfer and efficiency. But **corrosion by nitridation** was to be expected and confirmed in exposures of various steels at 500 ^{o}C in 80%NH_3-30%H_2O. Iron and low alloy steels were less affected, but with increasing Cr-content the ferritic and austenitic 1-20%Cr steels showed internal nitridation and cracking by the volume increase due to CrN formation [29], so, the application of the Kalina-cycles appears to be risky, due to the high probability of materials nitridation.

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Dependence of the Hydrogen Permeation in Stainless Steel on Carbon Content, Heat Treatment and Cold Work
steel res. 71, 255-260 (2000)

The hydrogen permeation behaviour in austenitic stainless steel (1.4301, AISI 304) was studied between 25 to 85 ^{o}C using the electrochemical double cell permeation technique. Influences of parameters like carbon content, grain size and cold work were investigated. Using the current transient plots from the permeation experiments, apparent diffusion coefficient, D_{app} values were calculated. Values ranging from $5.8 \cdot 10^{-12}$ to $2.7 \cdot 10^{-10}$ cm^2/s were obtained for various conditions of the material. The increase in carbon mass content from 0.045 to 0.085 % resulted in a decrease in D_{app} by a factor of 8. This was attributed to the increased blocking of interstitial sites by higher carbon in the latter steel. The annealing treatment, resulting in a slight grain growth caused a decrease in D_{app} to about its half, in contrast to the reduced trapping effect of the grain boundaries. This was explained to be due to a longer hydrogen transport path required through the grain and less contribution of fast diffusion paths in the larger grain size material. A slight cold work (5% reduction in thickness) decreased the D_{app} whereas higher cold working (30%) increased the D_{app}. The cold working results in an increase in dislocation density and the dislocations act as traps for hydrogen transport. This results in a decrease in D_{app} values for 5 % cold work material. Strain induced martensite (α', bcc phase) formation in the matrix occurred in the higher cold worked material (10 and 30%). The presence of this bcc phase overcame the trapping effect of increased dislocation density resulting in an enhancement of hydrogen transport. From the activation energy calculated, it was concluded that the α' phase present did not provide a continuous medium for hydrogen transport, but added to the overall increase in the hydrogen transport process.

Grabke, H.J.
Carburization and Metal Dusting of Steels and High Temperature Alloys by Hydrocarbons
In: Proceed. Int. Conf. Corrosion in Refinery, Petrochemical and Power Generation Plants, Venice May 2000, Ass. Italiana di Metallurgia. ISBN 88-85298-36-2, Milano, Italien 2000, 1-11

Carbonaceous gases can cause deterioration of metals and alloys either by carburisation, an internal carbide formation occurring generally at high temperatures > 900 ^{o}C and $a_C < 1$, or by metal dusting, a disintegration into graphite and metal particles occurring mostly at lower temperatures and $a_C > 1$ (carbon activity $a_C = 1$ in equilibrium with graphite). Carburisation is a problem mainly in the steam-cracking of hydrocarbons, it can be retarded by the presence of sulfur and suppressed by a protective oxide layer. The oxide layer may fail by several reasons, most dangerous are too high temperatures > 1050 ^{o}C where the layer (Cr_2O_3) is converted to unprotective carbides.

Metal dusting by hydrocarbons has recently been observed in heaters of platformer units. Under these conditions, the protection by sulfur appears to be most important, but again it is most dangerous to exceed a certain temperature (~ 625 ^{o}C).

Grabke, H.J.
Corrosion by Carbonaceous Gases, Carburization and Metal Dusting, and Methods of Prevention
Mat. at High Temperatures 17(4), 1-5 (2000)

Exposure of metallic materials to carbonaceous gases can lead to (i) carburization, i.e. internal carbide formation causing embrittlement and failure especially at high temperatures of cracking tubes for olefine production, (ii) metal dusting, a disintegration of metals to a dust of carbon and fine metal particles, occurring at intermediate temperatures, e.g. in synthesis gas for ammonia or methanol production or in direct reduction of iron ores, and (iii) coking, the carbon deposition which is an annoying phenomenon in many processes. The mechanisms of these phenomena are well understood now and they can be suppressed or effectively retarded either by the presence of some sulphur in the process gases and/or by a protective dense oxide scale. This review describes the mechanisms and kinetics of corrosion by carbonaceous gases and the fundamentals of prevention.

Grabke, H.J.
Nickel-Based Alloys in Carbonaceous Gases
Corrosion 56(8), 801-808 (2000)

High temperature corrosion in carbonaceous gases can occur by carburization (i.e., internal carbide formation at C activities ($a_C < 1$ and at temperatures > 800 ^{o}C) or by metal dusting, a disintegration of alloys into graphite and metal particles observed at $a_C > 1$ and in a lower temperature range. In both cases, C entry and diffusion in the metal matrix is a decisive step, and in comparison to high alloy steels, the C ingress in Ni-based alloys is retarded by the decrease of C solubility and diffusivity with increasing Ni content. Therefore, Ni-based alloys are recommended for applications in carbonaceous gases (e.g., for the steam-cracking of hydrocarbons). Since operating temperatures > 1,100 ^{o}C are desired in ethylene (C_2H_4) production, where chromium oxide (Cr_2O_3) is no more stable, the alloys must contain Si and/or Al to form a protective scale. At temperatures ≥ 25% Cr and some Al proved to be very resistant to metal-

dusting attack by the carbonaceous syngas (CO-H_2) environment. Such alloys showed no attack in laboratory and pilot plant exposures for up to 10,000 h, whereas all high-alloy steels were susceptible.

austenitic stainless steels in a strongly carburizing H_2-CO-H_2O atmosphere at 600 ^oC. Fine grain size and surface deformation (grinding) clearly improve the metal dusting resistance of the steels.

Grabke, H.J.
Surface and Interface Segregation in the Oxidation of Metals
In: Proceedings ECASIA '99, 4-8 Oct., Sevilla, Spain. Surface & Interface Analysis 30, 112-119 (2000)

For the protection of high-temperature alloys against corrosion, a slowly growing, dense, well-adherent scale must be formed. At elevated to high temperatures either chromia (Cr_2O_3) or alumina (Al_2O_3) can act as such a protective scale. Surface and interface phenomena in the nucleation, growth and adherence of oxide scales have been studied, mainly by AES; these phenomena are described and their mechanisms are discussed.

Various positive effects on nucleation, growth and adherence are exerted by alloying with reactive elements (i.e. Ce, Y, La, Ti, Zr …) in small concentrations. They are acting in their oxidized state, segregated on the metal surface in oxide nucleation and segregated in oxide grain boundaries in the oxide growth mechanism.

Non-metal elements such as nitrogen and carbon can enhance Cr_2O_3 nucleation by intermediate co-segregation with chromium, in contrast sulphur impedes chromia formation. Segregation of sulphur to the surface of voids and cracks forming at the metal/oxide interface deteriorates the scale adherence. The detrimental sulphur can be scavenged in precipitates formed by the reactive elements (oxides and oxysulphides) and at their interfaces.

Grabke, H.J.; Müller-Lorenz, E.M.
Use of Stainless Steels in a Strongly Carburizing Environment
Proc. JSPS Conference Tokyo, Sept. 2000, Research Reports of the 123. Committee Meeting for High Temperature Alloys. Tokyo, Japan 2000, 307-316

Stainless steels are convenient for use at elevated temperatures and in aggressive environments, i.e. under conditions too demanding for low alloy steels and not requiring high alloy steels. However, they should form a dense protective Cr-rich oxide scale and for that, Cr-diffusion must be enhanced by providing fast diffusion paths in the steels. This is achieved by a fine grain microstructure and/or surface working of the steels; the grain boundaries, subboundaries and dislocations act as fast diffusion paths supplying sufficient Cr to the surface upon exposure to the aggressive atmosphere. This is demonstrated by studies on the metal dusting of

Grabke, H.J.; Müller-Lorenz, E.M.; Eltester, B.; Lucas, M.
Formation of Chromium Rich Oxide Scales for Protection against Metal Dusting
Mat. at High Temp. 17, 229-346 (2000)

Metal dusting is a disintegration of metals and alloys into graphite and metal particles, caused by strongly carburizing gas mixtures mainly in the temperature range 400 – 700 ^oC. Protection of steels against metal dusting is possible through the formation of dense chromium rich oxide scales but it is not guaranteed that such scales are formed at low temperatures, even on high Cr-steels.

Surface analytical studies have been conducted on the formation and composition of the oxide scales on 9 – 20 % Cr steels. The growth of oxide films was followed by AES for 3 hours at 10^{-7} mbar O_2 great differences were observed in dependence on surface finish. On ground samples, Mn and Si appeared early and Cr-rich oxide was formed, whereas on chemically etched samples Fe-rich oxides grew.

After long term exposures (240 h) under metal dusting conditions, i.e. in CO-H_2-H_2O mixtures at 600 ^oC, thin Cr-rich scales were observed on ground steels which were impermeable to carbon whereas on chemically etched steels thick Fe-rich scales had grown and carbon penetration was detectable. Accordingly, the oxide formation on Cr-steels at relatively low tempertures strongly depends on the surface treatment. Any surface working such as grinding and sand-blasting etc. introduces dislocations and causes a fine-grained microstructure near the surface, and the dislocations and grain boundaries act as rapid diffusion paths for supply of Cr to the surface in the first minutes of exposure, which leads to the formation of a protective oxide scale.

Grabke, H.J.; Riecke, E.
Absorption and Diffusion of Hydrogen in Steels
Materiali in Tehnologije 34(6), 331-342 (2000)

To understand and control hydrogen-induced cracking and hydrogen-induced stress-corrosion cracking in steels, the fundamental processes of hydrogen absorption and diffusion are of interest.

The electrochemical hydrogen permeation method has been extensively applied to obtain data on hydrogen absorption and diffusion in iron, iron alloys and steels. Steady-state permeation measurements yield the permeation coefficient and the hydrogen concentration and activity a_H, which are established on the surface in electrolytes. This information was

used to study the effects of alloying elements on a_H present during corrosion.

Permeation transients from non-steady-state measurements yield the hydrogen diffusivity, which is affected by the presence of hydrogen traps. For shallow traps with low binding energies a distribution equilibrium between trap and lattic sites applies, deep traps are already saturated at low a_H and hydrogen in deep traps is immobile at ambient temperature. The effects of Mo, V, Nb, Ti, Zr and their carbides and nitrides on the hydrogen diffusivity were studied and information was derived on the numbers and binding energies of traps which are caused by strain fields around big atoms of alloying elements or in the neighbourhood of their precipitates.

For some pipeline steels with different microstructures, and after welding simulation, hydrogen diffusivities and trapping were studied. The results were related to hydrogen-induced stress-corrosion cracking, which was observed in constant-extension-rate tests. The work of fracture decreased with increasing hydrogen activity, i.e. the mobile hydrogen is decisive for failure, and the hydrogen in deep traps has no obvious effect on the fracture behaviour of steels.

Lindemann, J.
Effects of Phosphorous and Sulphur on the Grain Boundary Self-Diffusion in Alloy 800 and the Creep Properties of Alloy 800
Fortschritt-Ber. VDI Reihe 5 No. 592 VDI Verlag Düsseldorf, 1-144 (2000)

In Alloy 800, an austenitic steel with its specifications LC, H and HT and in melts with additions of P and S, diffusion, segregation and creep were measured to demonstrate the effects of impurities and to find correlations between microstructure, creep behaviour and self-diffusion. The grain boundary diffusivity was determined by the method of residual activity using ^{59}Fe in the temperature range 800 to 1000 ^oC. Impurities such as P and S retard the grain boundary self-diffusivity of ^{59}Fe in Alloy 800 by grain boundary segregation and enhanced precipitation. Creep curves, recorded at constant temperature and stress, showed that P addition causes an increase of creep life and a reduction of creep rupture strain. The minimal strain rate is for Alloy 800 with 0.09wt%P slower by a factor 100, compared to the other modifications of Alloy 800, this is caused by precipitation of phosphides in the grain and enhanced precipitation of $Cr_{23}C_6$ at the grain boundaries.

Müller-Lorenz, E.M.; Grabke, H.J.
Metal Dusting and Coking on Steels by Synthesis Gas
Proceed. Int. Conf. Corrosion in Refinery, Petrochemical and Power Generation Plants, Venice May 2000, Ass. Italiana di Metallurgia. ISBN 88-85298-36-2, Milano, Italien 2000, 213-220

Metal dusting and coking are coupled phenomena, often occurring in synthesis gas, i.e. CO-H_2 from methane conversion. High carbon activities $a_C > 1$ cause metal dusting, a disintegration of metals and alloys in graphite and metal particles, which are catalysts for carbon deposition (coking). The kinetics of both reactions have been studied in detail on several low and high alloy steels. Rate equations and Arrhenius plots are presented for description of metal wastage by metal dusting and for carbon deposition. These kinetics can be explained by well-understood mechanisms. Metal dusting and coking can be suppressed by sulfur addition to the atmosphere and/or a stable dense protective oxide layer.

Piehl, C.; Tökei, Zs.; Grabke, H.J.
Influence of Chromium Diffusion and Different Surfaces Finishes on the Oxidation Behaviour of Chromium Steels
Mat. at High Temp. 17, 243-246 (2000)

The present contribution is focused on the systematic investigation of the effects of different surface finishes (ground, polished, electropolished) on the oxidation behaviour of chromium steels. The specimens were oxidized in a H_2-2.5%H_2O atmosphere at 872 K for 1 h to 100 h. depth profiles were recorded by secondary neutral mass spectrometry (SNMS) to determine the elemental composition of the oxide scale and the diffusion profiles below the scale. The surface finish was found to influence both the thickness of the oxide scale and the depletion of the selectively oxidized elements.

Sämann, N.; Spiegel, M.; Grabke, H.J.
Effects of Surface Working on the High Temperature Corrosion of Stainless Steels in Oxidizing and Chloridizing Atmospheres
Proceedings EUROCORR' 2000, London, CD-ROM, Eds. Institute of Materials, London and Secure Data Services, Hants, www. secure-data.co.uk

Effects of different surface treatments such as sandblasting, grinding and electropolishing on the corrosion of 18Cr-10Ni-steels were studied in different environments at 600 ^oC. Effects of roughness were expected and of surface deformation which provides fast-diffusion paths for Cr-diffusion to the surface and formation of a protective scale. Thermogravimetric studies of the oxidation in He-5%O_2 showed a prevailing influence of the roughness: the initial rate increases in the sequence grinding < sandblasting (fine sand) < sandblasting (coarse sand). Also under oxidizing and chloridizing conditions, in He-5%O_2-0.05%HCl the effect of roughness prevails, the corrosion rate being fast after sandblasting with coarse sand but strongly diminished after sandblasting and electropolishing. In contrast, providing fast-diffusion paths proved to improve

corrosion resistance in exposures simulating waste incineration conditions: i.e. in N_2-5%O_2-0.05%HCl-0.05%SO_2-2.5%H_2O, samples embedded in fly ash. Under these condition corrosion attack increased in the sequence: sandblasted (coarse sand) < sandblasted (fine sand) < ground (#120) < ground (#600) < electropolished. The more resistant, sandblasted samples develop a more protective Cr-rich scale, because the fast-diffusion paths obtained by the surface deformation favored Cr-diffusion and chromia formation.

Schlüter, T.; Grabke, H.J.
Hydrogen Absorption, Permeation and Diffusion in Hot Strip
In: Nichtmetalle in Metallen 2000, (Ed.) D. Hirschfeld, DGM, ISBN 3-9806913-1-4, Clausthal-Zellerfeld 2000, 109-118

In connection with problems in galvanising of hot rolled steel strip the hydrogen absorption during pickling was studied on two steels. The trapping properties of the steels were characterized by permeation trials in the electrochemical double cell. Great care was applied for the hydrogen determination after pickling, dependences on steel quality, pickling time, acid concentration (HCl) and presence of iron ions in the solution were studied. The hydrogen absorption generally goes through a maximum with time, and is enhanced by presence of iron ions and for the steel DP600 (with 0.5%Cr) compared to the ELC steel (extra low carbon). Due to the Cr-content the steels DP600 shows lower hydrogen permeation and diffusivity compared to the ELC-steel.

Schneider, A.; Inden, G.; Grabke, H.J.; Wei*, Q.; Pippel*, E.; Woltersdorf*, J.
Effect of H_2S on Formation and Decomposition of Fe_3C and Fe_5C_2 under Metal Dusting Conditions
steel res. 71(5), 179 – 184 (2000)

The high temperature corrosion process metal dusting leads to the formation and decomposition of metastable iron carbides at the surface of iron samples. A small amount of H_2S in the carburising atmosphere causes the adsorption of sulphur onto the sample surface, which decreases the carbon transfer rate and retards or suppresses the start of metal dusting. The extent of retardation of metal dusting depends on temperature, carbon activity and H_2S content. The higher the carbon activity the higher the H_2S content required for suppression of metal dusting. At very high carbon activities a second iron carbide, Fe_5C_2 (Hägg carbide), forms on the cementite surface. The carburisation experiments were conducted at 500 ^oC using CO-H_2-H_2O-H_2S gas mixtures. The microstructural investigations show that both metastable carbides decompose during metal dusting.

*Max Planck Institut für Mikrostrukturphysik, Halle

Strauß, S.; Vogel, D.; Grabke, H.J.
Oxidation and Nitridation of Materials in NH_3-H_2O Gas Mixtures
In: Nichtmetalle in Metallen 2000, (Ed.) D. Hirschfeld, DGM, ISBN 3-9806913-1-4, Clausthal-Zellerfeld, 153-164 (2000)

For increased efficiency in power plants, the Kalina-cycle, i.e. the use of NH_3-H_2O mixtures instead of steam only, was proposed. Reservations exist concerning the possible corrosion problems, therefore tests were conducted at 500 ^oC in flowing 70%NH_3-30%H_2O mixtures on Fe, Ni and eight 1-20%Cr steels and the Ni-base alloy 600 for 200 hours. Oxide layers are formed on the materials but the scales are not dense and protective. Therefore internal nitride formation takes place in the Cr-containing materials. Fine CrN precipates are formed causing stresses and cracking, the more severe, the higher the Cr-content. Least corrosion was observed for iron and the 1%CrMo-steel, whereas nickel is destroyed by Ni_3N formation. The high probability of nitridation obviously prohibits the use of the Kalina-cycle in power plants.

Tökei, Zs.; Hennesen, K. ; Viefhaus, H.; Grabke, H.J.
Diffusion of Chromium in Ferritic and Austenitic 9-20wt% Chromium Steels
Mater. Sci. Technol. 16, 1129-1138 (2000)

Radiotracer ^{51}Cr diffusion experiments were conducted on 9 – 20 wt-% chromium ferritic and austenitic steels. Volume diffusion coefficients have been determined in the temperature range 881 – 1281 K, and triple product values of grain boundary diffusion between 795 and 1281 K. Compared with dilute solid solutions, high ratios of grain boundary and volume diffusion activation energies have been obtained. This is discussed in view of the chemical composition of the grain boundaries measured by Auger electron spectroscopy. Furthermore, in the case of ferritic steels the effects of α - γ and paramagnetic-ferromagnetic phase transitions are illustrated, while for austenitic steels a classical Arrhenius relationship has been found in the investigated temperature range.

Tökei, Zs.; Viefhaus, H.; Grabke, H.J.
Initial Stages of Oxidation of a 9CrMoV-Steel: Role of Segregation and Martensite Laths
Appl. Surf. Sci. 165, 23-33 (2000)

The initial stages of oxidation of steel P91 were studied in a UHV system at oxygen partial pressures ranging from 10^{-8} mbar up to 10^{-5} mbar. Experiments were conducted at 600 – 650 ^oC for heating times 5 – 120 min. The oxide scales were analyzed by means of

Auger electron spectroscopy (AES), scanning Auger microscopy (SAM), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The very initial stages up to growth of the first few oxide layers correspond to a complex surface situation and are influenced by Cr-nitride formation, P segregation and SiO_2 formation. After the first monolayers of oxides have grown the process becomes simpler and different oxidation kinetics accounts for the further growth. The microstructure of steel P91, tempered martensite along with chromium carbide precipitates leads to preferential chromium-rich oxide formation along martensite laths. The results are also discussed in view of diffusion data taking into account material transport by bulk and fast diffusion paths.

Tökei, Zs.; Viefhaus, H.; Hennesen, K.; Grabke, H.J.
Role of Fast Diffusion Paths in the Initial Stages of Oxidation of High Temperature Chromium Steels
Solid State Phenomena 72, 3-8 (2000)

The first stages of oxidation of 9-20 wt% commercial high temperature chromium steels were studied in a UHV system. The possible chromium supply by bulk diffusion from the metal and the Cr-content of the scales is compared. In coarse grained austenitic steels the contribution of fast diffusion paths remains local, while for ferritic/martensitic steels the presence of martensite laths influences significantly the overall oxidation process by enhanced Cr-supply.

Zahs, A.; Spiegel, M.; Grabke, H.J.
Chloridation and Oxidation of Iron, Chromium, Nickel and their Alloys in Chloridizing and Oxidizing Atmospheres at 400 – 700 °C
Corr. Sci. 42, 1093-1122 (2000)

The corrosion behavior of Fe, Cr, Ni, the ferritic alloys Fe-15Cr and Fe-35Cr and the austenitic alloys Alloy 800, Alloy 825 and Alloy 600 was investigated in N_2-5 vol% O_2 and He-5 vol% O_2 with additions of 500 – 1500 vppm HCl at temperatures between 400 and 700 °C using discontinuous exposures and thermogravimetric experiments. The corrosion products were analyzed by scanning electron microscopy with EDX-analysis, X-ray analysis and Auger electron spectroscopy. The main corrosion process, especially at temperatures above 500 °C, is 'active oxidation', i.e. the formation of volatile metal chlorides at the metal/oxide interface, which evaporate, diffuse outwards and are converted into oxides in regions of higher oxygen partial pressure. The characteristic differences concerning the corrosion behavior of the different metals and alloys at different temperatures are largely determined by thermodynamics, that means the free energy of chloride formation, the vapor pressure of the chlorides and the oxygen pressure necessary for conversion of the evaporated chloride to the oxide.

Oral and Poster Presentations

***Grabke**, H.J.:* 1. Thermodynamische Grundlagen der Hochtemperaturkorrosion, 2. Mechanismen der Oxidation reiner Metalle und von Legierungen, 3. Korrosion von Hochtemperaturlegierungen in aufkohlenden, sulfidierenden und chlorierenden Atmosphären, DGM-Fortbildungsseminar 'Hochtemperaturkorrosion'. Jülich, 08.11.-10.11.2000.

***Grabke**, H.J.:* Application of Surface and Interface Analysis in Metal Science, Session 'Advances in Materials Analysis', Analytica Conference 2000. München, 11.04.-14.04.2000.

***Grabke**, H.J.:* Carburisation and Metal Dusting of Steels and High Temperature Alloys by Hydrocarbons, Keynote lecture: Int. Conference 'Corrosion in Refinery, Petrochemical and Power Generation Plants'. Venezia, 18.05.-19.05.2000.

***Grabke**, H.J.:* Hochtemperaturkorrosion - von einfachen zu komplexen Bedingungen, Kolloquium Werkstoffwissenschaften. Universität Erlangen, 01.02.2000.

***Grabke**, H.J.:* Hydrogen Absorption and Diffusion in Steels, Opening lecture: 8. Conference on Materials and Technology. Portoroz, Slovenia, 10.10.-12.10.2000.

***Grabke**, H.J.:* Mechanisms and Prevention of Corrosion in Carbonaceous Gases, Keynote lecture: 5th Int. Symposium on High Temperature Corrosion and Protection of Materials. Les Embiez, France, 22.05.-26.05.2000.

***Grabke**, H.J.:* Metal Dusting of Steels and Nickel-based Alloys, Symposium honoring Ib Alstrups 40 years in Haldor Topsoes R & D division. Havreholm Castle, Denmark, 07.01.2000.

***Grabke**, H.J.:* Surface and Interface Reactions in the High Temperature Corrosion of Steels, Keynote lecture, DIMAT 2000, 5th Int. Conference on Diffusion in Materials. Paris, 17.07.-21.07.2000.

***Grabke**, H.J.; Strauß, S.; Vogel, D.:* Oxidation und Nitrierung von Stählen in NH_3-H_2O-Gasgemischen, 8. Symposium Nichtmetalle in Metallen. Inst. für Physikal. Chemie, Univ. Münster, 16.03.-17.03.2000.

***Müller-Lorenz**, E.M.; Grabke, H.J.:* Metal Dusting and Coking on Steels by Synthesis Gas, Int.

Conference 'Corrosion in Refinery, Petrochemical and Power Generation Plants'. Venezia, 18.05.-19.05.2000.

***Müller-Lorenz**, E.M.; Grabke, H.J.:* Metal Dusting of Modified Stainless Steels, "Posterschau", 5th Int. Symposium on High Temperature Corrosion and Protection of Materials. Les Embiez, France, 22.05.-26.05.2000.

***Müller-Lorenz**, E.M.; Grabke, H.J.; Schneider, A.:* Carburization and Metal Dusting of Iron, Invited Lecture, CAMP Current Advances in Materials and Processes. The Iron and Steel Institute of Japan. Nagoya, 01.10.-03.10.2000.

***Piehl**, C.; Tökei, Zs.; Grabke, H.J.:* The Role of Fast Diffusion Paths in the Selective Oxidation of Chromium Steels, "Posterschau", DIMAT 2000, 5th Int. Conference on Diffusion in Materials. Paris, 17.07.-21.07.2000.

***Piehl**, C.; Tökei, Zs.; Grabke, H.J.:* Surface Treatment and Cold Working as Tools to Improve Oxidation Behaviour of Chromium Steels, "Posterschau", 5th Int. Symposium on High Temperture Corrosion and Protection of Materials. Les Embiez, France, 22.05.-26.05.2000.

***Sämann**, N.; Spiegel, M.; Grabke, H.J.:* Influence of Surface Preparation on the Corrosion of Steels in Aggressive Atmospheres, "Posterschau", 5th Int. Symposium on High Temperature Corrosion and Protection of Materials. Les Embiez, France, 22.05.-26.05.2000.

***Schlüter**, T.; Grabke, H.J.:* Wasserstoff-Löslichkeit, -Permeation und -Diffusion in Warmband, 8. Symposium Nichtmetalle in Metallen. Inst. für Physikal. Chemie, Univ. Münster, 16.03.-17.03.2000.

***Spiegel**, M.; Grabke, H.J.; Tacke, K.H.:* Kinetic Studies in the Oxidation of Fe-Si Steels in the Temperature Range from 1000 - 1400 ^{o}C, 10th IUPAC, Conference on 'High Temperature Materials Chemistry'. Jülich, 10.04.-14.04.2000.

***Tökei**, Zs.; Grabke, H.J.:* Diffusion of ^{51}Cr in Cold-rolled 18Cr-8Ni Steel, "Posterschau", DIMAT 2000, 5th Int. Conference on Diffusion in Materials. Paris, 17.07.-21.07.2000.

Department of Interface Chemistry and Surface Engineering

M. Stratmann

The Department of Interface Chemistry and Surface Engineering was established in January 2000 with the appointment of Martin Stratmann as department head and scientific member of the Max-Planck-Institut. The Department of Physical Chemistry has been incorporated into the new department after the retirement of Prof. H.J. Grabke at the end of May.

The Department of Interface Chemistry and Surface Engineering has scientific interests in the areas of physico-chemical degradation mechanisms of surfaces and interfaces induced by electrolytic corrosion, high-temperature corrosion, loss of adhesion and tribologic attack; engineering of new and stable surfaces and interfaces; physico-chemical analysis of processes and reactions, by which new surfaces layers and modified surfaces are prepared.

In order to fulfil these tasks successfully, the department will be equipped with numerous spectroscopic techniques ranging from sophisticated surface analytical UHV-systems to optical spectroscopy and scanning probe microscopy. Due to construction work within the institute, the department could build up these techniques in the year 2000 only to a small extent.

The department will in the final state include 5 scientific groups; during the year 2000 only 3 of them have been established: molecular structures and surface modification (Michael Rohwerder), electrochemistry and corrosion (Achim Walter Hassel) and high-temperature reactions (Michael Spiegel). The highly interdisciplinary research is focussed on the following major subjects:

Buried interfaces

The research is aimed to the understanding of the stability of metal/polymer interfaces and is strongly based on new experimental techniques like the Scanning Kelvinprobe or the Scanning Kelvinprobe Force Microscope. Using these techniques is was possible to detect for the first time changes of the electrode potential at buried metal/polymer interfaces with a high local resolution, which are associated with deadhesion due to electrochemical reactions. The metallic material has a strong impact on the reaction kinetics and mechanisms. In the past these deadhesion reactions have been analysed in detail for materials like iron or galvanised steel which form electron conducting oxides. During 2000 for the first time Al-based substrates have been analysed which are characterised by non-electron conducing oxides locally interrupted by electron conducting intermetallic phases. This gives rise to very specific deadhesion reactions which are strongly localised (filiform-corrosion). The electrochemical properties of the buried interface may further be varied by activation and passivation cycles during cyclic wet/dry/wet exposure; in order to understand such phenomena a world-wide new scanning Kelvinprobe inside a climate chamber has been constructed and successfully established.

Surface modification

Surface modification is performed as well by ordered monolayers of organic molecules on metallic substrates as by ultra thin plasma polymers. In order to study plasma polymers on construction materials a microwave plasma chamber has been installed and the chemistry, morphology and stability of some 10 nm thick plasma polymers have been studied on galvanised steel. For these studies the combination of corrosion stability and ultra-hydrophobicity is of particular interest. During the plasma treatment the electronic properties of the oxidic metal surface can be changed significantly. This is of particular importance for the kinetics of electrochemical reactions and of central importance for actual research. Furthermore the stability of organic monolayers on different materials has been of ongoing interest. The studies have concentrated on organic phosphonates as possible molecular adhesion promoters.

Intelligent repair systems

Interfaces should not only withstand an electrochemical or mechanical attack, they should also have the possibility to repair defects and a local loss of adhesion. Such phenomena are of increasing importance; during 2001 in particular the repair of interfaces in the presence of Mg-ions has been studied in detail.

Stability of alloys

The understanding of corrosion phenomena on a very local and even atomistic scale is of considerable interest for actual research. For an example in a detailed investigation the dissolution of CuAu single crystals has been studied using in-situ scanning tunnelling microscopy on atomically defined surfaces. These studies will be extended also to the high temperature oxidation using a new variable temperature STM.

Molecular Structures and Surface Modification

M. Rohwerder

In 2000 the activities within the newly formed research group “Molecular Structures and Surface Modification” (Michael Rohwerder) covered a wide field of different aspects of the protection mechanisms and stability of ultra-thin films. Especially scanning probe techniques such as STM, AFM and the Scanning Kelvin Probe Force Microscope (SKPFM) are methods central to a great number of projects in this group.

In the project “**Fundamental Processes of Delamination**” (DFG, MPIE: **Elke Hornung**) nanoscopic and molecular aspects of delamination are at the centre of interest. The deadhesion of polymers from metallic substrates is usually based on electrochemical reactions at the metal/polymer interface. In particular, in the case of cathodic delamination oxygen is reduced at the delamination front and reactive inter-

mediates which are formed during the electrochemical reduction destroy the organic backbone of the polymer layer therefore diminishing the adhesive strength between the substrate and the coating.

In the recent years the Scanning Kelvin Probe (SKP) has proven to be a useful tool for the investigation of delamination of polymer coatings [1]. The typical resolution is usually not better than 20 µm. This is usually sufficient to detect local anodes and cathodes, to follow the reaction kinetics and therefore to elucidate the principle reaction mechanism.

However, a more microscopic or even nanoscopic view of the reaction at the buried interface is still missing. For example, localized forms of corrosion such as pitting corrosion or filiform corrosion are extremely dependent on existence and character of intermetallic particles in the matrix material. Often these particles are of micron or even submicron size.

AFM in the Kelvin mode (SKPFM) allows on specially prepared model samples to study fundamental aspects of delamination with submicroscopic resolution. This way it is possible to study the very initial stages of delamination and also the details at the delamination front, the reaction zone. A detailed information has been achieved on the dimension of the reaction zone and the influence of imperfections within the materials surface on the reaction mechanism.

Fig. 1 shows topography and potential mappings on a mechanically polished AA2024-T3 surface. A comparison shows that in the marked areas there is a significantly higher potential while the topography is basically the same. The surface of the matrix material is substantially Al_2O_3, the intermetallic particles contain increased amounts of Cu, Fe, Mn and Si. While the Al-matrix surface behaves passive, the surface of the intermetallic particles is active and thus in air positively charged.

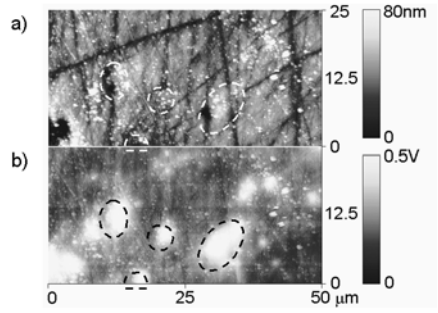

Figure 1: *Al-alloy AA2024-T3 with intermetallic particles; a) topography; b) potential*

First delamination experiments on specially prepared samples show formation of small blisters in the delaminated part of the only 100 nm thin plasma polymer film; also to be seen is the potential gradient typical for cathodic delamination: more negative potentials in the already delaminated area, more positive potentials in the still intact area. As can be seen in **fig. 2** the delamination front in the potential map (see broken white line) precedes the topographic delamination by about 10µm. The processes in this very delamination front are of ultimate interest and are subject of current research [2].

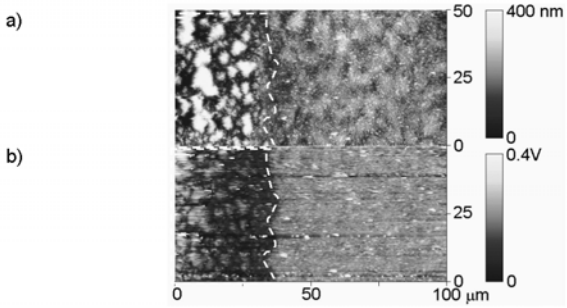

Figure 2: *Delamination of a HMDS-plasma polymer coated Au sample; progress of the delamination: left → right. a) topography; b) potential*

Another project (**Nanoscopic Aspects of the Forming Behaviour of Ultra-Thin Plasma-Polymer Films,** ECSC: **Birgit Baumert**) focuses on the reaction of ultra-thin plasma-polymer films deposited on electro-galvanised steel (ZE) on tensile stretching.

ZE has a z-range of about 1µm, in contrast with the film thickness of about 100nm. This large roughness makes AFM investigations, due to the necessarily rather slow scan velocities, very time consuming and tedious. The roughness of the substrate also makes it difficult to detect any nano-size cracks in the plasma-film itself. However, first steps could be made to investigate in-situ the forming behaviour of the plasma-polymer coated ZE, yielding so far predominately information about the reaction of the zinc coating on tensile stretching.

The performance of zinc coatings can be significantly improved by adding magnesium to the zinc. The underlying mechanisms of the improved corrosion protection achievable with these new alloy coatings are poorly understood so far.

Hence, electrochemical and surface analytical measurements were carried out on certain model systems, in order to elucidate the role of Mg in the **corrosion protection mechanisms of Zn-Mg alloy coatings** (BMBF: **René Hausbrand**). Such basic knowledge is of great importance, in particular for optimising the structure and properties of the coatings, and hence, the production process.

It has been suggested that the enhanced corrosion resistance of magnesium containing zinc coatings could be attributed to the formation of protective corrosion products of zinc, slower anodic dissolution of Mg-Zn intermetallic phases and the formation of protective MgO. The results, however, were obtained with different kinds of technical substrates containing at least two distinct phases, making well defined electrochemical experiments difficult.

Because of the complex and, depending on the deposition process, strongly varying microstructure of the Zn-Mg coatings, the main focus of the present study is to investigate the role of the different phases which may be contained in the coatings using single phase samples and the study of their corrosion behaviour.

Experiments consisted of immersion of single phase samples (Zn, MgZn2, Fe) in different electrolytes with chloride, with and without additional magnesium. The surface layers were analysed with XPS and the electrochemical behaviour was characterised with voltammetry. Additional corrosion experiments were performed on galvanised steel samples.

From these experiments it can be concluded, that $MgZn_2$, which is known to be present in many Zn-Mg coatings, exhibits similar electrochemical behaviour to zinc when immersed in a bulk electrolyte. Therefore, it is expected to release magnesium cations under corrosive attack. This magnesium in the solution forms surface layers on zinc and iron, which decrease the corrosion of zinc and the formation of red rust by the inhibition of oxygen reduction. The main effect is observed for the inhibition of oxygen reduction on iron.

If iron is immersed in solution containing magnesium at the corrosion potential, a magnesium-containing surface layer will form on cathodic sites while on regions of more metal dissolution, no magnesium can be detected on the surface. A cathodic shift in corrosion potential of almost 100 mV can be seen in comparison to iron in magnesium-free solution. This indicates an inhibition of the oxygen reduction. If iron is polarized to –0.8V, which will be the case on a technical substrate with strong galvanic coupling between iron and zinc, a thick layer of magnesium hydroxide forms shown through XPS measurements. The I/E curve of such a sample shows an strong inhibition of the oxygen reduction.

While this inhibition is not very large near the zinc corrosion potential, to which the iron will be polarised if the cathodic protection is strong (good galvanic coupling between zinc and iron), the inhibition is considerable if the galvanic coupling is weak, i.e. if the electrolyte layer is thin. Since oxygen reduction is then strongly inhibited, the galvanic drop is not as large as without Mg and consequently the iron dissolution much lower. This is why the Mg-Zn alloy coatings reduce the occurrence of red rust in thin electrolytes, as they are common in atmospheric corrosion [3].

An even stronger effect is observed for the delamination inhibition of organic coatings from Zn-Mg alloy coatings as compared to pure Zn coatings. The reason for this is not yet completely understood and subject of current research.

Also a very effective way to improve the resistivity against delamination is to use adhesion promoters at the interface between the metal surface and the organic coating. Phosphonates have proven to greatly inhibit delamination from aluminium and aluminium alloy surfaces [4,5]. The **potential of phosphonates on iron and steel surfaces** (MPIE: **Sascha Frenznick**) for the same application was topic of a diploma thesis. Contrary to aluminium no formation of well ordered phosphonate films could be observed. However, on iron electrochemical passivation during adsorption from aqueous solution could prevent the formation of thick precipitation layers. Contact angle studies on the wetting behaviour of alkylphosphonate modified iron surfaces showed that the ultrathin films are remarkably stable on this reactive surface; delamination rates could be reduced by a factor of two.

In the recent years conducting polymers were frequently claimed to effectively protect from delamination. A new project is dedicated to find out if this is true and to understand the **protection mechanisms of conducting polymers** (ECSC: **Adam Michalik**).

Electrochemistry and Corrosion

A. W. Hassel

Among all light metals aluminium is the most important one. On one hand alloying elements such as copper are necessary to increase the hardness to a value that allows the aluminium to be used as a construction material in automobiles, ships and aircrafts. On the other hand these elements are discussed to be responsible for corrosion phenomena such as filiform corrosion. This special corrosion type takes place only under specific conditions in the presence of chloride ions and only in a certain range of humidity. The need for an efficient corrosion protection is obviously mandatory for an investment like the fleet of aircraft. Chromate containing paintings are very efficient, but have a significant toxicity. For the development of a proper substitution it is essential to understand **the mechanism of filiform corrosion and the protective effect of the chromate (Jana vander Kloet)**. Kelvin probe measurements of the active head of filiform thread showed that anode and cathode are separated [6]. While the anodic metal dissolution takes place in the head of the corrosion thread, the cathodic oxygen reduction is localised in its tail. The ex-situ investigation of those samples, where the covering paint was removed, showed that chloride is accumulated in the head of the corrosion thread probably as counter ions. These investigations are now being continued with a focus on how a sudden addition of chromate into an active thread influences the corrosion.

Studies on **alternative anodising procedures** were performed **in oxalic acid electrolytes containing fluoride** [7]. These studies were performed in cooperation with the research group of **Dr. Alexander Mozalev** from the Belarus Institute of technology in Minsk. Beside the well known ELOXAL procedure for the preparation of protective oxide layers on aluminium there is a high industrial need for alternative anodising procedures. The anodising of aluminium in alternative electrolytes is one of the easiest techniques for the formation of evenly distributed and uniformly shaped honeycomb like pores in a chemically inert material such as aluminium oxide. This oxide films can be easily removed from the metal and are already used for highly sensitive filters that allow even a separation of the different hydrogen isotopes from a gas mixture.

In a co-operation with **Dr. Detlef Diesing** from Heinrich-Heine-Universität Düsseldorf the **Simmons theory of electronic tunnelling through thin insulation oxide films** was extended in order to explain:

- the current voltage plots of direct elastic tunnelling,
- the temperature dependence of the tunnel current,
- the potential and temperature dependence of the relaxation currents and
- the breakdown of metal-insulator-metal contacts.

The basic idea is to replace the simple asymmetrical trapezoidal barrier as supposed by SIMMONS [8] by the real image potential curve of the barrier. It takes into account that the band edges are smeared out due to the finite value of the insulators permittivity. In addition, concurrent tunnelling processes such as Fowler-Nordheim-tunnelling [9] and valence band tunnelling are allowed to contribute to the overall current [10]. Finally, image potential corrections are calculated for non-perfect insulators due to the local barrier deformation in the vicinity of a dipole defect within the insulating film. These defects are always present in a real material. A mayor problem is the fact, that the concentration as well as the position of these defects show a strong transient behaviour.

These theoretical extensions are based on a significant improvement in the preparation of MIM-contacts (metal-insulator-metal-contacts) with ultrathin anodic valve metal oxides as insulating material [11]. After electropolishing the unavoidable film from oxidation in air is converted into a well defined anodic oxide under stationary corrosion conditions. The sample is then potentiostatically polarised to the oxide formation potential. It is essential to hold the sample at this oxide formation potential until the current reaches the level of stationary corrosion. Under these conditions an extremely high field strength of several hundred MV m^{-1} (e. g. 625 MV m^{-1} for aluminium) forms an almost perfect oxide with a very low concentration of defects. These samples are then evaporated with a thin silver top electrode.

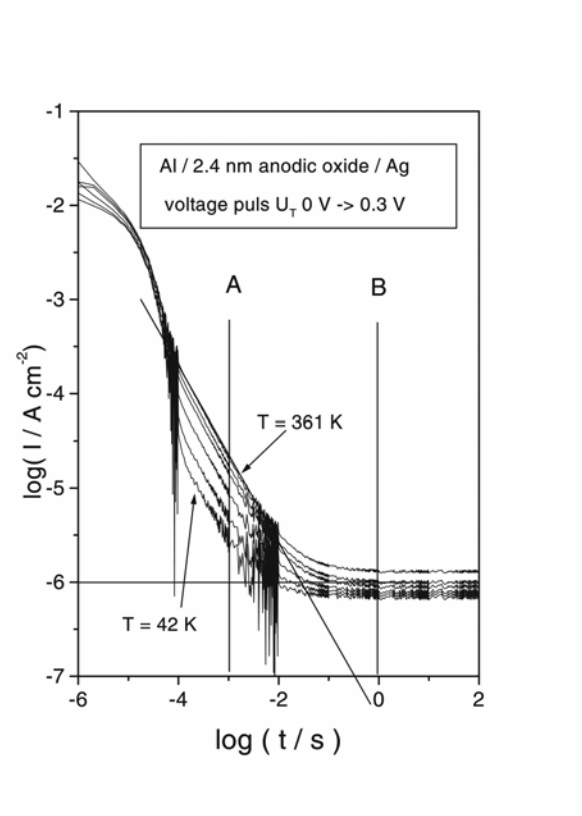

Figure 3: *Current transients after a voltage step from 0V to 0.3V of an aluminium / aluminium oxide / silver system at temperatures of 361K, 289K, 200K, 148K, 77K and 42K.*

In an approach to separate the various charge transport processes current transients of potentiostatic pulse steps have been recorded in the temperature range from 42 K to 420 K, **fig. 3** [12]. For the first 10 µs the capacitive charging of the oxide can be observed. Between 10 µs and 10 ms the current decreases with a slope of nearly -1 in the double logarithmic plot. Finally the current reaches its steady state value of direct tunnelling. Only the first process is almost independent on the temperature. In order to determine the activation energies of the processes the current densities at 1 ms and 10 s are plotted in **fig. 4** as a function of the temperature.

This extended model explains the relaxation current observed in the intermediate time range as a Poole Frenkel emission of electrons from traps within the oxide into the conduction band. Beside the direct elastic tunnelling through the entire film these traps can serve as resonance centre of tunnelling. Due to the exponential dependence of the tunnel current from the tunnel length this leads to a significant increase of the tunnel probability.

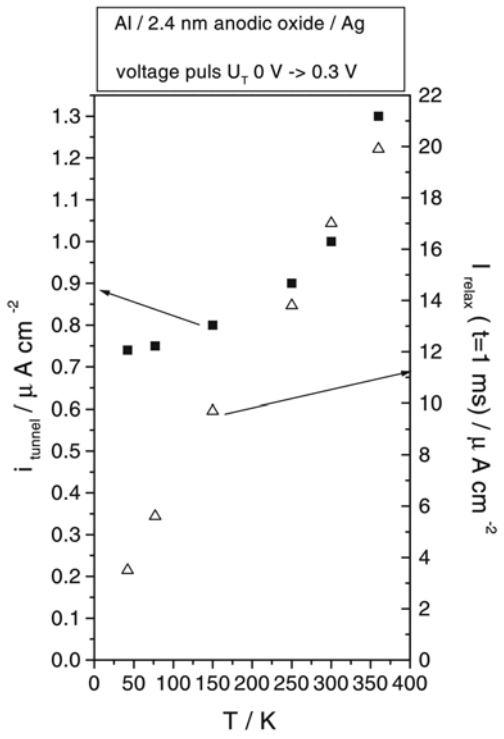

Figure 4: *Characteristic currents as a function of the temperature (taken from fig. 3).*

After the depletion of oxide traps the voltage is no longer buffered by electronic processes. At sufficiently high temperatures and field strength the activation of a thermally activated field assisted ionic hopping mechanism becomes possible. This ionic movement will introduce a dipole layer into the oxide which changes the shape of the tunnel barrier significantly. This change on the other hand gives rise to a sudden increase in the tunnel current which will heat the sample and through this feedback loop the current will exceed a critical value resulting in the breakdown of the film [13].

Studies on **the formation and the properties of porous Indiumphosphid** were continued. This work was initiated by **Prof. Masahiro Seo** at the Hokkaido University at Sapporo, Japan [14] and is now continued in a collaboration of the Hokkaido University and the Max-Planck-Institut für Eisenforschung in Düsseldorf. The goal is to prepare porous InP with a high efficiency of light emission through anodising in highly aggressive electrolytes [15]. Another approach is the preparation of watersplitting photoelectrodes by the deposition of a indium / platinum metal sandwich which allows an easy charge separation between semiconductor and metal on one hand and an efficient hydrogen evolution on the metal electrolyte interface on the other hand [16].

The research project **passive/active transitions in cyclic corrosion tests** was started in 2000 (ECSC, **Stephan Bonk**, **Mariusz Wicinski**, Partners: Thyssen Krupp Stahl, Irsid France, Voest Alpine Linz Austria). The goal is to understand the mechanism of activation and delamination of coated steel products under cyclic corrosion conditions on a more fundamental level and link the results from industrial corrosion tests to the chemistry and physics behind it. Up to now a new scanning Kelvin probe in an climatic chamber has been moved from Erlangen to Düsseldorf. The Software was completely rewritten and allows now an independent control of the SKP, the temperature and the humidity.

Another project deals with the behaviour of new types of **weathering steel under cyclic corrosion conditions** (Kawasaki Steel, **Shiro Tsuri**). For this purpose a dip and dry machine was constructed which allows an efficient simulation of corrosion conditions that form thick inhibiting rust layers. During this formation the corrosion potential is monitored as a function of time and cycle number. In parallel the corrosion potential and the corrosion rate are investigated during a wet dry transition using a special Kelvin probe combined with a oxygen consumption measurement. It was found that the current density shows reaches its highest value in the second cycle when a small amount of rust is already there but still thin enough to allow a fast diffusion of the oxygen through the film.

High Temperature Reactions

M. Spiegel

A research project was started together with the VGB (Vereinigung der Grosskraftwerksbetreiber) on the **influence of different ($PbCl_2$, $ZnCl_2$, KCl, NaCl, $FeCl_2$) salt mixtures** on the corrosion behaviour of 15 Mo 3 steel and HVOF-applied coatings of Alloy 625 in different (N_2-(5,10) vol. % O_2-(1000, 2000) vppm HCl-(3,10) vol. % H_2O) atmospheres at 400 °C (Spiegel, Strauch). All salt mixtures are molten at the reaction temperature. The corrosive attack on the Alloy 625 coating is much less than on the 15 Mo 3 steel. By variation of the salt mixtures, it was found that the low melting mixtures $39ZnCl_2$-50KCl-$11PbCl_2$ and 52KCl-$48ZnCl_2$ with 275 and 250 °C melting point cause more corrosion damage than the mixtures $35ZnCl_2$-48NaCl-$17PbCl_2$ (350 °C)- und 47KCl-$53FeCl_2$ (355 °C) with the higher melting points. Additionally, the effects of the salt mixtures are superimposed by the variation of the gas atmosphere. In general, the corrosion damage increases with increasing amount of oxidizing gas i.e. H_2O, O_2 and HCl. The composition of the corrosion products, formed on both alloys are a mixture of chlorides and oxides of the base metal components. The nature of the products slightly varies as a function of salt composition and gas atmosphere. It turns out that the viscosity of the salt melts plays a major role in its corrosive effect, rather than the influence on the na-

ture of the corrosion products. Experiments will be conducted by varying the temperature gradient upon the salt melt and the metallic sample in order to quantify this effect.

Thermogravimetric and electrochemical **investigations for the determination of corrosion mechanisms in presence of molten and solid chlorides** ($KCl,NaCl,ZnCl_2$) have been started **(Miguel Sanchez)**. For further performances of electrochemical experiments in a NaCl-KCl-melt at 630°C different $Ag\text{-}AgCl_2$ reference electrodes including membranes of Mullit, Duran and Supremax-glas have been tested. It was found that the electrodes consisting of Supremax-glas show a better time dependent constancy of the potentials. Experiments with different amounts of $AgCl_2$ (1, 2, 5 mol.%) let to an optimum amount of 5 mol.% $AgCl_2$ in the NaCl-KCl melt. First experiments were conducted with pure iron. During these experiments a gas mixture of N_2-5 vol.% O_2 bubbled through the chloride melt. The free corrosion potential of iron reaches a constant value and after the experiment the metal surface is covered with iron oxide. Obviously there is enough soluble oxygen or H_2O in the melt. Further experiments with chromium and nickel are planned as well as investigations of the influence of the O_2, H_2O and HCl partial pressures.

In order to **develop corrosion resistant materials for molten carbonate fuel cells (MCFC)**, experiments were conducted on the corrosion of Fe-17Cr-model alloys with different concentrations of Mn, Co, Mo and Ni. The experiments were carried out beneath a Li_2CO_3-K_2CO_3-mixture at 650 °C in an N_2-O_2-CO_2 atmosphere **(Michael Spiegel, Elke Strauch)**. All model alloys show a satisfactory corrosion behaviour after 5000 h of exposure, high amounts (14 wt. %) of nickel and silicon (0.5 wt. %) favour the corrosion resistance. Different pretreatments (hot- and cold rolling, vacuum annealing) have no major influence on the corrosion scale thickness.

The corrosion products are $FeCr_2O_4$ spinels, containing dissolved manganese and cobalt, however, significant outward diffusion of manganese and cobalt was observed after 5000 h of exposure. In addition, enrichment of chromium at the metal/oxide interface occurs. SNMS investigations should clarify whether there is a separation of lithium, which is important for a good conductivity of the corrosion products, and if the isolating $LiCrO_2$ is formed at the metal/oxide interface. The set-up for the determination of in-situ conductivities was built up and measurements were carried out on the components (Ni, NiO(Li)), as well as on the steel AC 66 **(Ivana Parezanovic).** The Ohmic resistivity of AC 66 and the formed corrosion products increases with time and was determined to be 100 $m\Omega cm^2$ in the beginning and 700 $m\Omega cm^2$ after 150 h. According to the high chromium content of the alloy this value is reasonable.

Adhesion and Thin Films

N.N.

The activities within the "**Adhesion and Thin Films"** group (**N.N.** (will be headed in 2001 by **Guido Grundmeier**), provisional head in 2000: **Michael Rohwerder**) were focussed on plasma-polymerisation.

Thin film technology is of increasing interest for the corrosion protection of reactive metals, such as steel and galvanised steel. Plasma polymerisation is a process which allows the preparation of polymeric films onto almost any surface. Microwave plasma polymerisation enables the deposition of a large range of high-quality films at high rates; it also produces very little waste. By varying the process parameters of the plasma polymer deposition, it is possible to control the coating properties.

The oxygen content of the gas mixture during plasma polymer deposition plays an important role in the resulting chemical structure of the coating (industry financed: **Petra Thiemann).** Surface analysis shows that with increasing oxygen concentration in the plasma, the oxygen content in the film increases and the carbon content decreases. The Si-O-Si peak is of particular interest as shifts from 1070 to 1120 with increasing oxygen content of the films. The peak becomes split. This suggests the formation of a few Si-O-Si bridges at low oxygen partial pressure and silicone-silica networks at higher partial pressures. The Si-H peak was no longer measurable when oxygen was introduced into the plasma. The low intensity of the C=O stretch absorption and absence of an O-H stretch band indicates that little oxygen is bound to carbon.

XPS Analysis shows that the silicon environment becomes more inorganic when the oxygen is added to the plasma. The oxidation states moves from +1 and +2, for the polymer without added oxygen, to mostly +3 and +4, for the polymer with oxygen.

The mechanisms and chemical structure are described in greater detail in Shirtcliffe et al. [17].

The surface morphology of the films was strongly affected by both the pressure in the plasma and the oxygen partial pressure. **Fig. 5** shows AFM pictures of the surfaces of two films on silicon wafers. The films were produced at the same total pressure but under different oxygen partial pressures. Both films show the presence of spherical grains, the scale of these being smaller at high oxygen concentration. A reduction in the total reaction pressure in the absence of oxygen produced a similar reduction in the roughness of the films.

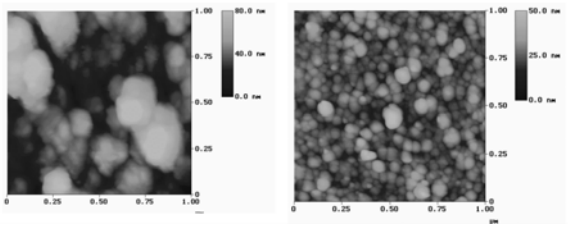

Figure 5: *1×1 µm AFM scans of approx. 100 nm thick HMDS films on Si-wafers. Left: HMDS plasma-polymer (conditions 1) Right: HMDS/oxygen plasma-polymer (conditions 2)*

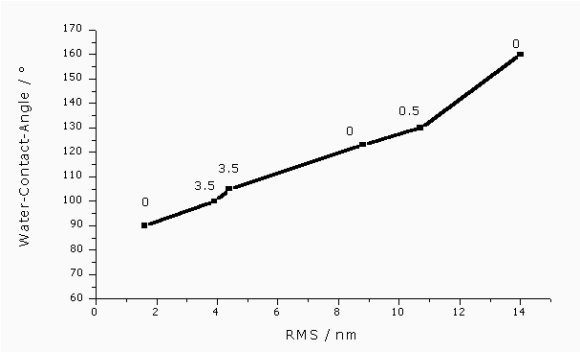

Figure 6: *Graph of stationary water contact angle on HMDS plasma-polymer-films plotted against roughness; the values above each point denote the oxygen to HMDS partial pressure ratio in the depositing plasma ([O_2]/[HMDS].*

The films were all hydrophobic, having a water contact angle of greater than 90º. The water contact angle correlated well with the roughness, as shown in **fig. 6**.

Samples of plasma-polymer coated galvanised steel were tested for corrosion and adhesion resistance after they were painted with organic coatings. Thin films (50-100nm) showed performance approaching that of standard phosphate chromate pre-treatment. The samples were also tested for their protection against delamination from a scratch to zinc and one to steel. The films provided protection of a level similar to that provided by standard treatments.

Adhesion tests showed that smooth plasma polymers have a good adhesion but rougher films performed worse. The oxygen content of the films appeared not to have an effect on the results of this test. Small spot XPS measurements of the surface exposed by the peeled off paint showed high concentrations of zinc, oxygen and carbon and only a little silicon, indicating that the plasma polymer remains on the paint film. This suggests a weakness in the adhesion of the rough films to the metal. It also shows that adhesion of a polyurethane paint to a surface with barely any polar groups and a water contact angle of 160° is surprisingly good.

Another project focuses on the **effect of plasma treatment on metals and metal oxides** (MPIE: **Neil Shirtcliffe**).

As well as depositing films and removing material, plasma treatment can be used to reactively alter the surface of different materials. On metals this is normally restricted to oxide formation and reduction but suitable gas mixtures enable formation of other metal compounds. These could be of interest, as they are thin and regular. It is possible that some of these materials are formed during plasma polymerisation at the interface between metal and organic material; consequently suitable systems are subject of current research.

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Publications and Abstracts

Enders, M.; Spiegel, M.; Albrecht**,J.; Putnis*, A.*
Mineralogical problems in advanced power systems: The contribution of slag and gaseous chemical species to the fly ash
Eur. J. Mineral 12, 639-650 (2000)

The study focuses on a mineralogical and chemical characterization of the particulate matter collected from flue gases of a pilot plant for pressurized pulverized coal combustion (PPCC) under slagging conditions. The material collected on temperature resistant filter materials was analysed by X-ray diffraction, WDS-electron microprobe, electron microscopy and thermoanalysis.

The particles in the flue gas are in the micrometer and submicrometer range. The most important crystalline species are $CaSO_4$, $K_2Ca_2(SO_4)_3$ and $K_3Na(SO_4)_2$. Minor components of the flue gas stream are spinels ($FeAl_2O_4$, Fe_3O_4, $FeCr_2O_4$, and $(Fe,Cr)_2O_3$). The only silicate phase are siliceous glassy spheres which originate from solidified slag droplets. Half of the collected fly ash was generated during complex reactions from the gaseous phase to crystalline and nanocrystalline solids.

*Univ. Münster, **Lurgi, Frankfurt

Fili, T.; Rohwerder, M.; Stratmann, M*
Influence of Surface Plasma Pretreatment on the Interface Properties of a-SiC:H Covered Steel Substrates
Adv. Engineering Mater. 2, No. 6, 378-380 (2000)

The effect of an oxidising and a reducing plasma pre-treatment of steel surfaces on the stability of plasma-deposited a-SiC:H layers (of 200nm thickness) was investigated by means of Kelvin probe measureents, XPS and corrosion tests. The interfacial structure was analysed by XPS depth profiling. The Volta potential of the samples was influenced by the kind of pre-treatment. The oxygen plasma pre-treated sample showed a higher potential in comparison to the hydrogen plasma treated sample. The reason for this behaviour is the different state of oxidation of the iron in the interface layer. The ratio of Fe^{2+} to Fe^{3+} in the oxide determines the Volta potential. This potential was stable for weeks, which is a good proof for the impermeability of the a-SiC:H films. The interface of the systems was approximately 40 nm thick and varied with the pre-treatment. While the coating protected the samples very effectively at extreme humidity around 100% r.h., at 85% r.h. the delamination of the a-SiC:H-films was surprisingly fast and followed filiform corrosion characteristics. The oxygen-pretreated samples showed a slightly higher stability against filiform corrosion than the hydrogen-pretreated samples.

*Univ. Erlangen-Nürnberg

Fürbeth, W.; Stratmann, M.*
Scanning Kelvin Probe investigations on the delamination of polymeric coatings from metallic surfaces
Progress in Organic Coatings 39, 23-29 (2000)

The corrosion behaviour of zinc- and polymer-coated steel has been investigated from a very fundamental approach in order to derive the important parameters for suitable short-term corrosion tests, which are capable of simulating outdoor exposure behaviour. A very simple model system has been investigated mainly by in situ Scanning Kelvin Probe measurements and surface analysis after removal of the polymer. Both types of defect have been considered. The delamination from a defect with an intact zinc layer is due to the formation of

a galvanic element. The oxygen reduction in the delaminated area leads to an alkalinization of the interface and therefore anodic reaction with the consequence of oxide growth. Cathodic delamination is strongly influenced by the CO_2-concentration in the atmosphere. The delamination starting from a defect down to steel has shown to be a complex combination of anodic undermining and cathodic delamination, the latter one becoming more important with increasing corrosion time and therefore influencing the cathodic protection of the defect.

*DECHEMA, Frankfurt

Grundmeier, G.; Jüttner**, K.-M.; Stratmann, M.*
Novel electrochemical techniques in corrosion research
In: M. Schütze: Corrosion and environmental degradation, Wiley-VCH, Weinheim, Germany 2000, 285-382

This chapter is part of a series on materials science. Novel electrochemical techniques such as impedance spectroscopy, scanning reference electrotechniques and the Scanning Kelvin Probe nowadays used in corrosion research are discussed. For all techniques the physical basis is discussed in detail. Applications include pitting corrosion, passivity, atmospheric corrosion, corrosion of electronic materials and in particular the corrosion of polymer coated materials.

*TKS Dortmund, **DECHEMA, Frankfurt

Grundmeier, G.; Schmidt, W.; Stratmann, M.*
Corrosion protection by organic coatings: electrochemical mechanism and novel methods of investigation
Electrochimia Acta 45, No. 15/16, 2512-2533 (2000)

The application of electrochemical techniques for corrosion studies of organic coatings on reactive metals is considered from the analytical and mechanistic standpoint. Techniques such as electrochemical impedance spectroscopy (EIS),

scanning vibrating electrode and scanning Kelvinprobe (SKP) are powerful tools to better understand the fundamental processes of corrosion at defects and underneath coatings. In the first part of this paper these three techniques are discussed in more detail as they present a very complementary approach to understand the ensemble of coating degradation, processes in defects and corrosion underneath coatings, respectively. The second part of this paper focuses on the two important mechanisms of cathodic delamination and filiform corrosion (FFC). Since both forms of corrosion are characterised by certain electrochemical reactions underneath coatings and are localised in nature, the discussion focuses on the application of the SKP to give new insights in these corrosion phenomena.

Hassel, A.W.; Aihara*, M.; Seo*, M.
Formation and corrosion of InP/In contacts in hydrochloric acid
Electrochim. Acta 45, 4682 (2000)

Flatband potentials, charge carrier concentrations and their frequency dispersions of p-type and n-type InP in 1.0 M HCl were determined. The cathodic decomposition of InP in this acidic solution is compared with

the deposition process of indium from 1.0 M HCl containing 0.1 M $InCl_3$. The shares of the involved reactions: hydrogen evolution, InP decomposition and indium deposition are investigated. The reaction rates

are generally smaller on p-type InP and the reaction speed is much slower but the principal reactions are the same. The kinetics of the indium deposition and dissolution are studied in detail. These reactions

are discussed in terms of the preparation of watersplitting photoelectrodes with modified surfaces.

*Hokkaido University

Hassel, A.W.; Seo*, M.
Localised Photoelectrochemical Measurement with the Scanning Droplet Cell
In: "Passivity and Localized Corrosion": International Symposium in Honor of Professor Norio Sato", (Eds.) R. G. Kelly, B. MacDougall, M. Seo, and H.Takahashi Proceedings of the Electrochemical Society PV 99-27 (1999)

337

All common electrochemical techniques can be localised with the scanning droplet cell (SDC). In this work, a modified cell type (PSDC) for photoelectrochemical measurements is presented. Light from an argon ion

laser or from a high power light emitting diode is coupled into the glass capillary and illuminates the small area of the working electrode, which is covered by the electrolyte droplet. The resolution of the PSDC is 150 µm with further potential for down-sizing. Two different constructions were realised. Details of the construction process are presented. The problem of a proper illumination is discussed in detail. The selectivity or degree of localisation of the PSDC as compared with other methods is discussed briefly.

Hokkaido University

Hassel, A.W.; Seo*, M.
Local Analysis of Anodic Oxide Films on Titanium by Scanning Droplet Cell and Scanning Electrochemical Microscope
In: "Localized In Situ Methods for Investigating Electrochemical Interfaces" eds. A. C. Hillier, M. Seo, and S. R. Taylor. Proceedings of the Electrochemical Society PV 99-28 (1999) 166

An improved type of the scanning droplet cell (SDC) was constructed with a tip size of 100 µm. It was used to form a 2x3 pattern of 100 µm oxide spots on a single grain of a polycrystalline titanium specimen. The

crystallographic orientation of the grain was determined by a scanning micro Laue method to be near-XXX0 with an angle of 12° between mean axis and surface normal. The distance between these spots was 100 µm or less. All oxide spots had different oxide thicknesses resulting from the different polarisation potentials (3 to 8 V(Ag/AgCl)). The inhomogeneity of the surface reactivity was then evaluated by using a SECM. Size,

shape and position of the pattern could be clearly monitored with SECM current images. Differences in the reactivity due to the differences in oxide thickness could be determined as well.

*Hokkaido University

Kowalik*, T.; Adler*, H.-J.; Plagge**, A.; Stratmann, M.
Ultrathin layers of physphorylated cellulose derivatives on aluminium surfaces
Macromol. Chem. Phys. 201, 2064-2069 (2000)

In recent works the self-assembly process has been investigated to replace the present chromating procedure on reactive metals like aluminium and to improve the lacquer adhesion and corrosion inhibition. These self-assembling layers were formed of small bifunctional organic molecules with phosphate or phosphonic acid groups attached to the metal substrate. The idea of this work was to apply these results and techniques to cellulose derivatives on implant metals. The formation of ultra-thin layers of phosphorylated cellulose

derivatives has been reported previously. These ultrathin layers were built on metal substrates like aluminium, titanium or steel fur adhesion promotion

and corrosion inhibition. Hydroxy-propyl-2-phosphatepropyl cellulose was synthesised for adhesion on hydrophilic metallic surfaces. Hydroxypropyl-2-cinnamoylpropylester cellulose was prepared in order to crosslink the adsorbed layers. The layers were formed on metal surfaces via dip coating from dilute solutions and characterised by means of contact angle measurements, SEM investigations and FT-TR spectroscopy. Initial corrosion tests were performed.

*IFW Dresden, **Univ. Erlangen-Nürnberg

Kowalik*, T.; Adler**, H.J. ; Plagge, A.; Stratmann, M.***
Neue Wege der Haftungsvermittlung mit wasserbasierten Celluloselackfilmen für Keramik-, Stahl- und Titanoberflächen
Farbe und Lack 11, 48-55 (2000)

Cellulose is interesting as a natural, non-toxic material for biological applications. Its poor solubility in technical solvents can be improved by incorporating alkyl-side chains. Polymers modified with phosphate groups can be used as excellent adhesion promoters on stainless steel, titanium and on the bone substance hydroxyl-apatite. Medical implants are pre-treated with UV-radiation, then coated with the modified cellulose which is finally activated by hot water application just before implantation. The adhesion properties of these implants are comparable to the ones observed for conventional PMMA systems.

*TU Dresden, **Univ. Erlangen-Nürnberg

Müller*, R.; Heckmann*, K.; Habermann*, M.; Paul*, T.; Stratmann, M.
New adhesion promoters for copper leadframes and epoxy resin
Journal of Adhesion 72, 65-83 (2000)

New primer molecules have been synthesized to increase the adhesion strength between a copper leadframe and an epoxy molding compound in microelectronical devices. The coupling agents were preliminarily chemisorbed at the surface of copper plates via special binding groups like thiol, disulfide, ethylene diamine and phthalocyanine. Binding to the epoxy resin was performed via an hydroxyl group, linear hydrocarbon spacers with various chain lengths connected the copper- and epoxy-binding groups. The self-assembled layers of the organic coupling agents at the metal surface were characterized by X-ray photoelectron spectroscopy.

Thermogravimetric analysis was used to study the coating with respect to its corrosion oxidation inhibition. Shear tests clearly indicated that the coupling agents increase adhesion strength and are stable even in extreme humidity and thermal conditions in analogy to IPC-Level-1 pretreatment. Thus, delamination of the microelectronical packages was prevented.

*Univ. Erlangen-Nürnberg

Plagge*, A.; Stratmann, M.; Kowalik**, T.; Adler**, H.J.
Selected Aspects of Surface Engineering with Cellulose Polymers
Advanced Engineering Materials, Vol. 2, No. 6, 376-378 (2000)

In this work cellulose polymers for a potential application in the field of medical technology are described. A certain phenomenon, the so called aseptic adhesion loss, especially encountered with prosthetic hip joints, is well known. To solve this problem common approaches do not use polymers, although they are cheap to produce, handle and apply. One part of our strategy to form adhesive layers between the implant surface and the natural bone was to use mixtures of cellulose polymers with different functions: To obtain layers which are stable against mechanical stress one cellulose polymer contained UV-crosslinkable groups. This polymer forms a crosslinked matrix in which the other polymer with phosphate groups is embedded. Such phosphate groups can interact very strongly with different technical surfaces containing oxides, such as steel or titanium alloy surfaces. This allows a completely new way of handling cellulose layers as adhesion system. First, the layers are transferred to the implant surface from an alcohol or water solution. In a second step, the activation, the coated implants are dipped in boiling water and pressed on the bone. No heat treatment is required for drying the joint. The adhesive force is built up after 24h. Adhesion force measurements were made for several polymer systems. The toxicity of such polymers was characterized by a test following ISO 10993/5.

*Univ. Erlangen-Nürnberg, ** TU Dresden

Spiegel, M.
Korrosionsmechanismen in Müllverbrennungsanlagen
In: Tagungsband zu VGB-Konferenz Essen. Verein der Großkraftwerk-Betreiber VGB, Essen 2000, CD-ROM

An overview is given on corrosion mechanisms on boiler tubes and superheaters in waste fired boilers by the presence of corrosive gas species like HCl and SO_2 in combination with ash deposits. Emphasis is given to the role of ash deposits, where molten phases of the chlorides KCl and $ZnCl_2$ and also sulfates are formed and the tube materials are severely attacked by molten salt induced corrosion. Especially chlorides cause detrimental corrosion at relatively low temperatures of 250-400 °C. Sulfate melts are

less harmful and corrosion occurs at higher tempertures of 550-600 °C. The HCl-induced 'active oxidation' plays a minor role at temperatures higher than 400 °C.

Spiegel, M.

Electrochemical investigations on the corrosion of metals in a (Ca, Na, K)-Sulfate Melt

In: Proceedings EUROCORR '00. European Federation of Corrosion EFC, Institute of Corrosion, London, 2000, CD-ROM

Potentiostatic experiments were carried out on the corrosion of Alloy 2.25Cr-1Mo steel, 625 and AC 66 (32Ni-27Cr) in a 50 wt.% $CaSO_4$-29 wt.% K_2SO_4-21 wt.% Na_2SO_4 mixture with and without addition of 0.01 - 1 g $ZnSO_4$ at 850 °C in an N_2-5 vol.% O_2 atmosphere. As reference electrode membranes, zirconia and also mullite were tested, where mullite behaves much better than zirconia. In this electrode, a Ag-wire dipped into the Ca,K,Na-sulfate melt, containing 10 mol.% of $AgSO_4$. The stability range of the sulfate melt was found to be in the range from –2 to +0.5 V referred to the Ag/Ag^+ electrode. Anodic polarization curves have shown that the 2.25Cr-1Mo steel shows higher anodic currents with respect to Alloy 625 and AC 66. The sample dissolves in the sulfate and Fe_2O_3 particles are formed in the entire melt. In addition, FeS was formed in the inner parts of the remaining sample. The corrosion products on AC 66 and Alloy 625 were mainly sulfides of chromium and nickel, along with layers of (Fe,Cr,Ni)-oxides in contact with the melt. In order to study the effect of Zn^{2+} on the corrosion of chromium containing alloys, potentiodynamic experiments were conducted with AC 66 in the 50 wt.% $CaSO_4$-29 wt.% K_2SO_4-21 wt.% Na_2SO_4 mixture with addition of 1 g $ZnSO_4$. Compared to the experiment in the melt without $ZnSO_4$ the anodic current decreases at the same potentials. As corrosion products, a thin $ZnCr_2O_4$ layer was found on the sample. The addition of $ZnSO_4$ obviously decreases the corrosion rate of the chromium containing alloy AC 66 by the formation of $ZnCr_2O_4$. In order to study the formation of $ZnCr_2O_4$ in more detail, cyclic voltammograms of AC 66 in the $ZnSO_4$ containing melt are carried out.

Spiegel, M.

Influence of gas phase composition on the Hot Corrosion of steels and nickel-based alloys beneath a (Ca,K,Na)-sulfate mixture containing $PbSO_4$ und $ZnSO_4$

Mat. Corr. 51, 303-312 (2000)

The corrosion of steels and of nickel-based alloys was studied in exposure experiments at 600 °C beneath a molten $CaSO_4$-K_2SO_4-Na_2SO_4-$PbSO_4$-$ZnSO_4$ sulphate mixture in N_2-5 vol.% O_2 with and without additions of 1000 vppm HCl, 1000 vppm SO_2 and 1000 vppm HCl in combination with 250 vppm SO_2. In the N_2-5 vol.% O_2 atmosphere, the corrosion products are iron- and nickel-rich but chromium-free precipitates of oxides in the solidified melt. Additionally, pits filled with layered corrosion products are formed, growing into the metal substrate. These layers consists of less soluble chromium-rich oxides, containing varying amounts of zinc, ($ZnCr_2O_4$) alternating with potassium-rich sulfates, most probably $K_2S_2O_7$. The addition of 1000 vppm SO_2 leads to a seperation of the melt in a $K_2S_2O_7$ part close to the metal surface and a Ca-rich part on top in contact with the gas atmosphere. Compared to the N_2-5 vol. % O_2 atmosphere accelerated corrosion was observed. In the $K_2S_2O_7$ part of the melt dissolved iron and nickel are identified, whereas in the Ca-rich part iron- and nickel-oxide precipitates are formed. Underneath the solidified salt, thin layers of sulfides are detected. In the N_2-5vol.% O_2-1000 vppm HCl containing gas, the corrosive attack is also accelerated compared to the N_2-5vol.% O_2-atmosphere. Much more oxide precipitates are found in the melt on every sample and the inward growth of the zinc-free chromium-rich oxides is significantly enhanced. Underneath the inward growing oxide small amounts of metal-chlorides are detected. Compared to the SO_2 containing gas, the corrosive attack is enhanced for the iron-based materials, but retarded for the nickel-based alloys. In the 1000 vppm HCl-250 vppm SO_2 containing gas, the corrosive attack is similar to the atmosphere containing only 1000 vppm HCl. In addition, sulfides are formed next to chlorides at the metal/scale interface.

Spiegel, M.; Warnecke, R.*

Korrosion thermisch gespritzter Schichten unter simulierten Müllverbrennungs-Bedingungen

In: Tagungsband zu VGB-Konferenz Essen. Verein der Großkraftwerk-Betreiber VGB, Essen 2000, CD-ROM

Coupons of 15 Mo 3 were coated with different materials, predominantly Alloy 625 based compositions, embedded in a KCl-$ZnCl_2$-$PbCl_2$ salt mixture and reacted at 350 °C for 360h in N_2-5 vol.% O_2-1000 vppm HCl gas with and without additions of SO_2. In general, the corrosive attack of the Alloy 625 coatings is less than at the 15 Mo 3 reference material. It turns out that Alloy 625 coatings, applied by APS behave less protective than HVOF-sprayed coatings. The reason for this is the lower chromium content and the higher amount of oxide phases, which are preferentially attacked. Nickel-based coatings with a low amount of oxide phases, more than 20 wt. % chromium and silicon additions behave most protective. The addition of SO_2 decreases the corrosive attack on every material.

*NOELL-KRC, Augsburg

Zahs, A.; Spiegel, M.; Grabke, H.J.
Chloridation and oxidation of iron, chromium, nickel and their alloys in chloridizing and oxidizing atmospheres at 400-700 °C
Corr. Sci 43, 1093-1172 (2000)

The corrosion behaviour of Fe, Cr, Ni, the ferritic alloys Fe-15Cr and Fe-35Cr and the austenitic alloys Alloy 800, Alloy 825 and Alloy 600 was investigated in N_2 - 5 vol% O_2 and He – 5 vol% O_2 with additions of 500-1500 vppm HCl at temperatures between 400 and 700 °C using discontinuous exposures and thermogravimetric experiments. The corrosion products were analyzed by scanning electron microscopy with EDX-analysis, X-ray analysis and Auger electron spectroscopy. The main corrosion process, especially at temperatures above 500 °C, is 'active oxidation', i.e. the formation of volatile metal chlorides at the metal/oxide interface which evaporate, diffuse outwards and are converted into oxides in regions of higher oxygen partial pressure. The characteristic differences concerning the corrosion behavior of the different metals and alloys at different temperatures are largely determined by thermodynamics, that means the free energy of chloride formation, the vapor pressure of the chlorides and the oxygen pressure necessary for conversion of the evaporated chloride to the oxide.

Oral and Poster Presentations

Hornung, E.; Rohwerder, M.; ***Stratmann****, M.:* Elektrochemische Reaktionen an verborgenen Metall/Polymer-Grenzflächen, GDCh-Jahrestagung, Fachgruppe "Angewandte Elektrochemie". Ulm, 27.09.-29.09.2000.

Hornung*, E.; Rohwerder, M.; Stratmann, M.:* Metal/Organic Coating Interfaces – Influence of the Potential Distribution on the Stability of the Interface, European Research Conference "Surface Engineering for Protection of Metals and Alloys". Acquafredda di Maratea, Italy, 30.09.-05.10.2000.

Rohwerder*, M.:* The Scanning Kelvinprobe - a New Technique to Study the Stability of Metal/polymer Bonds, Second International Symposium on Adhesion Aspects of Polymeric Coatings. Newark, New Jersey, USA, 25.05.-26.05.2000.

Sämann*, N.; Spiegel, M.; Grabke, H.J.:* Influence of surface preparation on the corrosion of steels in simulated waste incineration environments, Posterschau, European Research Conference "Surface Engineering for Protection of Metals and Alloys". Acquafredda di Maratea, Italy, 30.09.-05.10.2000.

Seo*, M.; Aihara, M.; Hassel, A.W.:* Cathodic Decomposition and Changes in Surface Morphology of InP in HCl, The Electrochemical Society, 198th Meeting. Phoenix, Arizona, 22.10.-27.10.2000.

Stratmann*, M.:* Elektrochemische Reaktionen an Metall/Polymer-Grenzflächen, Festvortrag, Kolloquium 100 Jahre Institut für Physikalische Chemie und Elektrochemie. Dresden, 14.04.2000.

Stratmann*, M.:* Neue Erkenntnisse und Konzepte zum Korrosionsschutz metallischer Werkstoffe durch Polymere, GDCh-Kolloquium. Marl, 14.06.2000.

Stratmann*, M.:* Neue Methoden zur Charakterisierung von Grenzflächen in Verbundsystemen, Workshop "Haftung". Frankfurt, 09.05.-10.05.2000.

Stratmann*, M.:* Untersuchung der Stabilität von Metall/Polymer-Grenzflächen mit der Raster-Kelvin-Sonde, 162. Vollsitzung des Werkstoffausschusses VDEh. Düsseldorf, 13.04.2000.

Stratmann*, M.; Rohwerder, M.; Hornung, E.:* On the origin of the electrode potential at the intact metal/polymer interface, ISE 2000, Symposium 'Electrochemistry in Surface Finishing and Protection against Corrosion'. Warsaw, Poland, 03.09.-08.09.2000.

GENERAL INFORMATION ON THE INSTITUTE

Lectures and Teaching

K.-H. Tacke, TU Berlin: Werkstoffprozeßtechnik: Gießprozesse und Produkteigenschaften : SS 2000

G. Frommeyer, Technische Universität Clausthal: Physikalische Metallkunde und Technologie der hexagonalen Metalle Ti, Zr, Hf, SS 2000

D. Raabe, RWTH Aachen: Ethymologie und Geschichte der Metalle, WS 2000/2001

D. Raabe, RWTH Aachen: Prozeß-und Werkstoffmodellierung, WS 2000/2001

D. Raabe, Carnegie Mellon University Pittsburgh, USA: Computer Simulation in Materials Science, WS 2000/2001

P. Neumann, Universität Düsseldorf: Versetzungen in Metallen, WS 2000/2001 P. Neumann, Universität Düsseldorf: Werkstoffwissenschaftliche Mechanik, WS 2000/2001

G. Sauthoff, RWTH Aachen: Spezielle Probleme der Metallphysik II/ Theoretische Metallkunde II, SS 2000

A. W. Hassel, Heinrich-Heine-Universität Düsseldorf: Thermodynamische Rechenübungen für Chemiker, SS 2000

M. Spiegel, RWTH Aachen: Korrosion keramischer Werkstoffe, WS 1999/2000, SS 2000

Institute Colloquia

M. Wenderoth, Göttingen, Nichtlineare dynamische Instabilität beim Sprödbruch von GaAs, 25. Januar 2000

E. Tolksdorf, Essen, Potentiale und Grenzen der Anwendung der neu entwickelten 9-12% Cr-Stähle für die Kraftwerkstechnik, 15. Februar 2000

H. Zimmermann, Duisburg, Oberflächenrisse beim Dünnbandgießen von Stahl, 04. März 2000

J. Hald, Lyngby, Dänemark, 9-12 %Cr power plant steels – Microstructure stability and alloy optimisation, 28. März 2000

B. Zeumer, Düsseldorf, Wege zu Innovationen in der Stahlindustrie, 11. April 2000

M. Hillert, Stockholm, Schweden, Solute drag, solute trapping and diffusional dissipation of Gibbs energy, 12. April 2000

M. Zehetbauer, Wien, Österreich, Kristallplastizität - Theorie und Experiment, 17. April 2000

S. Ahzi, Strasbourg, Frankreich, Texture Modeling, 02. Mai 2000

K. Helming, Clausthal, Texturen in der modernen Festkörperforschung, 16. Mai 2000

T. Miyazaki, Birmingham, UK, Computer simulation of microstructure formation in real alloy systems based on the Discrete Type Phase Field Method, 06. Juni 2000

E. Nembach, Münster, Experimentelle Untersuchungen der intermetallischen Phase Fe_3Al: Ordnungszustände und Versetzungsprozesse, 15. August 2000

V. Lantari, Maizieres-lés-Metz Cedex, Frankreich, Scaling phenomena during hot rolling: kinetic and mechanical aspects, 12. September 2000

S. Takaishi, Tokyo, Japan, Katana - Japanische Schwertkunst, 19. September 2000

L. Kestens, Gent, Belgien, Orientation selection during the nucleation and growth of recrystallized grains in cold rolled low carbon steels, 17. Oktober 2000

T. Al-Kassab, Göttingen, Die Tomographische Atomsonde (TAP): Nanaoanalytische Spektrometrie in der Materialphysik, 31. Oktober 2000

H. Vehoff, Saarbrücken, Gefüge und Riss – lokale Messmethoden, Modelle, Anwendungen –, 28. November 2000

Events Organized by the Institute

D. Raabe, Co-Organizer and Discussion Leader of the Session Metalle / Alloys / Composites during the EU Workshop on strategies for future areas of basic materials science, June 13-15 2000 in Ludwigsburg near Stuttgart, Germany.

The Meeting of the Fachausschuß Computersimulation of the DGM entitled "Modellverknüpfungen und Hybridmodelle in der Werkstoffsimulation" was organized by Dr. F. Roters and held at the Max-Planck-Institut für Eisenforschung on 20. September 2000. 12 papers were presented to more than 50 participants from 3 countries.

D. Ponge, Hamburg, Metallkundliche Konzepte bei Feinkornbaustählen, 11. Juli 2000

G. Grundmeier, Dortmund, Elektrochemische und oberflächenanalytische Untersuchungen an neuartigen Dünnschichten für die organische Bandbeschichtung von Stahl: SiO2-Flammen-pyrolyse, Plasmapolymerisation, UV-Härtung, 24. August 2000

H. Takahashi, Sapporo, Japan, Patterning of the surface of aluminium by laser irradiation and AFM probe processing, 08. September 2000.

M. Seo, Sapporo, Japan, Surface stress of noble metal electrode and stress of anodic oxide film on metal, 08. September 2000

N. Tsuji, Osaka, Japan, Ultra-grain refinement of steels and aluminium alloys by a novel intense straining process, ARB – Microstructure formation and mechanical property of ultra-fine grains –, 11. September 2000

M. Winning, Aachen, Einfluss mechanischer Spannungen auf die Korngrenzenbewegung, 24. Oktober 2000

K.J. Bowman, West Lafayette, USA, Texture and anisotropy in piezoelectric materials, 16. November 2000

T. Hirano, Ibaraki, Japan, Fabrication of Ni_3Al thin foil by cold-rolling, 06**.** Dezember 2000

A symposium was organized by M. Stratmann (Department of Interface Chemistry and Surface Technology) on 7 and 8 December 2000: With this symposium Profs. H.-J. Engell and H.J. Grabke were honoured. There were 150 participants from industry and other research organizations. The after dinner speech “H.J. Grabke” was held by R. A. Rapp, Ohio State University USA.

E. Mittemeijer, Stuttgart, Festkörperreaktionen in dünnen Schichten

R. Schlögl, Berlin, Heterogene Katalyse mit Eisenoxiden

R. Mast, Schwerte, Grenzflächensegregation von Verunreinigungselementen in Eisen und Stählen – Einflüsse auf Materialeigenschaften

F. Blekkenhorst, Ijmuiden, Korrosionsbeständigkeit, Ein Fall für zwei Phasen

J. Behm, Ulm, Struktur und Dynamik der Cu(100)-Korrosion

G. Eckstein, Erlangen, In-situ STM-Untersuchungen zur selektiven Korrosion von niedrig-indizierten Au_3Cu*(hkl)*- und Cu_3Au*(hkl)*-Legierungseinkristallen

H. Möhwald, Golm, Funktionalisierte Oberflächen und Kapseln

W. Rühe, Freiburg, Bürsten, Bojen, ultradünne Netzwerke – Neue Wege zu maßgeschneiderten Oberflächen von Materialien

G. Grundmeier, Dortmund, Neue Wege in der Oberflächenveredelung von Stahlband – Dünnste funktionale Schichten an Grenzflächen

M. Schütze, Frankfurt, Erhöhung der Oxidationsbeständigkeit von Titanaluminidlegierungen durch den Halogen-Effekt

P. Biedenkopf, Jülich, Werkstoffe und Reaktionen an Phasengrenzen in der Energietechnik

A. Schneider, Düsseldorf, Phasenumwandlungen bei der Aufkohlung von Eisen in hochaufkohlenden Gasatmosphären

Scientific Honours

Prof. Dr.-Ing G. Frommeyer and Dr.-Ing. O. Grässel received the "Steel Innovation Award" in the category: honourable statement for their outstanding work on new classes of TWIP/TRIP steels.

Doctoral Theses

Dr. rer. nat.	Brehm, Holger	Univ. Jena
Dr.-Ing.	Grässel, Oliver	TU Clausthal
Dr.rer.nat.	Herrmann, Jutta	RWTH Aachen
Dr.-Ing.	Pramono, Adika	RWTH Aachen
Dr.rer.nat.	Schroer, Carsten	Univ. Dortmund
Dr.rer.nat.	Steinert, Ingo	RWTH Aachen
Dr.-Ing.	Weidig, Ursula	RWTH Aachen
Dr.-Ing.	Wettlaufer, Marc	RWTH Aachen