

INSTITUTE IV:
CORROSION SCIENCE AND
SURFACE TECHNOLOGY



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4.4 Institute IV: Corrosion Science and Surface Technology

4.4.1 General

The Institute of *Corrosion Science and Surface Technology* within the Department of Materials Science and Engineering, which is one of the largest of its kind, is regarded as an interdisciplinary institute between science and technology. The Institute is as well interested in basic phenomena of surface science, electrochemistry and interfacial chemistry as in technical applications of this fundamental knowledge in modern surface technology. Therefore, the scientific staff is mixed between physicists, chemists and engineers of materials science.

The general scientific scope is the modification of interfaces and surfaces of materials in order to improve their technological properties. The modification usually consists of ultrathin and well defined layers like highly organized organic monolayers, plasmapolymers and inorganic CVD or PVD layers on surfaces of Fe-, Al- or Mg-based alloys. The layers are used to improve the corrosion resistance of the base material or the adhesion between the base material and thick coatings. In future research also the improvement of the tribological or tribochemical properties will play an important role. The main focus of the Institute of *Corrosion Science and Surface Technology* lies in the scientific understanding of how the ultrathin layers are formed of real surfaces and what link exists between the chemical and morphological structure of these layers and their technological properties like corrosion, adhesion or tribology. The technology of the industrial surface coating process is of minor interest.

The scientific interests are also reflected in teaching. Students, who chose this subject as their major course, are well trained in the basic subjects of physical chemistry of surfaces and interfaces, of electrochemistry including semiconductor electrochemistry and of interfacial chemistry. Technological subjects include an extensive course in aqueous corrosion, high temperature corrosion, stress corrosion cracking, adhesion and tribology. Additionally, specific subjects of industrial interest like corrosion in chemical plants are taught by colleagues from the industry.



4.4.2 Staff

Teaching Faculty:

Prof. Dr. Martin Stratmann (Head of Institute)

Prof. Dr. Elsbeth Wendler-Kalsch

Prof. FH Dr. Ralf Feser

PD Dr. Gernot Grötsch, lecturer from industry (Intra Serve Hoechst, Frankfurt)

PD Dr. Bernd Stellwag, lecturer from industry (Siemens AG, Erlangen)

Secretary:

Heide Kreisel

Administration, Teaching and Research Scientists:

Dr. Hermann Kaiser (Academic Director)

Dr. Werner Auer (Chief Engineer)

Dr. Andrea Dakkouri

Dr. Michael Rohwerder

Dipl.-Ing. Elke Hornung

Dipl.-Ing. Wolfgang Schmidt

Research Associates:

Dipl.-Ing. Margrit Dannenfeldt

Mgr. Andrea Dziakova

Dipl.-Chem. Gerald Eckstein

Dipl.-Ing. Thomas Fili*

Dipl.-Ing. Bodo Gerold

Dipl.-Ing. Thomas Hebner

Dipl.-Phys. Uta Hecht

Dipl.-Chem. Stefan Maupai

Dipl.-Min. Roger Meier

Dipl.-Chem. Andreas Plagge

Dipl.-Phys. Matthias Rebhan

Dipl.-Chem. Christof M. Schilz*

Dipl.-Ing. Wolfgang Schmidt

Dipl.-Phys. Michael Unger *

*Now in industry



Technical Staff:

Anja Friedrich

Helga Hildebrand

Martin Kolacyak

Manfred Pirzer

Hans Rollig

Dipl.-Ing. FH Petra Thiemann

Ingeborg Tontsch

Italo Wassermann

Karl Werner

Visiting Graduate Students & Scientists:

Aaron Neufeld, CSIRO-Building, Construction and Engineering Highett Labs, Victoria,
Australia



4.4.3 Laboratory and Offices

Accommodation:

Total space: 1 328 m²

Laboratory space: 717 m²

Main Equipment:

Surface Analysis / Electrospectroscopic Methods

- SEM incl. EDX
- AES/XPS with transfer into a preparation chamber for gas-adsorption & electrochemical cell
- XPS/UPS/ISS incl. sample transfer into a UHV-preparation chamber
- UHV-preparation chamber (cleaning by sputtering, heating) incl. SIMS, AES, LEED; sample transfer into a reaction chamber
- SAM incl. fracture apparatus and transfer vessel to XPS
- XRD

Optical Spectroscopy Methods

- FT-IR spectroscopy incl. in-situ cell for plasma-polymerisation, gas-adsorption incl. quartz crystal microbalance
- Raman spectroscopy
- Spectroscopic ellipsometry
- Surface plasmon spectroscopy
- Brewster angle microscopy (BAM)

Scanning Probe Techniques

- STM/AFM (non-contact) / friction microscopy in air and in electrolytes
- STM/AFM for electrochemical investigations, incl. in-situ tensile creep machine for measurements constant stress
- UHV-high-temperature STM (temperatures up to 1500 K for semi-conductors, up to 750 K for metals)



Electrochemical Investigation Methods

- 2 Common electrochemistry set-ups
- 2 EIS set-ups
- Rotating ring-disc electrode
- Electrochemical quartz crystal microbalance (EQCM)
- 3 Set-ups for the measurement of local Volta-potentials (Kelvin-Probe)

High Temperature Corrosion Investigation Methods

- Thermo-gravimetric methods
- Volumetric method

Methods for Surface Preparation

- High-vacuum-vapour deposition system (electron-beam, thermal, Magnetron-sputtering)
- Langmuir-Blodgett troughs
- Plasma-coating-chamber (integrated in FT-IR and ESCA)
- Plasma-coating-chamber with microwave source

Material Testing

- 2 Temperature-humidity chambers
- Salt-spray chamber



4.4.4 Teaching (weekly hours)

Winter Semester 1998/99 (WS 1998/99):

Basic Studies (Grundstudium, till Vordiplom):

Lectures:

- Materials science III, 2 h (M. Stratmann)
for students of materials science and engineering
with experiments (T. Hebner, E. Hornung)

Laboratory Courses:

- Basic laboratory course in materials science

Advanced Studies (Hauptstudium, after Vordiplom):

Lectures:

- Physical-chemistry fundamentals of corrosion and surface techniques,
2 h (M. Stratmann)
for students of materials science and engineering
with exercises, 1 h (T. Fili, H. Kaiser)
- Electrolytic corrosion, part I, 2 h (M. Stratmann)
- Electrochemical characterization methods, 2 h (M. Stratmann, A. Dakkouri)
lecture with exercises
- Practical surface techniques, 1 h (E. Wendler-Kalsch)

Seminars:

- Corrosion and surface technology II, 2 h (E. Wendler-Kalsch)
- Current research topics, 2 h (A. Dakkouri)

Laboratory Courses:

- Advanced laboratory course: Corrosion and surface techniques, part II



Summer Semester 1999 (SS 1999):

Basic Studies (Grundstudium, till Vordiplom):

Laboratory Courses:

- Basic laboratory course in materials science

Advanced Studies (Hauptstudium, after Vordiplom):

Lectures:

- Kinetics of electrochemical reactions (M. Stratmann)
for students of materials science and engineering
with exercises, 1 h (T. Fili, H. Kaiser)
- Electrolytic corrosion, part II, 2 h (H. Kaiser)
- Interfacial chemistry, 2 h (M. Stratmann)
- Materials science II, 2 h (E. Wendler-Kalsch)
for students of chemical engineering

Seminars:

- Corrosion and surface technology I, 2 h (E. Wendler-Kalsch)
- Current research topics, 2 h (H. Kaiser)

Laboratory Courses:

- Advanced laboratory course: Corrosion and surface techniques, part I

List of Optional Lectures offered during WS 1998/99 and SS 1999

(A total of 7 h weekly is required for majors):

- Surface analysis, 1 h (M. Stratmann)
- Corrosion and corrosion protection in power plants, 2 h (B. Stellwag)
- Corrosion of technical materials in industrial plant buildings, 1 h (R. Feser)
- Tribology, 1 h (H. Kaiser)
- High temperature corrosion, 1 h (W. Auer)
- Corrosion in the chemical industry, 1 h (G. Grötsch)
- Corrosion monitoring and prediction in industrial plants, 1 h (B. Stellwag)
- Stress-corrosion cracking, 1 h (E. Wendler-Kalsch)



4.4.5 Graduates

Studienarbeiten:

- **Ritter, Stefan**
Untersuchung der Adhäsion dünner Polymerfilme auf Aluminium mittels Zugversuchen
- **Frensnick, Sascha**
Untersuchung der Kristallisation von aufgedampften Metallfilmen auf Si (111)
- **Eibisch, Harald**
Elektrochemische Untersuchungen an Au_3Cu - und Cu_3Au -Dünnschichtfilmen

Diploma Theses:

- **Schmidt, Elke**
Untersuchungen zur atmosphärischen Korrosion von Eisen-Aluminium-Legierungen

Doctorate Theses:

- **Schilz, Christof Matthias (November 1995 till June 1999)**
Untersuchungen zu den Grundlagen der Haftung des Systems Aluminium/Polycyanurat
- **Unger, Michael (November 1995 till May 1999)**
Partikelinduzierte Korrosion von Kupfer durch Ammoniumsulfat und deren Inhibition
- **Jung, Christian (October 1994 till January 1999)**
Alkylphosphonsäuren als molekulare Haftvermittler für Aluminium und Zinkwerkstoffe



4.4.6 Research Projects / Co-operation with Industry

Survey of Research Projects

The Institute of *Corrosion Science and Surface Technology* has broad research interests ranging from very fundamental studies of elementary processes of surface modification or corrosion to technological studies related to the coating processes of real materials under industrial plant conditions. Major research areas are:

- Atomistic studies of elementary steps of corrosion and oxidation
- Aqueous corrosion
- High temperature corrosion
- Atmospheric corrosion and corrosion of electronic materials
- Surface modification by ultrathin inorganic and organic layers
- Delamination of organic coatings

Materials under investigation range from electronic materials to structural materials like steel or galvanized steel and modern light-weight alloys. Many research projects are based on an international collaboration and are financed from international sources.

In the following part a summary of the funding sources and a survey of all research activities are given.

Funding Sources	Total Expenses in 1999, DM	Funding granted in 1999, DM
Deutsche Forschungsgemeinschaft	597 490.00	310 800.00
Bundesministerium für Bildung und Forschung	73 641.00	0.00
European Community	162 108.00	423 735.00
Funding by Industry	195 434.00	578 320.00
Tasks for Industry	49 543.00	30 000.00
State/Federal Investment Programs	123 952.00	154 409,00
Total	1 202 168.00	1 497 264.00



List of Research Projects

Research project: Corrosion characteristics and surface properties of high-strength light alloys based on Fe-Al

Project leader: M. Stratmann

Responsible researcher: M. Dannenfeldt

Research partners: Thyssen Krupp Stahl AG, MPI f. Eisenforschung, Düsseldorf

Funded by: BMBF

Beginning of project: August, 1995

Duration: 4 years

Research project: Cellulose - Adhesion promoter and corrosion protection

Project leader: M. Stratmann

Responsible researcher: A. Plagge

Research partner: MPI f. Polymerforschung, Mainz

Funded by: DFG-Schwerpunkt "Cellulose"

Beginning of project: July, 1996

Duration: 4 years

Research project: Investigation of the delamination of polymer coated zinc and steel surfaces with the scanning Kelvinprobe in a climatic cycle test

Project leader: M. Stratmann

Responsible researcher: T. Hebner

Research partners: Verein Deutscher Eisenhüttenleute, Thyssen Krupp Stahl AG, Preussag AG, IRSID, OCAS, Stahlwerke Bremen, VOEST-Alpine Stahl Linz

Funded by: European Community for Steel and Coal

Beginning of project: July, 1996

Duration: 3 years

Research project: Corrosion resistance of hydrogenated amorphous silicon carbon alloys deposited on steel

Project leader: M. Stratmann

Responsible researcher: T. Fili

Research partner: FhG Braunschweig

Funded by: DFG

Beginning of project: October, 1995

Duration: 4 years

Research project: Fundamental aspects of adhesion of metal-polymer systems

Project leader: M. Stratmann

Responsible researchers: C. M. Schilz, U. Hecht

Research partners: IZM Teltow, DaimlerChrysler AG

Funded by: BMBF

Beginning of project: November, 1995

Duration: 3.5 years



Research project: Mechanism of Al-alloy corrosion and the role of chromate inhibitors

Project leader: M. Stratmann

Responsible researcher: W. Schmidt

Research partners: Research Foundation: Ohio State University, Rockwell, State University of New York, Brookhaven National Laboratory

Funded by: US Air Force

Beginning of project: January, 1998

Duration: 5 years

Research project: Atmospheric corrosion of copper in the presence of submicron ammonium sulfate

Project leader investigator: M. Stratmann

Responsible researchers: M. Unger, R. Lobnig

Funded by: DFG

Beginning of project: October, 1995

Duration: 4 years

Research project: Investigation of the growth and electrochemical properties of silicides formed on iron

Principal investigator: M. Stratmann

Responsible researcher: M. Rebhan

Funded by: SFB "Mehrkomponentige Schichtsysteme"

Beginning of project: January, 1996

Duration: 3 years

Research project: Investigation of basic processes of the delamination of organic corrosion protection coatings

Principal investigator: M. Stratmann

Responsible researcher: E. Hornung

Funded by: DFG

Beginning of project: June, 1997

Duration: 3 years

Research project: Corrosion protection of zinc-coated steel by deposition of optimized plasma polymers induced by microwave linear sources

Project leader: M. Stratmann

Responsible researcher: P. Thiemann

Research partners and funding: BASF Coatings, DaimlerChrysler AG, Chemetall, Laminoir de Dudelange, TKS, VASL

Beginning of project: September, 1998

Duration: 2 years



Research project: Electrochemical features of passive layers on ion implanted and PVD coated aluminum alloys

Project leader: M. Stratmann in co-operation with Prof. Dr. Luis F. P. Dick, Universidade Federal do Rio Grande do Sul, Porto Alegre

Funded by: DFG

Beginning of project: January, 1997 **Duration:** 3 years

Research project: Nanostructuring of alloy-surfaces with in-situ scanning tunneling microscopy

Project leader: A. Dakkouri

Responsible researcher: S. Maupai

Funded by: DFG-Schwerpunkt: "Grundlagen der elektrochemischen Nanotechnologie."

Beginning of project: July, 1997 **Duration:** 2 years

Research project: Investigation of de-alloying mechanisms on atomic scale by EC-STM

Project leader : A. Dakkouri, H. Kaiser

Responsible researcher: G. Eckstein

Funded by: DFG

Beginning of project: September, 1997 **Duration:** 3 years

Research project: Initial states of high temperature corrosion – in-situ UHV-STM investigations

Project leader: M. Stratmann

Responsible researchers: R. Meier, A. Dziakova

Funded by: DFG

Beginning of project: July, 1996 **Duration:** 4 years

Research project: Changes in grain structure and typical properties of FeCr-alloys after quick heating and cooling down with an excimer laser

Project leader: E. Wendler-Kalsch

Responsible researcher: B. Gerold

Research partners: Universität Bayreuth, Universität Göttingen, ATZ EVUS

Funded by: DFG-Schwerpunkt "Kurzzeitmetallurgie"

Beginning of project: August, 1996 **Duration:** 4.5 years

Specific Projects

Research Group of M. Stratmann

- **Investigation of the delamination of polymer-coated zinc and steel surfaces with the Scanning Kelvinprobe in a climatic cycle test (T. Hebner)**

Objectives

Polymer-coated zinc and steel surfaces are increasingly used for many applications, especially in the automotive industry. Therefore, intense studies have been performed in the steel producing industry to develop suitable short term corrosion tests to simulate long term behavior. To reveal the differences in the corrosion behavior of variously pretreated and coated steel substrates the critical corrosion parameters of these systems have to be determined. In co-operation with the steel works Thyssen Krupp Stahl AG, Stahlwerke Bremen, VOEST Alpine Stahl Linz AG (A) and the research institutes IRSID (F) and OCAS (B) a suitable short term corrosion test for cyclic conditions should be developed by comparison of laboratory and outdoor investigation results.

Experimental set-up

The delamination processes can be investigated in situ with the so-called Scanning Kelvinprobe (SKP) [1]. The SKP allows the high resolution mapping of the distribution of the electrode potential even beneath the polymer coating. At the defect the values are negative, at the intact interface polymer/metal positive. Thus, the delamination can be monitored in-situ. To determine the influence of relative humidity and temperature on the corrosion

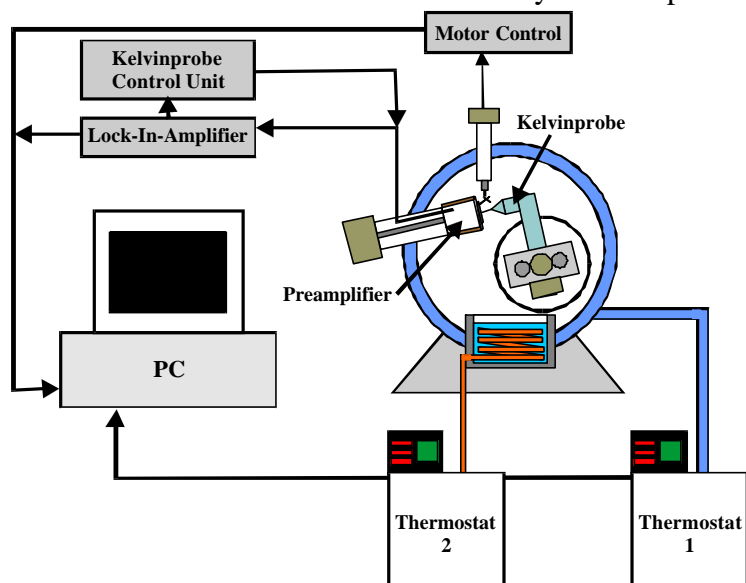


Fig. 4.4.6.1: Set-up of the new scanning Kelvinprobe in a climatic chamber.



potential a complex SKP set-up has been designed (Fig. 4.4.6.1). The model-samples will be prepared according to Leng [2] using a epoxy-ester/amine lacquer on electrodeposited zinc. Technical coatings will be provided by the industrial partners dependent on the outdoor exposure results.

Fundamental Studies

Aim of the project is to find ways to replace long term outdoor exposure testing by exposing samples, that have been prepared with well defined defects, to a high number of short term cycles in temperature and humidity and monitoring early stages of delamination. Changes in humidity are important to simulate passivation and reactivation of the defect in dry and humid atmosphere, respectively.

Also differences in the delamination process, that depend on whether the defect only extends down to the zinc coating or even runs through it to the steel, are investigated.

Parallel to these investigations at our Institute the very early stages of the delamination, the starting reactions at the defect, are investigated at the IRSID. Here, the Scanning Vibrating Electrode Technique (SVET) is employed to obtain detailed information about the reactions at the defect and their effect on the delamination process.

Also different cyclic corrosion tests - ProhesionestTM (IRSID), VDA(621-415)-test (Thyssen Krupp Stahl AG), VW-test (OCAS) - are carried out on a number of differently pretreated samples. Based on these tests samples are selected for the experiments at our Institute and at IRSID.

For outdoor exposure different combinations of surface treatments, e.g., pure, galvanealed, and electrogalvanized steel with or without phosphate pretreatments are used at different exposure sites - industrial and marine environment.

References

- [1] A. Leng
Untersuchungen zur Delamination polymerbeschichteter Eisenoberflächen; Ph.D. thesis, University of Düsseldorf (1995).
- [2] M. Stratmann, R. Feser and A. Leng
Corrosion protection by organic films; *Electrochimica Acta*, **39** (1994) 1207-1214.



- **Biomedical applications of new cellulose-composite layers** (A. Plagge)

Introduction

This research project concerns the synthesis of new cellulose polymers and investigation of their potential application as coatings on different materials. Cellulose polymers are ideal materials for use in medical products; the polymer is often used in dialyser membranes and its biocompatibility is proved several times. Coating metals with such polymers could help to prevent corrosion. This is sometimes a problem in implants consisting of steel, where toxic ions (like nickel or chromium) are released in the presence of chloride-containing blood, causing inflammation. Another potential application of cellulose polymers is the field of adhesion promotion. It is a problem that implants often loose the structural support to the natural bone after a couple of years due to deadhesion and have to be replaced. To avoid this problem new cellulose layers seem to be ideal materials.

Idea

The chosen strategy to obtain cellulose polymers which give strong interaction on different substrate surfaces, like titanium, steel or hydroxyapatite (a calcium phosphate and main

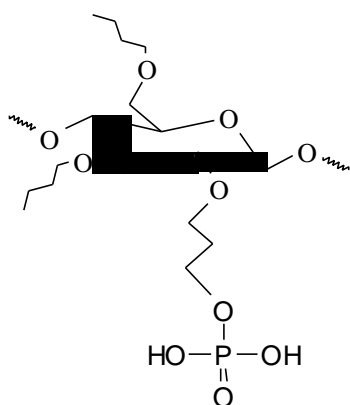


Fig. 4.4.6.2: Diagram of one mono-mer-unit of the new cellulose phosphate, representing the introduced alkyl-spacer-groups which are necessary for LB-capability and the alkyl-phosphate-group. The synthesis was carried out by the project partner of this work, the work group of Prof. Adler at the TU Dresden. The polymer is an example of a hairy-rod like cellulose polymer - first described by the work group of Prof. Wegner [1] at the MPI in Mainz - that is well known to form homogenous layers ideal for surface techniques.

part of the human bone) surfaces, was to introduce phosphate groups well known to adsorb strongly at reactive metals. One has only to substitute a part of the polymers native hydroxyl groups. For the first part of the project basic studies were carried out with model systems described below. The substrates were coated with the polymers by the Langmuir-Blodgett-technique. (cp-titanium, titanium alloy TiAl6V4, steel DIN 1.4441 - all typical implant metals - and hydroxyapatite ceramic as a model for the human bone). The sophisticated LB-technique was necessary to obtain layers with defined and reproducible layer thickness.

Instead of using only one polymer a mixture of a phosphate and a cinnemate containing cellulose was used. The cinnemate polymers can be crosslinked by UV-radiation to form a mechanical stable matrix, in which the phosphate polymers are embedded.

Layer formation - model systems

The polymer coated metal surfaces are analyzed using scanning auger microscopy, AFM and other techniques. Examples are represented below. The thickness of each layer was determined by ellipsometry.

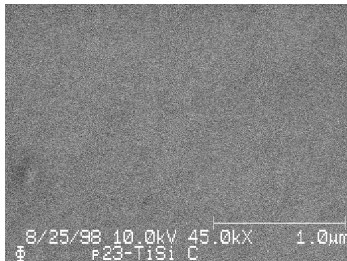


Fig. 4.4.6.3: 2D Auger-signal distribution for the polymer-carbon in a LB-multilayer of cellulose phosphate. A unique grey tone reveals a homogenous layer composition. The layer is about 15 nm thick.

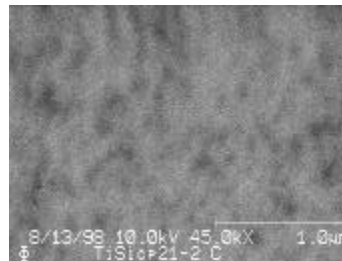


Fig. 4.4.6.4: 2D Auger-signal distribution for the polymer-carbon in a LB-multilayer of the mixture cinnemate-phosphate, ratio 2:1, 17 nm thick. Regions of lower density shown as dark regions, due to defects in the layer.

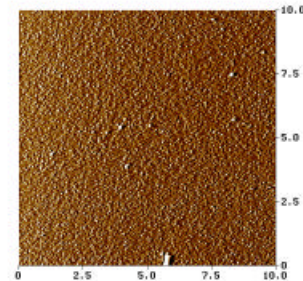


Fig. 4.4.6.5: AFM image: Topography (contact mode) showing a very smooth surface structure in the case of the polymer mixture CP 21. The roughness is 3.1 nm on 20 μm.

Summarized results

Phosphate cellulose forms homogenous layers on all substrate surfaces. With increasing layer thickness (up to 30 nm) a mixture with low phosphate content becomes homogenous, too. Only mixtures with high content of phosphate keep defects with increasing layer thickness (up to 60 nm). In the case of the matrix component cinnemate cellulose the defects seem to be specific for each substrate. On steel 1.4441 homogenous layers with no defects can be obtained, whereas the film on titanium surfaces always contain a significant part of defects.

The promising results with model systems and the positive effect of phosphate cellulose have led to the development of two component systems. The phosphate cellulose has a higher content of phosphate groups giving rise to a stronger interaction with oxide surfaces than the model systems. These systems are actually characterized by spectroscopic and electrochemical methods to find out more about their behavior under a corrosive environment typical for chloride containing blood.

References

- [1] M. Schaub, G. Wenz, G. Wegner, A. Stein, D. Klemm, *Adv. Mater.*, **5** (1993) 919

• **Corrosion protection of steel and zinc substrates by deposition of optimized plasma polymers** (N. Shirtcliffe, P. Thiemann)

Steel and zinc-coated steel are still the most widely used materials in the manufacturing of cars or household appliances. Especially in the automotive industry the use of zinc-coated steel has become more important in the last few years. Steel as well as zinc-coated steel are often phosphated (with or without chromate rinsing) and electrocoated before being lacquered with several layers of organic coatings. Because of the increasing importance of environmental concerns, the steps of phosphating/chromating and electrocoating should be replaced by new technologies.

A possible alternative is the use of plasma technology for cleaning the metal substrate and for depositing ultra-thin plasma-polymers. First research on the development of plasma polymer coating on steel was performed at the Institute by G. Grundmeier and continued by M. Brettmann to zinc-coated surfaces.

The aim of the studies was to develop a plasma polymer with optimized structural features in order to obtain an improved stability at the interfaces.

The metal substrates are cleaned in an oxygen plasma and then a plasma polymer is deposited which binds strongly to the metal oxide. In order to improve the adhesion of the primer, the surface of the plasma polymer is finally modified by plasma-etching (Fig. 4.4.6.6).

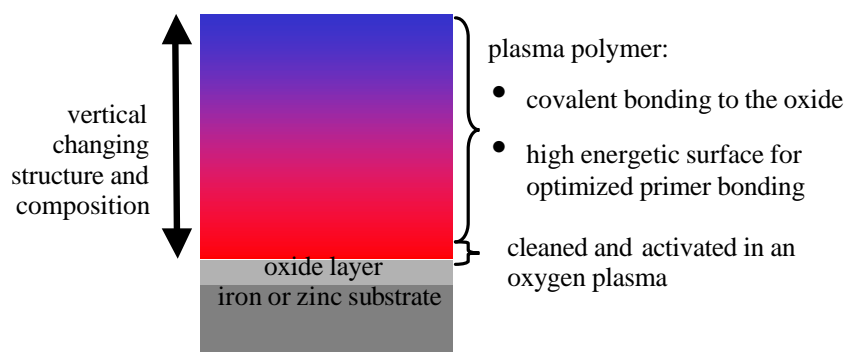


Fig. 4.4.6.6: Scheme of an optimized interfacial plasma polymer for enhanced bonding to the substrate and the primer.

All steps of the plasma treatment, i.e., cleaning of the metal surface and the deposition of the polymer, can be controlled in situ in a custom-made plasma-cell, combining quartz-crystal-nanoweighing and infrared reflection-absorption spectroscopy with monolayer sensitivity. This experimental set-up allows us to elucidate the structure of the metal(oxide)/plasma polymer and plasma polymer/primer interface, respectively.

The delamination of the primer starting from an artificially prepared defect was monitored with the scanning Kelvinprobe (Fig. 4.4.6.7). The results show that the delamination rate of the primer can be reduced significantly by this kind of plasma polymer of about 15 nm thickness, on steel as well as on zinc-coated steel substrates.

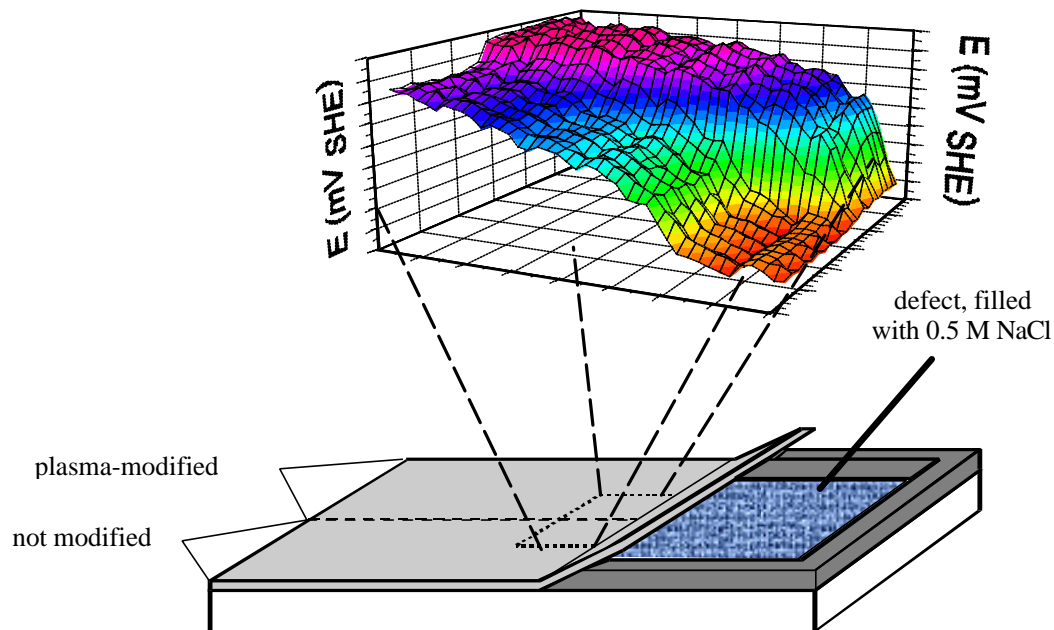


Fig. 4.4.6.7: Sample preparation for the investigation of delamination processes with the SKP.

The technique described above shows commercial promise, therefore, we have begun to upscale the process. Currently, we are using A4 sized, zinc-coated steel sheets as an intermediate to a full scale pilot plant. Previously, a glow discharge plasma had been used in all of the plasma treatment stages, the larger set-up uses microwave sources to induce the plasmas. This should improve the homogeneity of the larger plasmas.



- **Selective dissolution and nanostructuring of Cu-Au single crystal alloys: An in-situ STM Study** (A. S. Dakkouri, G. A. Eckstein, S. Maupai)

Alloys are of great technological importance because their properties can be tailored by changing the chemical composition. Detailed information about the surface properties of alloys is essential for a deeper understanding of complex interfacial reactions in fields like selective corrosion and heterogeneous catalysis. Binary alloys are of particular regard in materials science because of their widespread usage in technical applications. At present a detailed understanding of the selective corrosion of binary alloys is still lacking.

De-alloying, the selective dissolution of one or more of the elements of an alloy owing to large differences in their reactivities, is important in the passivation, pitting and stress-corrosion of technologically significant materials. Various mechanisms of de-alloying have been proposed, but a full understanding of this important process is still an open issue.

The need for an atomic-level understanding of the de-alloying process has motivated us to focus our studies on investigations of the selective anodic dissolution of Cu - the less noble component - from Cu-Au alloys. These studies are mainly performed with electrochemical scanning tunneling microscopy (STM). With this method it is possible to follow the atomistic processes during selective corrosion in real time and, simultaneously, to image the corroded surfaces with atomic resolution. For the development of a microscopic understanding of these corrosion processes, the experiments are performed with single-crystal electrodes. To gain more insights into de-alloying phenomena is also of importance with respect to the observation that alloys with an ordered arrangement of atoms are more stable against corrosion than disordered ones. By varying the degree of ordering, the reason for its influence on the so-called critical potential (below which bulk de-alloying does not occur) should be clarified. Moreover, the role of the crystallographic orientation of the alloy surfaces and the composition of the electrolyte in the dissolution mechanism are studied.

The results of the in-situ STM investigations on low index Au_3Cu and Cu_3Au single crystals are used to evaluate the mechanism of selective copper dissolution and formation of the Au-rich protective layer in the low current ($E < E_C$) potential region during anodic polarization of Au_xCu_y alloys.

Single crystals were prepared under UHV conditions and characterized by LEED, UHV-STM and surface X-ray diffraction (SXRD). These surface studies revealed new structural models for the topmost surface region and represent an ideal starting point for electrochemical and in-situ EC-STM studies on defined surfaces.

Electrochemical studies in sulfate media by cyclic voltammetry and current-time transients enabled us to get a deeper understanding on different electrochemical behaviour of low index single crystals. The Au_3Cu and Cu_3Au surfaces showed different critical regimes

dependent on the netplanes. In comparison to sulfate media, chloride caused a decrease in E_C which is also dependent on the netplanes.

In situ EC-STM is used to study the nature of surface morphology during dealloying of Au_3Cu and Cu_3Au at potentials below the critical potentials. The surface morphology of the ordered $\text{Cu}_3\text{Au}(001)\text{-p}(1\times 1)$ surface at different potentials is shown in Fig. 4.4.6.8 and indicates the influence of crystallographic orientation on selective corrosion. The electrochemical behaviour is correlated with alteration of surface morphology observed by in situ EC-STM and UHV structural models of these surfaces. The results reveal new insights into the mechanisms of selective corrosion and enabled us to modify existing models in the literature.

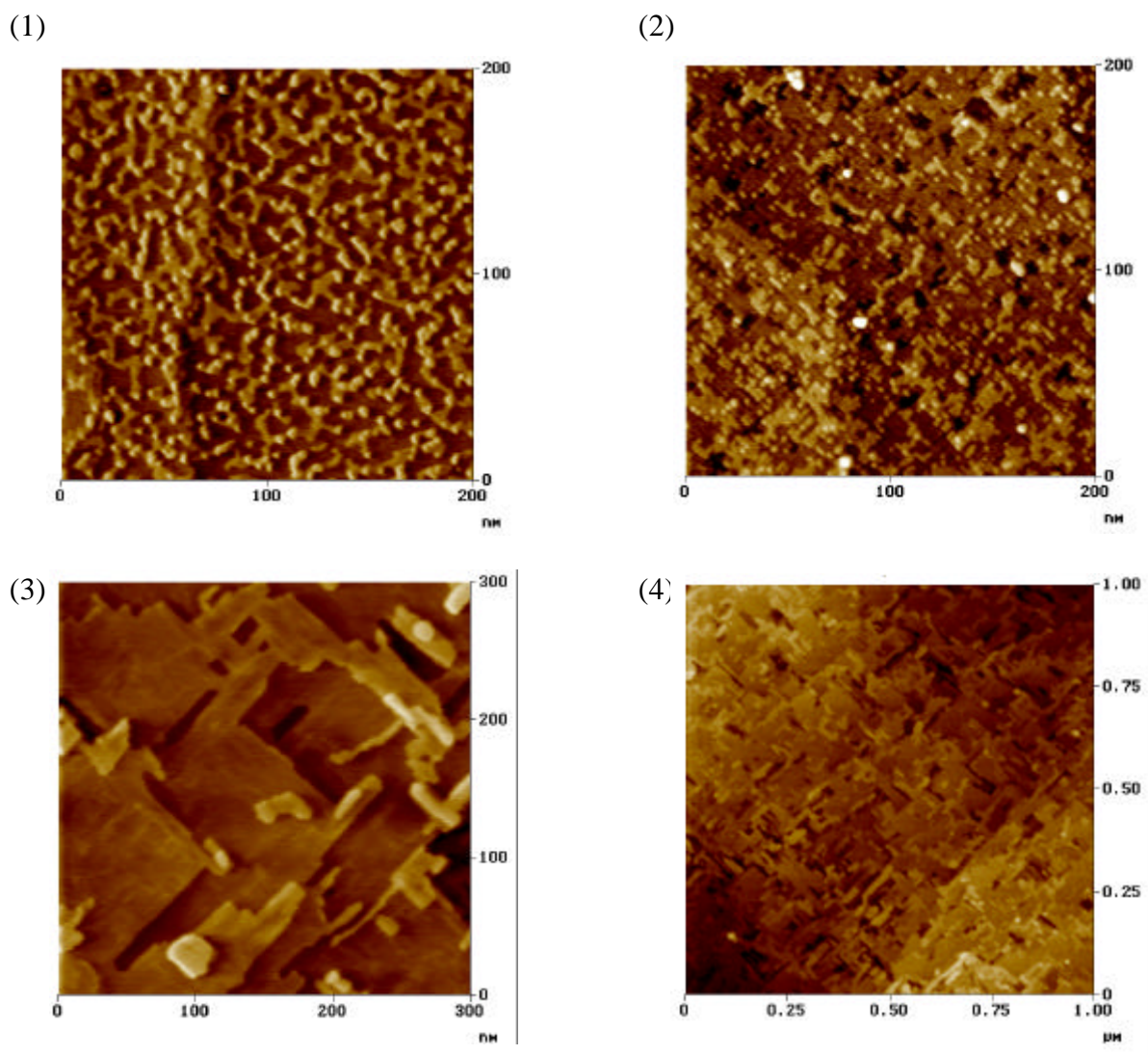


Fig. 4.4.6.8: In-situ STM images of different stages on selective corrosion on $\text{Cu}_3\text{Au}(001)\text{-p}(1\times 1)$ in 0.1 M H_2SO_4 : (1) $E_{\text{Sample}} = +253$ mV, (2) $E_{\text{Sample}} = +353$ mV, (3) $E_{\text{Sample}} = +593$ mV, (4) $E_{\text{Sample}} = +960$ mV (all potentials vs. NHE).

Furthermore, we use the electrochemical STM not only to image these alloy surfaces and to follow surface structural changes but also as a tool for generating structures at a nanometer scale on Cu-Au surfaces. This nanostructuring which is induced by the STM tip is performed by selective, local dissolution of an alloy compound and by local metal deposition leading to small metal clusters. Thus the chemical composition of the alloy surface is laterally modified which leads to new physical, chemical and mechanical properties. Therefore, for example, new local catalytic properties, magnetic domains or areas with changed or even induced electric conductivity can be created.

We have developed - in co-operation with Prof. D.M. Kolb, Department of Electrochemistry, University of Ulm, Germany - a technique that allows the generation of small metal clusters typically 2-4 atomic layers in height, with the help of an STM-tip, and place them at will onto single crystal electrode surfaces. Two examples are shown in Fig. 4.4.6.9.

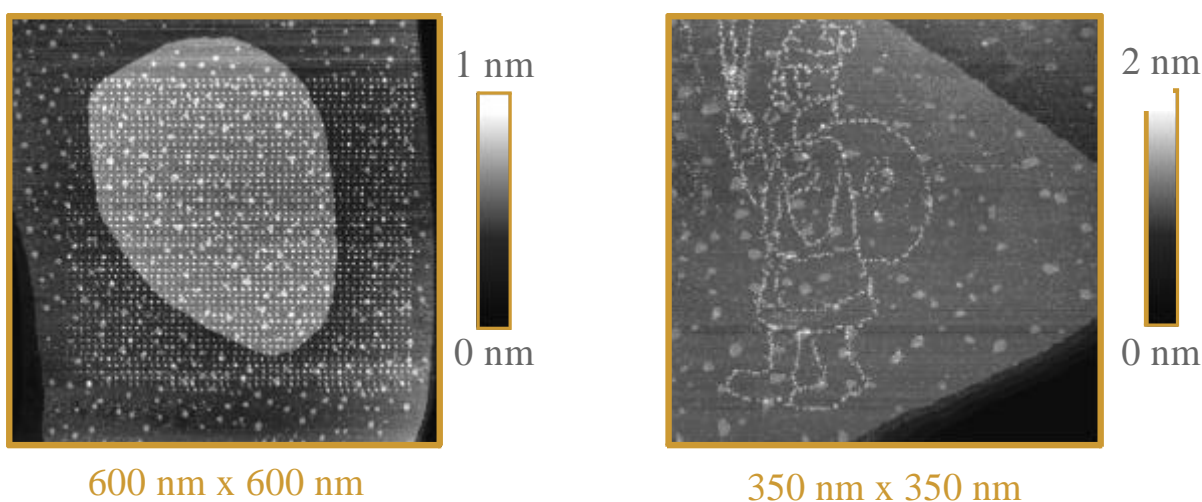


Fig. 4.4.6.9: STM image of an array of 50 x 50 Cu clusters on Au(111) in 0.05 M H_2SO_4 + 0.5 mM CuSO_4 , $E_{\text{sample}} = 10$ mV vs. Cu/Cu^{2+} , $E_{\text{tip}} = -50$ mV vs. Cu/Cu^{2+} (left); STM image of a nanoscale “Santa Claus” made of 1109 Cu clusters on Au(111) in 0.05 M H_2SO_4 + 0.5 mM CuSO_4 , $E_{\text{sample}} = 10$ mV vs. Cu/Cu^{2+} , $E_{\text{tip}} = -50$ mV vs. Cu/Cu^{2+} (right).



Research Group of E. Wendler-Kalsch

Laser-Surface-Modification of Binary FeCr-Alloys (B. Gerold)

Introduction

In many cases rather the surface than the bulk determines the materials technological properties (e.g. wear resistance and corrosion resistance). The corrosion behaviour of passivating metals and alloys is governed by the thin passive layer on the surface. Alloy chemistry and structure at nanoscale depth determine formation, growth, composition and structure of the passive film and with that it's electrochemical properties. Alternation of the surface structure and composition consequently lead to alternation of the film properties.

Motivation

With a short pulse of high intensity ultraviolet radiation from an excimer laser heat is introduced rapidly into the material's surface so that melting of a thin layer, evaporation and plasma formation take place. Subsequently the melt is rapidly cooled by self-quenching [1]. Since the process is extremely fast the heat affected zone between melted material and bulk is exceedingly small. Thus the properties of the bulk material remain unchanged. The basic aspects of the excimer laser treatment that affect electrochemical behaviour are: 1.) structural changes through remelting and rapid solidification which result in extremely fine segregations and/or microstructures. 2.) changes in the chemical composition through a) selective evaporation of elements and/or phases. The result is an enrichment of the melt with the remaining components. b) introduction of new elements and/or phases from reactions of the melted metal with the ambient atmosphere (e.g. background gas) [2].

We assume that a fine grain structure combined with the additional introduction of dispersed oxides and nitrides, respectively, affect the composition and structure of the passive film in a positive way. A more stabile passive layer would exceed an higher resistance against general and localized corrosion [3, 4]. For that reason an excimer laser surface melting technique is used to modify the surface of binary FeCr_x-alloys (x = 0, 6, 10, 13) to study the correlation between laser process parameters (intensity [H] = J/cm², number of pulses P, ambient atmosphere (Argon, Nitrogen = N), chemical composition, structure and the electrochemical characteristics (passivation-activation behaviour, pitting corrosion) of the laser remelted and laser gas alloyed surfaces, respectively.



Results of laser gas alloying in nitrogen atmosphere

Results from X-ray diffraction (XRD) confirm the stabilization of the ϵ - and the austenitic γ -phase in pure ferritic FeCr-alloys after laser treatment in 0.2 MPa nitrogen atmosphere. For an nitrogen pressure of 0.5 MPa no ϵ -phase formation could be observed (Fig. 4.4.6.10), while the γ -fraction and the nitrogen content of the γ -phase (Fig. 4.4.6.11) is reduced. We found not evidence for nitride formation inside the modified layer. All the nitrogen is in solid solution. Only an thin film of nitrides $(\text{Cr,Fe})_2\text{N}_{(1-x)}$ was detected on the surface by ESCA-investigations.

Pitting potential measurements have been performed mainly by the potentiodynamic method to determine the breakdown potential E_b . The results of such measurements clearly show an shift of E_b to more noble potentials by nitrogen (Fig. 4.4.6.12). On the other side nitrogen produces only a minor effect on the E_r where pits can firstly initiate but also re-passivate [6]. So the favourable effect of nitrogen is the broadening of the potential range between E_r and E_b by promoting the repassivation kinetics rather than by suppressing pit initiation (Fig. 4.4.6.13).

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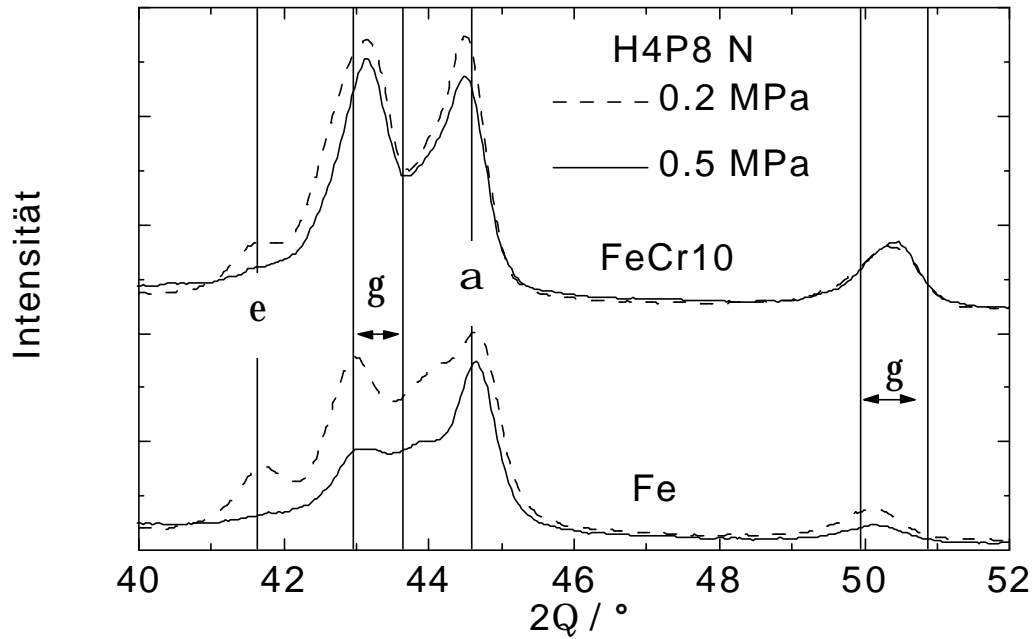


Fig. 4.4.6.10: XRD-Spectra of pure iron and FeCr10. Laser treatment: Energy 4 J/cm^2 (H4); 8 pulses (P); Ambient atmosphere: Nitrogen 0.2 and 0.5 MPa (N).

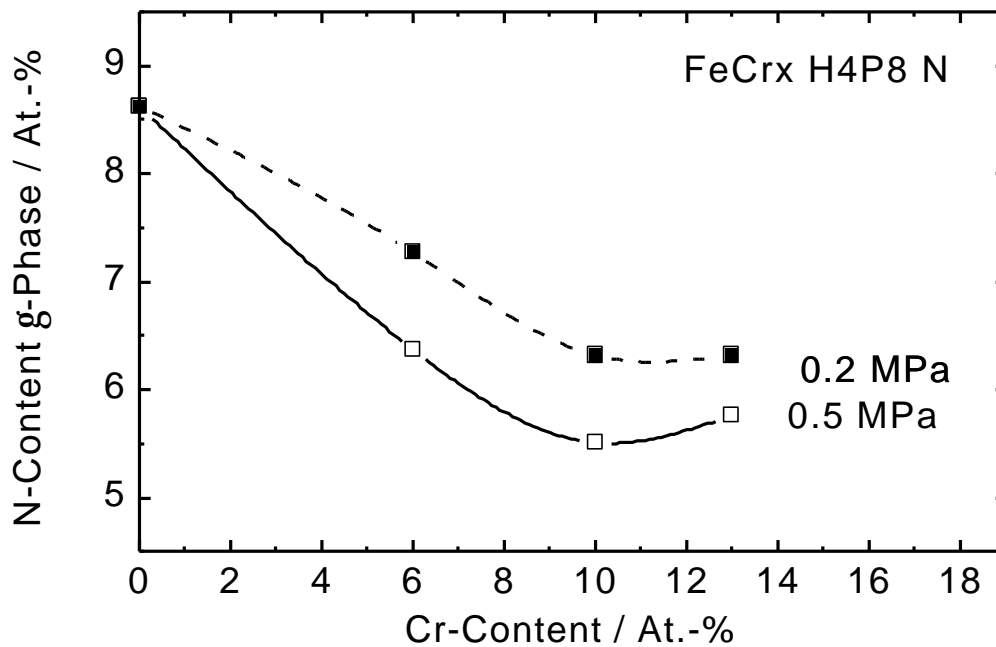


Fig. 4.4.6.11: Comparison of the Nitrogen content of the γ -phase after laser treatment with 8 pulses at 4 J/cm^2 in nitrogen atmosphere. Evaluation follows [5].

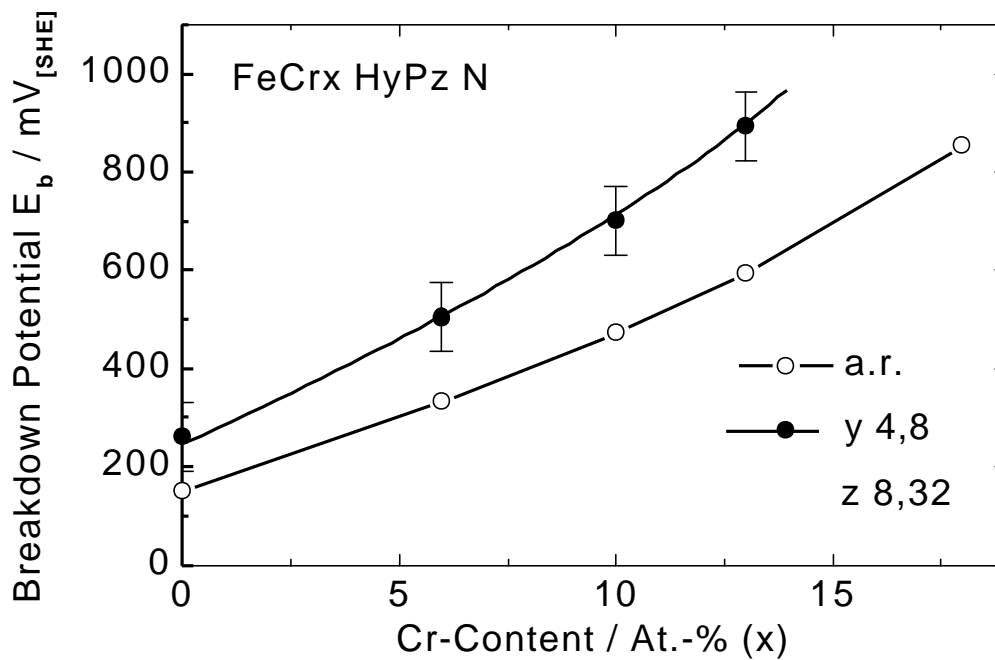


Fig. 4.4.6.12: Pitting potentials of the as received (open symbols) and laser modified (full symbols) samples (Cr-content x: 0, 6, 10, 13). Energy y: 4 and 8 J/cm², respectively; number of pulses z: 8 and 32, respectively.

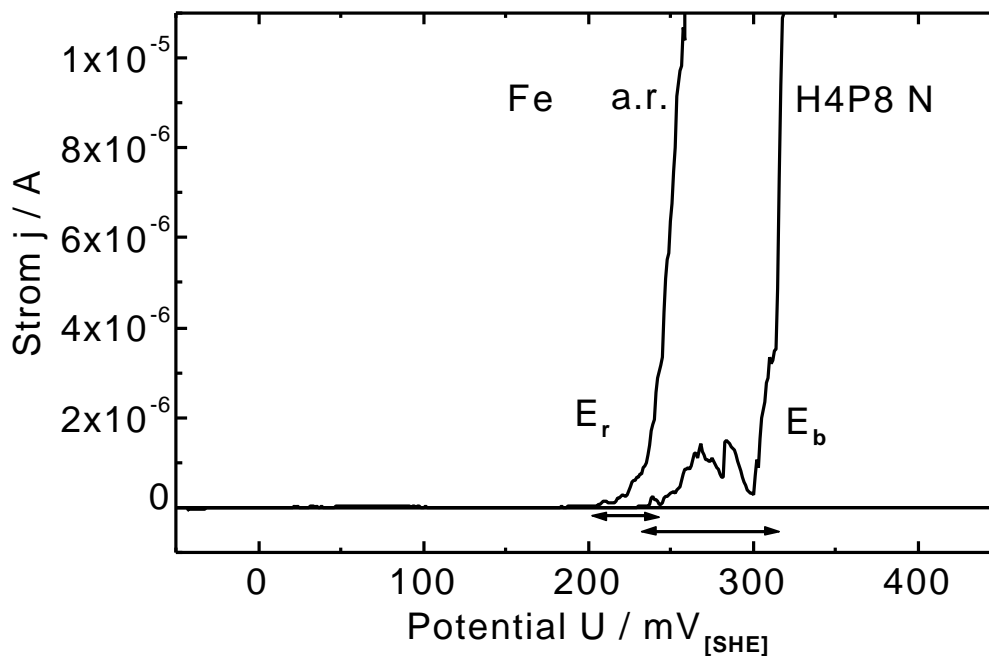


Fig. 4.4.6.13: Current-potential-curve of pure iron and of laser treated iron.



4.4.7 Publications (Papers, Conference Proceedings, Books)

Papers

- 1/99 **M. Rebhan, M. Rohwerder and M. Stratmann**
CVD of silicon and silicides on iron; Applied Surface Science **140** (1999) 99-105
- 2/99 **K. Lübbert, J. Kopp and E. Wendler-Kalsch**
Corrosion behaviour of laser beam welded aluminum and magnesium alloys in the automotive industry; Materials and Corrosion **50** (1999) 65-72
- 3/99 **A. Leng, H. Streckel and M. Stratmann**
The delamination of polymeric coatings from steel, Part 1: Calibration of the Kelvinprobe and basic delamination mechanism; Corrosion Science **41** (1999) 547-578
- 4/99 **A. Leng, H. Streckel, K. Hofmann and M. Stratmann**
The delamination of polymeric coatings from steel, Part 2: First stage of delamination, effect of type and concentration of cations on delamination, chemical analysis of the interface; Corrosion Science **41** (1999) 579-597
- 5/99 **A. Leng, H. Streckel and M. Stratmann**
The delamination of polymeric coatings from steel, Part 3: Effect of the oxygen partial pressure on the delamination reaction and current distribution at the metal/polymer interface; Corrosion Science **41** (1999) 599-620
- 6/99 **G. Grundmeier and M. Stratmann**
Influence of oxygen and argon plasma treatments on the chemical structure and redox state of oxide covered iron; Applied Surface Science **141** (1999) 43-56
- 7/99 **M. Rohwerder and M. Stratmann**
Surface modification by ordered monolayers: New ways of protecting materials against corrosion; MRS Bulletin **24** (1999) 43-47
- 8/99 **G. A. Eckstein and S. Maupai**
Reinstwasseraufbereitung für elektrochemische STM-Anwendungen; Labo. Magazin für Labortechnik **6** (1999) 46-48
- 9/99 **G. A. Eckstein, S. Maupai, A. S. Dakkouri and M. Stratmann**
Surface structure of Au₃Cu(001); Physical Review **B60** (1999) 8321-8325
- 10/99 **G. A. Eckstein, S. Maupai, M. Stratmann, A. S. Dakkouri, J. H. Zeysing and R. L. Johnson**
Atomically flat Au₃Cu(111) thin films prepared by magnetron sputter deposition; Applied Surface Science (submitted 1999)



Conference Proceedings

11/99 **B. Gerold and E. Wendler-Kalsch**

Gefüge- und Eigenschaftsänderungen von FeCr-Legierungen durch hohe Aufheiz- und Abkühlraten mittels Excimer-Laserbelichtung; Handbuch zum DFG - Schwerpunkt: Kurzzeitmetallurgie, 1999

12/99 **C. M. Schilz, U. Hecht and M. Stratmann**

Nanostrukturierung von Phasengrenzen zur Verbesserung der Haftungseigenschaften von Metall/Polymer Fügeverbunden; DGM-Tagung; Tagungsband, 1999, pp. 117-120

13/99 **M. Dannenfeldt and M. Stratmann**

Korrosionsschutz durch Oberflächenstrukturierung an Eisen-Aluminium-Legierungen; Werkstoffe für Energietechnik/Werkstoffe und Korrosion, Werkstoffwoche 1998, Wiley-VCH, Weinheim, vol. III, 1999, pp. 327-331

14/99 **M. Rebhan and M. Stratmann**

Korrosionsschutz von Eisen durch Beschichtung mit Silizium
Werkstoffwoche 1998, Wiley-VCH, Weinheim, vol. IX, Symposium 11, Oberflächentechnik, 1999, pp. 161-164



4.4.8 Conferences, Seminars, Invited Lectures

Conferences and Seminars organized by members of the Institute

- **75. Bunsenkolloquium** "Elektrochemische Modifizierung von Oberflächen mit Rastersondenmethoden", 22.03.-23.03.1999, Leipzig
- **Seminar E-30-409-111-9 im Haus der Technik** "Vermeidung von Schäden an metallischen Bauteilen", 20.04.-21.04. 1999, Essen
- **Fachveranstaltung E-30-935-111-9 im Haus der Technik** "Die Rolle des Wasserstoffs bei Korrosionsprozessen an Metallen, 30.11-01.12.1999, Essen

Invited Lectures

February, 1999

M. Stratmann

"Die Modifizierung von Metalloberflächen durch ultradünne organische Schichten - Neue Wege des Korrosionsschutzes für Gebrauchsmetalle", Bunsenkolloquium, Ulm

March, 1999

E. Wendler-Kalsch

"Korrosionsverhalten von Werkstoffen", Hochschulpraktikum: Schadenanalyse, München, Germany

E. Wendler-Kalsch

"Eigenschaften von Beschichtungssystemen", Hochschulpraktikum: Schadenanalyse, München, Germany

E. Wendler-Kalsch

"Gefügebildung und Eigenschaften der nichtrostenden Stähle", Seminar: Werkstoffe/Schweißen; Nicht rostende Stähle, Haus der Technik, Essen, Germany

E. Wendler-Kalsch

"Spannungsriß- und Schwingungsrißkorrosionsverhalten der nichtrostenden Stähle", Seminar: Werkstoffe/Schweißen; Nicht rostende Stähle, Haus der Technik, Essen, Germany

April, 1999

E. Wendler-Kalsch

"Metallische Überzüge und anorganische Schutzschichten", DECHEMA - Weiterbildungskurs: Korrosion und Korrosionsschutz, Frankfurt a. Main, Germany



E. Wendler-Kalsch

"Die Bedeutung der mechanischen Belastungsarten bei der Rißbildung und geeignete Prüfverfahren", Seminar: Vermeidung von Schäden an metallischen Bauteilen, Haus der Technik, Essen, Germany

E. Wendler-Kalsch

"Schäden an Armaturen und Wärmetauschern aus Kupfer und Kupferlegierungen und ihre Vermeidung", Seminar: Vermeidung von Schäden an metallischen Bauteilen, Haus der Technik, Essen, Germany

E. Wendler-Kalsch

"Vermeidung von Schäden an Aluminiumwerkstoffen im Leichtbau", Seminar: Vermeidung von Schäden an metallischen Bauteilen, Haus der Technik, Essen, Germany

M. Stratmann

"Neuartige wissenschaftliche Ansätze zur Untersuchung und Verbesserung der Stabilität von Metall/Polymer-Grenzflächen", Colloquium Universität Saarbücken/Institut für Neue Materialien

June, 1999

E. Wendler-Kalsch

"Eigenschaften und Anwendungen von Kupfer und Kupferlegierungen", Seminar: Unterschiede im Korrosionsverhalten metallischer Werkstoffe und ihre Auswirkungen auf den praktischen Einsatz, Haus der Technik, Essen, Germany

E. Wendler-Kalsch

"Eigenschaften und Anwendungen von Aluminium und Aluminiumlegierungen", Seminar: Unterschiede im Korrosionsverhalten metallischer Werkstoffe und ihre Auswirkungen auf den praktischen Einsatz, Haus der Technik, Essen, Germany

E. Wendler-Kalsch

"Eigenschaften und Anwendungen von Nickel und Nickellegierungen", Seminar: Unterschiede im Korrosionsverhalten metallischer Werkstoffe und ihre Auswirkungen auf den praktischen Einsatz, Haus der Technik, Essen, Germany

E. Wendler-Kalsch

"Metallische Verbundwerkstoffe durch Plattieren", Seminar: Unterschiede im Korrosionsverhalten metallischer Werkstoffe und ihre Auswirkungen auf den praktischen Einsatz, Haus der Technik, Essen, Germany

G. Eckstein

"Struktur und Dynamik an Metall/ Elektrolyt Grenzflächen", Institut für Festkörperphysik, Lehrstuhl für Angewandte Physik, Universität Erlangen-Nürnberg, Erlangen, Germany



July, 1999

R. Meier

"In-situ observation of the initial stages of high temperature oxidation of iron with STM", Gordon Conference: Corrosion dry", New London, NH, USA

October, 1999

E. Wendler-Kalsch

"Schäden durch Wasserstoff", DECHEMA - Weiterbildungskurs: Korrosion und Korrosionsschutz, Teil A: Grundlagen und Untersuchungsmethoden, Frankfurt a. Main, Germany

E. Wendler-Kalsch

"Schäden durch Wasserstoff", DECHEMA - Kurs: Korrosion und Korrosionsschutz, Teil A: Grundlagen und Untersuchungsmethoden, Frankfurt a. Main, Germany

M. Stratmann

"The Scanning Kelvinprobe (SKP) as a new technique to analyze buried interfaces", 196th Meeting of The Electrochemical Society, Honolulu, Hawaii, USA

M. Rohwerder

"Ultrathin organic films for corrosion protection in microelectronic devices", 196th Meeting of The Electrochemical Society, Honolulu, Hawaii, USA

November, 1999

E. Wendler-Kalsch

"Wechselwirkung von Absorptionwasserstoff mit Metallen", Fachveranstaltung: Die Rolle des Wasserstoffs bei Korrosionsprozessen an Metallen, Haus der Technik, Essen, Germany



4.4.9 Seminar Presentations by External Lecturers

Lectures at the Institute

- 18.01.1999 **Dr. M. Spiegel**, MPI für Eisenforschung, Düsseldorf, "Salzschmelzinduzierte Hochtemperaturkorrosion"
- 18.02.1999 **Prof. Dr. Ch. Leygraf**, Royal Institute of Technology, Stockholm, "Research of atmospheric corrosion at Royal Institute of Technology"
- 12.03.1999 **Dr. M. Wolpers**, Voest-Alpine Stahl, Linz, "Die Rolle des Nickels bei der Phosphatierung verzinkter Feinbleche"
- 12.04.1999 **Prof. Dr. U. Stimming**, TU München, München, "Eigenschaften mesoskopisch strukturierter Oberflächen"
- 12.08.1999 **A. Neufeld**, CSIRO-Building, Construction and Engineering Highett Labs, Victoria, Australia, "Degradation of Metal Components used in Built Environment: Pollution Transport, Stochastic Simulations and Surface Potentials"

Lectures in the Departmental Materials Science Colloquium

- 19.01.1999 **Prof. Dr. O. Marti**, Universität Ulm, Ulm, "Kraftwechselwirkung in Raster-sondenmikroskopen am Beispiel von Nanostrukturen in Elektrolyten und Polymeren"
- 11.05.1999 **Prof. Dr. B. Bhushan**, The Ohio State University, Columbus (OH), USA, "Micro/Nanotribology and its Applications"

4.4.10 Activities in University Committees

M. Stratmann:

- Member of "Strukturkommission"

E. Hornung:

- Women's representative of Technische Fakultät



4.4.11 Activities in Professional Societies, Editorial Boards, Advisory and Organization Committees

Professional Societies

M. Stratmann:

- Member of Deutsche Bunsengesellschaft
- Member of Deutsche Gesellschaft für Materialkunde (DGM)
- Member of Gesellschaft Deutscher Chemiker (GDCh)
- Member of International Society of Electrochemistry (ISE)
- Member of Electrochemical Society (ECS)
- Member of Verein Deutscher Eisenhüttenleute e.V. (VDEh)
- Member of Gesellschaft für Korrosionsschutz e.V. (GfKORR)

Editorial/Advisory Boards of Journals and Conferences

M. Stratmann:

- Member of Editorial Board of the Journal Materials and Corrosion
- Member of Editorial Board of the Journal Steel Research