



DECHEMA

FORSCHUNGSINSTITUT

Stiftung bürgerlichen Rechts

Corrosion

Research Activities 2017

Preface

DECHEMA-Forschungsinstitut *Interdisciplinary Research for Sustainable Technologies*

The DECHEMA-Forschungsinstitut (DFI) stands at the forefront of interdisciplinary research for sustainable materials, processes and products for the industrialized society. It is a scientific research center where chemists, engineers and biotechnologists jointly work on creating novel concepts and innovative interdisciplinary solutions based on materials science, chemical engineering and biotechnology.

The institute has a staff of approx. 80 who are involved in

- Basic and preindustrial **research** in Chemical Engineering, Biotechnology, Environmental Technology, and Materials Sciences
- **Teaching activities** at German universities in the fields mentioned above
- **Continuing professional development** courses for participants from industry and universities
- Development of solutions to **industrial problems**
- **Scientific support** for DECHEMA working parties and conferences

The structure of the institute is undoubtedly unique in Germany: based on the competencies of five academic research groups:

- High Temperature Materials
- Corrosion
- Electrochemistry
- Chemical Technology
- Industrial Biotechnology

These groups, together with additional service units, strive for novel ideas and scientific concepts to target the needs of our industrialized society.

It focuses on three main areas of research, covering the whole spectrum from fundamental aspects to application:

- Energy Efficiency
 - Fuel Cells
 - Metal-Air-Batteries and other energy storage systems
 - Photocatalytic Systems
- Conservation of Resources
 - Innovative Corrosion Protection Systems
 - Recycling of precious metals
 - Water Treatment

- Biotech for Chemical Production
 - Utilization of Renewable Resources
 - Biotechnological Production Routes for Chemical Products

Driven by the needs of HiTech industries in the fields of biotechnology, materials, and chemical engineering and other industrial areas including energy conversion, automotive and aircraft technologies, the research activities at the DECHEMA-Forschungsinstitut cover the whole spectrum from fundamental aspects to application.

These activities reflect the institute's commitment to bridging the gap between academia and industry in the scientific and technological fields represented by DECHEMA.

Fields of expertise at the DECHEMA-Forschungsinstitut are:

- High temperature materials
- Corrosion protection in extremely aggressive environments
- Development of novel coating systems
- Advanced investigation methods for high temperature corrosion
- Nanoparticle-based coatings
- Modification of anodic oxide layers
- High resolution methods for corrosion investigations
- Microbially influenced corrosion
- Redox-flow batteries
- Metal-air energy storage systems
- Fuel cells
- Reaction engineering
- Photocatalysis
- Functional surfaces
- Molecular electrochemistry
- Electrochemical water treatment
- Bioelectrochemistry
- Bioprocess development
- Enzymatic catalysis and microbial syntheses of fine chemicals
- Metabolic engineering of microorganisms for industrial production

Every year, we publish five *Research Activities* brochures, each presenting one research group.

For more information about the DECHEMA-Forschungsinstitut, please visit: www.dechema-dfi.de

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Corrosion Group - Overview

Main Interests

- investigation of corrosion mechanisms and modeling of corrosion processes
- corrosion and corrosion protection of light weight materials
- development of new coating systems based on biopolymers and chemical nanotechnology

The corrosion working group is on the one hand engaged in mechanism-based investigations and modeling of corrosion processes. On the other hand new coating systems are developed by using biogenic substances and chemical nanotechnology.

In the field of corrosion protection several actual projects are characterized by methods of chemical nanotechnology to be used for the synthesis or modification of coating systems. However, also for the generation of the coating matrix innovative methods like a metal treatment by ultrasound or plasma-electrolytic oxidation are being used. Furthermore biogenic substances are used for the development of protective coatings especially against biocorrosion.

In the second main field of work the focus is on corrosion investigations on new materials or for materials qualification for new technologies. The fundamental understanding of corrosion mechanisms should in some cases also lead to a modeling of corrosion processes. As new materials in the last years especially titanium alloys have been under investigation. For the time being this work is focusing especially on alloys for medical technologies like e.g. Ti-13Nb-13Zr. For this alloy besides the characterization of corrosion properties some work is also aiming at optimized implants by combining a partial heat treatment of the alloy with a localized surface treatment by plasma anodizing incorporating hydroxyapatite into the oxide layer.

Concerning alloy qualification for new technologies locally resolved corrosion measurements on compounds being friction stir welded under ultrasonic support will help for the future development of this new joining technology.

More mechanistic investigations have been done concerning dew point corrosion of aluminium heat exchangers. The aim is here to build the basis for corrosion modeling and thus for the modeling of heat exchanger failures. This should allow the supplier to optimize construction and working modes.

Furthermore the group is responsible for corrosion investigations, materials selection tasks and damage analysis in the frame of industrial research.

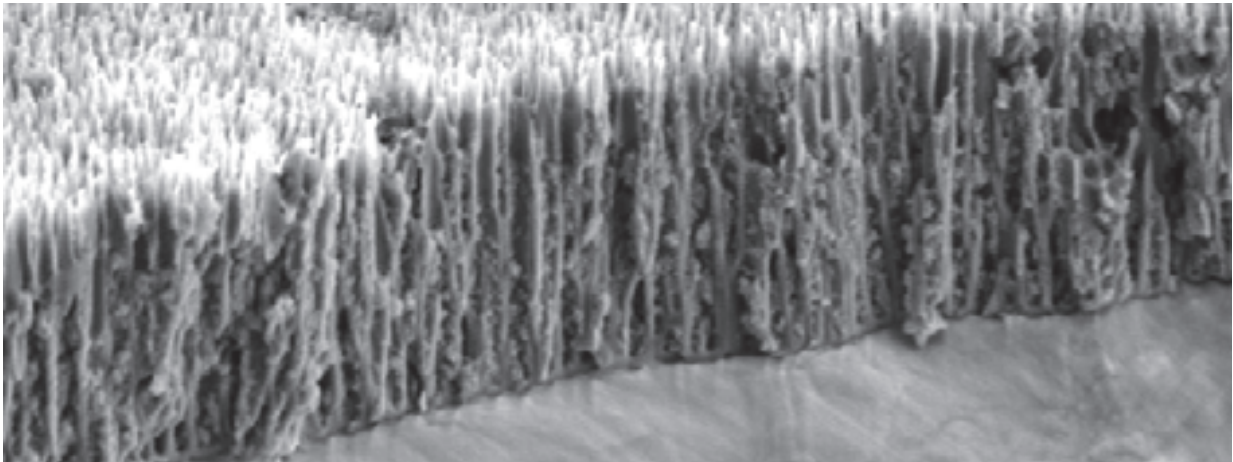
Methods to be used are:

- Conventional electrochemical techniques, e.g.
 - stationary current-potential curves
 - impedance spectroscopy
 - rotating disc and ring-disc electrodes
 - cyclic voltammetry
 - electrochemical noise analysis
- Electrochemical quartz crystal micro balance
- Scanning Kelvin probe / Kelvin probe force microscopy
- ex-situ methods
 - scanning electron microscopy with EDX-analysis
 - electron beam microanalysis
 - atomic absorption spectroscopy
 - ion chromatography
 - gas chromatography coupled with mass spectrometry GC-MS
 - FT-IR-spectroscopy
 - contact angle measurement
 - adhesion testing
 - particle size analysis and zeta potential measurement
- Electrochemical Atomic Force Microscopy
- Raman-Microscopy

Research Projects 2017

Nanoparticle-based coatings for corrosion protection

Nanoparticle modified anodizing-layers with increased alkali resistance



Period: 01.04.2016 - 30.09.2018
Partner: Fraunhofer IKTS Dresden
Funder: AiF

Motivation and Aim

Aluminum and Al alloys are nowadays used not only for automotive and aircraft construction, but also for building claddings, windows, etc., in the construction industry. In order to protect the base metal from corrosion, the surface is anodized, whereby the native / thin oxide layer is artificially thickened. The oxide layer thus produced is several microns thick and has pores whose diameters lie in the one to three-digit nanometer range (depending on the anodizing method). The present pores are generally sealed in a downstream process step (water vapor) or cold (chemical) in order to increase the corrosion resistance. However, the thus densified alumina as a passive layer is only stable up to a pH value of approx. 8.5, whereby recurring cleaning with strongly basic cleaning chemicals (pH 13.5) leads to a corrosive attack of the surface. However, an adequate long-term stability of anodized aluminum and Al alloys against alkaline media is required by the

user, which is to be achieved within the framework of the project by a corresponding surface modification.

Approach

The aim of the ongoing project is to develop an anodizing process based on sulfuric acid anodizing (SAA), which allows subsequent chemical nanotechnology impregnation to increase resistance to strongly alkaline media. The modification of the anodizing parameters (current-voltage regimes, temperature and bath composition) should directly influence the pore morphology, so that the pore diameter and shape are optimized for the subsequent impregnation. The impregnation is to be carried out using aqueous nanoparticulate zirconium dioxide dispersions since zirconium dioxide has a high resistance to strong acids and bases. In addition, the coefficient of expansion of zirconium dioxide is approximately equal to that of aluminum oxide, which means that thermal stress should not be a problem for the generated layers. The impregnated anodizing layers are then to be characterized by modern analytical methods and their corrosion behavior both electrochemically and by aging in typical basic cleaners.

Results

Aqueous zirconium dioxide dispersions (starting material: powder with a particle size of 5-25 nm) having a primary particle size of <10 nm, which are distinguished by a long-term storage stability (several weeks), can be produced. In addition, an ultrasonic method was developed with which "large" zirconium dioxide particles (5 μm and larger) could be milled to a single-digit nm range in a short time, which could drastically reduce the cost of the zirconia particles used. The pore diameter could be increased by optimizing the process parameters during sulfur acid modification, so that first immersion coatings or impregnations of the anodizing layers could be carried out.

Future work

The future work will include the further optimization of the pore design (expansion of the pores) on the other hand, the already available samples should be impregnated with aqueous zirconium dioxide dispersions and compared with industrially anodized samples (benchmark), which were also impregnated with zirconium dioxide. After successful impregnation, the samples should be characterized and tested for their corrosion resistance in basic media.

Supported by:



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on the basis of a decision
by the German Bundestag



Das IGF-Vorhaben Nr. 19082 BG der Forschungsvereinigung
DECHEMA e.V., Theodor-Heuss-Allee 25, 60486 Frankfurt am Main
wurde über die AiF im Rahmen des Programms zur Förderung der
industriellen Gemeinschaftsforschung (IGF) vom Bundesministerium
für Wirtschaft und Energie aufgrund eines Beschlusses des
Deutschen Bundestages gefördert.

Ultrathin polymer films

Corrosion protection of steels by analogues of extracellular polymeric substances (EPS) from renewable resources



Period: 01.11.1014 - 30.09.2017
Partner: Biofilmcenter University Duisburg-Essen
Funder: AiF

Many corrosion damage cases are associated with microbiological activity. Microbial biofilms and the extracellular polymeric substance (EPS) they excrete can both induce (MIC) and inhibit (MICI) corrosion processes. Both effects are particularly influenced by the interactions between the material and the EPS. Decisive here are functional groups such as glucuronic acid or carboxylic acid residues that appear to be also critical for cell adhesion.

In the precursor project 16953 N biogenic cyclodextrins were studied within the meaning of EPS analogous substances as a starting point for a modern and environmental friendly method of corrosion protection for metals in aqueous medium. By surface spectroscopic methods the adsorbate could be identified as polymerized cyclodextrins. Furthermore, the results suggest that the reaction of carboxyl and / or hydroxyl functional groups with dissolution products, which are released at the anode, affects a covering or blocking of these electrochemically active areas. Layers of correspondingly functionalized

cyclodextrins could reduce the attachment of harmful microorganisms briefly by up to 90%. As electrochemical studies prove, the layers also show a protective effect during abiotic corrosion.

The aim of this research project is the consistent further development of cyclodextrins. The layers are optimized to (a)biotic corrosion of (un)alloyed steel with regard to their corrosion-inhibiting effect; also their long-term stability should be increased.

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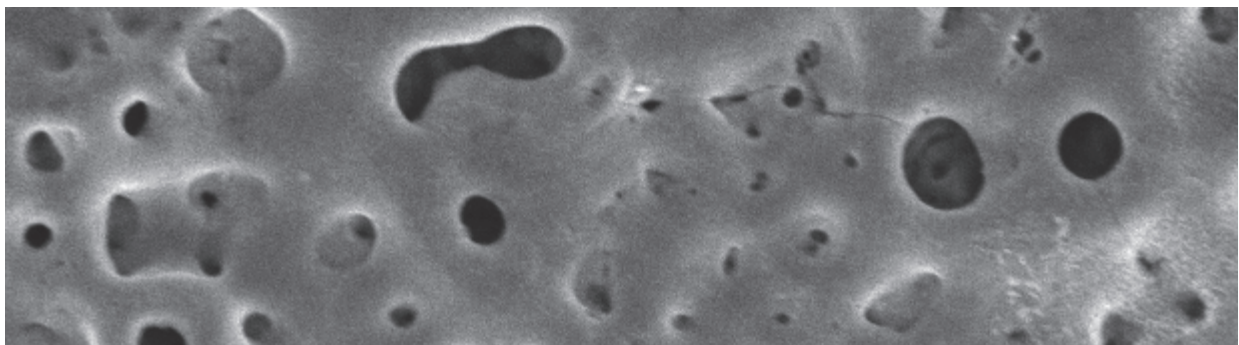
on the basis of a decision
by the German Bundestag

Das IGF-Vorhaben Nr. 18352 N der Forschungsvereinigung DECHEMA e.V., Theodor-Heuss-Allee 25, 60486 Frankfurt am Main wurde über die AiF im Rahmen des Programms zur Förderung der industriellen Gemeinschaftsforschung (IGF) vom Bundesministerium für Wirtschaft und Energie aufgrund eines Beschlusses des Deutschen Bundestages gefördert.



Corrosion investigations for new materials and technologies

Qualifying the Metastable, Biomedical -Titanium Alloy $Ti_{13}Nb_{13}Zr_{13}$ via Tuning of Gradiant Mechanical Properties and Partial Surface Modification



Period: 01.04.2014 - 30.09.2017

Partner: TU Braunschweig, Institut für Werkstoffe, Prof. Dr. J. Rösler

Funder: AiF

Introduction

The goal of the project IGF 18116 N is the tuning of gradiental mechanical and surface chemical properties on the alloy $Ti_{13}Nb_{13}Zr$. Today's implants, as for example a hip implant, need different chemical and mechanical properties on one piece of implant. The upper part of a hip implant for example needs to be wear resistant because of contact with the femoral head. At the same time the lower part of the implant, the stem, requires a high degree of bone growth promotion (biocompatibility).

Project goals

At DECHEMA-Forschungsinstitut (DFI) a partial anodizing process will be carried out. The upper part of the implant will be anodized by plasma electrolytic oxidation (PEO) to produce an abrasion and fretting corrosion resistant oxide layer. The lower part instead will be conventionally anodized in the presence of bone growth promoting substances.

Via this way a biocompatible oxide layer will be produced. At the project partner TU Braunschweig the corresponding areas will be treated mechanically and by heat treatment in order to produce the required mechanical properties.

Results

The influence of different electrical and chemical parameters on the characteristics of titanium surface layers obtained by plasma-electrolytic oxidation were examined. The focus of this research is on the Ti-13Nb-13Zr alloy, which was particularly developed as an implant material for medical use, unlike the Ti-6Al-4V alloy. Ti-13Nb-13Zr samples with four different microstructures (+; “; +“; ++“) were galvanostatically anodized at constant charge-carrier densities and current-densities reaching from 14 mA/cm² up to 817 mA/cm². Both a constant current mode and a unipolar pulsed mode with a duty-cycle of 50 % and frequencies of 1 Hz to 50 Hz were used. The surface layers were characterized by scanning electron microscope (SEM), electron dispersion X-ray spectroscopy (EDX), X-ray diffraction (XRD) and nanoindentation.

Several micrometer thick crystalline titanium oxide coatings with a porous structure could be generated in an undiluted and diluted electrolyte containing 1 M H₂SO₄ + 0.1 M H₃PO₄ and 0.1 M H₂SO₄ + 1 M H₃PO₄ respectively. The coatings consist of anatase and rutile, the phase composition of the coatings can be adjusted by the PEO current density. It can be shown that porosity can be reduced with increasing frequency.

The corrosion resistance of these layers was tested in a simulated body fluid (SBF) with the addition of 0.1 M H₂O₂ by open circuit potential measurements, potentiodynamic polarization and electrochemical impedance spectroscopy. Higher current densities during the PEO process formed thicker and denser coatings, which consequently resulted in lower corrosion currents. A pulsed process caused improved corrosion behaviour in the diluted electrolyte. This effect did not occur in the more concentrated electrolyte. The addition of zirconium oxide nano-particles into the electrolyte increased the surface hardness to an average value of 11.4 GPa, compared to that of an untreated sample (4.1 GPa) and a sample without particle addition (8.5 GPa).

The improvement of the biocompatibility of titanium implant surfaces by modification of its morphology and the application of hydroxyapatite (HAp) is an ongoing challenge for today's implant technology. As a result, PEO was used to generate HAp layers on the Ti-13Nb-13Zr alloy in an electrolyte consisting of 0.1 M Ca(CH₃COO)₂·H₂O + 0.05 M NaH₂PO₄·H₂O. At a current density of 14 mA/cm² only anatase and rutile could be detected within the XRD-spectrum. HAp was formed in-situ at current densities

of 139 mA/cm² and higher. The corrosion resistance of these apatite containing layers was analyzed again in SBF + 0.1 M H₂O₂. The higher corrosion potentials indicated that all HAp coated specimens offer a better protection than the untreated samples.

The specimens in their initial uncoated state show good corrosion resistance in artificial saliva + 1000 ppm NaF. The corrosion currents are higher, when both the alpha and the beta phase is present in one sample, due to the development of a local element.

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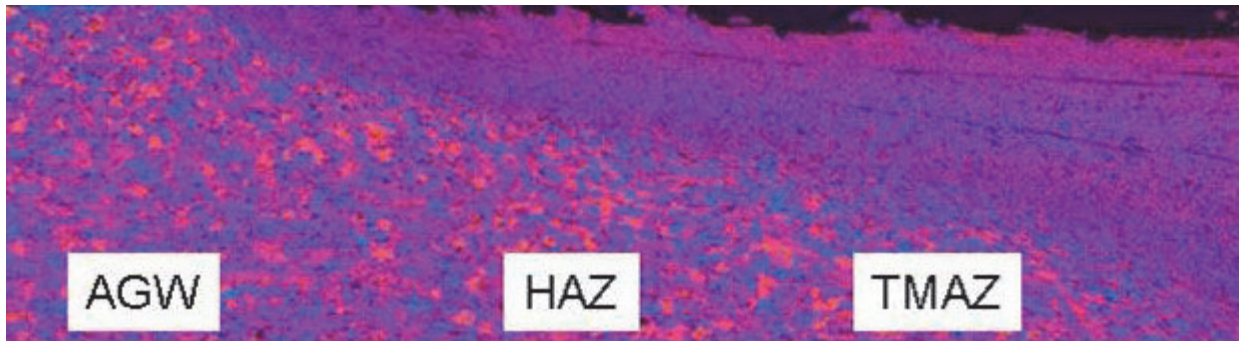
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Das IGF-Vorhaben Nr. 18116 N der Forschungsvereinigung DECHEMA e.V., Theodor-Heuss-Allee 25, 60486 Frankfurt am Main wurde über die AiF im Rahmen des Programms zur Förderung der industriellen Gemeinschaftsforschung (IGF) vom Bundesministerium für Wirtschaft und Energie aufgrund eines Beschlusses des Deutschen Bundestages gefördert.



Realization of Al/High Strength Steel: Joints by Ultrasound Supported Friction Stir Welding - Process and Robustness, Microstructure, Corrosion, and Joining Area Integrated Corrosion Protection



Period: 01.01.2013 - 30.04.2019
Partners: Prof. Dr.-Ing. G. Wagner, M. Thomä;
TU Chemnitz, Lehrstuhl Verbundwerkstoffe
Dr.-Ing. B. Wolter, Dr.-Ing. B. Straß;
Fh IZFP, Saarbrücken
Funder: DFG

Aim of the Project

Only with hybrid construction it is possible to combine the advantages of dissimilar materials. Force-fitted or form-closed joints can be realized in an easy manner, but the strength of welded joints can rarely be achieved. However, fusion welding of dissimilar materials is often impossible as a result of the different melting ranges. Moreover, in many cases undesirable mixed phases occur in the weld area, whereby the attainable strength of the joints will be reduced.

The aim of the research project is to use friction stir welding (FSW) to join material groups that are well established in industrial applications, but that cannot be joined by fusion welding. These are the light weight materials aluminum and magnesium as well as aluminum and steel. FSW enables a joining by plastic deformation. To eliminate strength reducing effects by occurring brittle phases and to improve the stirring in the joining area power ultrasound is additionally transferred into the welded area (USE-

FSW). An estimation of the quality of the produced welds will be carried out by monotonic and cyclic as well as non-destructive investigations. To determine the complex problems of corrosion of the hybrid material joints, detailed examination of the corrosion behavior, especially of the welding area, are made.

Results

The USE-FSW process has been successfully applied to Al/Mg-hybrid joints (see publications) and was now transferred to Al/steel-joints. Investigations on joints made out of an Al wrought alloy (EN AW-6061) and cold rolled DCo₄ steel have been in the focus of the second project period.

The hybrid joints were characterized by *Scanning Kelvin Probe* (SKP) measurements first. At the beginning of the measurements the Volta potential difference between the Al alloy and the steel is about 1.0 V. Both materials exhibit a shift of the Volta potential to more positive values within the measurement time due to surface oxidation processes. The Volta potential shift for the steel is about 0.1 V whereas the aluminum alloy shows a shift of 0.2 to 0.3 V. This leads to a slight reduction in the difference between the materials during the measurement. The Volta potential maps show an influence of the ultrasound on the welding area of Al/steel hybrid joints but it is much less pronounced than in the case of the Al/Mg-hybrid joints. This can be explained by the different joining parameters for the different joints. For the Al/Mg-hybrid joints the pin-offset was 1 mm to the Mg which results in a mechanical mixing of both materials during the process. In case of the Al/steel-hybrid joints, because of the high difference in the melting points of the materials, the pin only rotates within the Al with a distance of 0.3 mm to the faying surface of the steel. Therefore the influence of the ultrasound introduced via the steel sheet is less visible. Only the shoulder of the rotating tool has mechanical contact to the steel and may transport material from one side to the other. The SKP measurements resulted in about 1 V more negative Volta potential values for the EN AW-6061 Al alloy compared to the DCo₄ steel. This is a similar difference to that measured between AZ80 Mg alloy and AC-48000 Al alloy where the Al alloy has shown the more positive values. From that result one would expect that the EN AW-6061 Al alloy will show stronger corrosion in corrosive media than the steel particularly if both phases are in simultaneous contact to an electrolyte.

The measurements in air are not directly transferable to that of in a liquid electrolyte, as the *open circuit potential* (OCP) measurements in 0.5 molar NaCl solution show. The OCP

of the EN AW-6061 alloy exhibits a shift from about -0.7 V to -0.47 V within the first 5 to 10 min and then stabilises around that value. The OCP of the steel declines continuously from about -0.23 V to -0.45 V within the first 10 min and then further to -0.52 V. After 15 to 20 min the OCP value of the DCo4 steel is more negative than that of the EN AW-6061 Al alloy. This behaviour is different to that of the Al/Mg-hybrid joints where an OCP difference of 0.9 V was measured between the base materials in the sodium chloride electrolyte similar to the Volta potential difference in air (SKP measurement). The nugget area and the Al/steel transitional area show nearly constant OCP values immediately after the immersion in the electrolyte. The values are similar to that of the EN AW-6061 aluminum alloy. The OCP values of the base materials and the nugget phase within the hybrid joints are independent of the joining conditions. After the immersion time of 60 minutes the OCP difference between the materials is only about 50 mV or less. Therefore, the risk of an enhanced corrosion caused by a galvanic element is much less pronounced than in the case of the Al/Mg-hybrid joints.

The EN AW-6061 aluminum alloy exhibits a free corrosion potential (E_{oc}) around -0.46 V and a pitting potential around -0.42 V which is only slightly more positive than the free corrosion potential. The corrosion current density measured for the aluminum alloy at the E_{oc} is around 1-2 $\mu\text{A}/\text{cm}^2$ indicating a low corrosion rate. At the pitting potential the current density increases immediately up to values of several hundred $\mu\text{A}/\text{cm}^2$. The free corrosion potential of the DCo4 steel is around -0.54 to -0.53 V. The polarization curve of the steel shows a continuous increase in the anodic region. The corrosion current density at the E_{oc} is slightly higher than that of the EN AW-6061 aluminum alloy (2-3 $\mu\text{A}/\text{cm}^2$). The free corrosion potential of the nugget area shows during the potentiodynamic polarization a small shift to the anodic direction compared to the OCP measurement. The pitting potential of the nugget area is identical to that of the EN AW-6061 aluminum alloy. The corrosion current density of the nugget area of the FSW-hybrid joint at E_{oc} is somewhat higher than that of the USE-FSW-hybrid joint and higher than that of the EN AW-6061 aluminum alloy. This may be attributed to the higher amount of intermetallic phases within the measured area. These phases show a higher corrosion tendency. The E_{oc} value of the Al/steel transitional area of the FSW-joint is about 50 mV more negative than that of the USE-FSW-hybrid joint, which may be a result of a different Al to steel ratio or different phases within the measured area. However, both polarization curves exhibit in the anodic range first a continuous increase of the current density - comparable to the DCo4 base material - and then a pitting potential and further progress comparable to that of the EN AW-6061 aluminum alloy. The corrosion current density at the E_{oc} is lower than that of the DCo4 base material. This is a distinct difference to the Al/Mg-

hybrid joints where an increase of the corrosion current density of several orders of magnitude was observed at the Mg/nugget transitional area.

Outlook

The USE-FSW process will be used to join other alloy combinations (e.g. Al/high strength steel). The mechanical and corrosion properties of the new hybrid-systems will be characterized as well.

Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation – DFG-SPP1640 A2).



Selected publications

F. Depentori, F. Brunke, J. Laukart, C. Siemers, J. Rösler, W. Fürbeth

Oxidation of surface lanthanum precipitates in a free-machining titanium alloy investigated by in-situ AFM and cyclic voltammetry

Materials and Corrosion 65/4 (2014) 425-430

A new, free-machining titanium alloy of the composition $\text{Ti}_6\text{Al}_2\text{Fe}_1\text{Mo}_{0.9}\text{La}_{0.5}\text{Cu}_{0.3}\text{Si}$ was investigated for its corrosion properties in 1.5wt% NaCl solution. The alloy showed localized corrosion of metallic lanthanum precipitates. Localized corrosion kinetics were investigated via cyclic voltammetry and potentiodynamic polarization. Furthermore, the process could be visualized in situ via electrochemical atomic force microscopy (in situ AFM). Results show that before dissolution, the precipitates undergo a strong volume increase. This was attributed to the oxidation of lanthanum to $\text{La}(\text{OH})_3$. Investigations show that the oxidation process can be triggered by either applying electrochemical polarization to the alloy or by exposing the alloy for enough time in NaCl solution. The holes created after removal of the lanthanum precipitates can act as sites of further corrosion, but only at high anodic polarization of around 3 V versus normal hydrogen electrode.

M. Schneider, K. Kremmer, S.K. Weidmann, W. Fürbeth

Particle reinforced open porous anodizing layers on AA5005

Materials and Corrosion 68 (2017) DOI: 10.1002/maco.201609389

The present work deals with the target aimed design of anodic oxide films on AA5005 by modified phosphoric acid anodizing and reinforcement by subsequent impregnation with nanosized silicon dioxide by chemical nanotechnology. The authors show the influence of the anodizing time on the oxide layer thickness, the pore diameter and the morphology. It is revealed that silicon dioxide nanoparticles are successful when incorporated into the open structure pores of the layer. The anodizing and the incorporation process were carried out wet on wet. Complementary electrochemical measurements show the potential of the modified oxide layer in view of corrosion protection despite their deliberated open porosity.

C. Thyssen, D. Holuscha, J. Kuhn, F. Walter, W. Fürbeth, W. Sand

Biofilm formation and stainless steel corrosion analysis of *Leptothrix discophora*

Advanced Materials Research 1130 (2015) 79-82

Bioleaching and biocorrosion are based on similar biochemical processes. Microbe-surface interaction, biofilm formation and concomitant extracellular polymeric substance (EPS) production gained increasing interest in the past decades. Nowadays it is generally accepted that biofilm formation and an accompanying formation of manganese oxides by manganese oxidizing bacteria such as *Leptothrix* spp. account for one type of pitting corrosion of stainless steel (SS). However, little is known about biofilm formation, EPS composition of manganese oxidizing microorganisms and their influence on micro-biologically influenced corrosion. Consequently, we studied biofilm formation of *Leptothrix discophora*, the biooxidation of manganese in biofilms on floating filters as well as biofilm formation on stainless steel and the involved corrosion processes. Cells were visualized by epifluorescence (EFM) or confocal laser scanning –microscopy (CLSM). Additionally, the influence of biofilm formation and biooxidation of manganese by *L. discophora* on the open circuit potential (OCP) and pitting potential (Epit) of stainless steel was measured using a 3 electrode setup. *L. discophora* grew well in biofilms on floating filters and on SS coupons and incorporated in both conditions Mn²⁺ in the form of MnO₂ from the bulk phase into the biofilm. OCP measurements of actively manganese-oxidizing biofilms on stainless steel showed a significant ennoblement of ≥ 200 mV.

S. Benfer, B. Straß, G. Wagner, W. Fürbeth

Manufacturing and corrosion properties of ultrasound supported friction stir welded Al/Mg-hybrid joints

Surface and Interface Analysis 48 (2016) 843-852

Friction stir welding (FSW) allows to join Al and Mg alloys, which could hardly be welded by other techniques. Within the project a modified FSW process was developed, which uses additionally submitted power ultrasound during the joining of the Al-cast and Mg-cast alloys with the aim to improve the stirring in the welded area and to eliminate the formation of brittle intermetallic phases as coherent layers which reduce the attainable strength of the joints. To understand the development of the microstructure in the bonding zone a detailed analysis has been carried out. The resulting microstructure may

influence the corrosion properties, which have been investigated by different methods. Voltapential differences between the base alloys and the welded area were measured with the Scanning Kelvin Probe. Electrochemical measurements (open circuit potential, impedance spectroscopy and potentiodynamic polarization) were carried out at different positions on the hybrid joints by using an electrochemical minicell (\varnothing 3 mm). This allows to observe the passivation behavior and corrosion activity of the base alloys and the nugget phase separately. As expected the Mg alloy exhibits a much stronger corrosion in sodium chloride solution than the Al alloy. In the transitional area between the Mg alloy and the nugget phase the overall corrosion rate strongly increases while the corrosion of the nugget is reduced at the expense of the Mg alloy. Differences between hybrid joints processed with and without ultrasound support are discussed.

F. Depentori, C. Forcellini, F. Andreatta, E. Marin, S. Maschio, F. Brunke, C. Siemers, L. Fedrizzi, W. Fürbeth

Oxidation of Neodymium Precipitates in a Ti6Al4V2Nd Alloy in Sodium Chloride Solution

Materials and Corrosion 67 (2016) 277-285

The corrosion properties of a neodymium modified titanium alloy, Ti6Al4V2Nd were investigated in 1.5wt% NaCl and compared with Ti6Al4V. The modified alloy contains neodymium precipitates mainly located at grain boundaries. Ti6Al4V2Nd differs in corrosion behavior from Ti6Al4V by the oxidation of the neodymium precipitates. Electrochemical investigation by polarization measurements and cyclic voltammetry indicate that the precipitates undergo an oxidation process in the early stages of exposure. This is confirmed by SEM investigation and atomic force microscopy (AFM) investigation. Scanning Kelvin probe force microscopy (SKPFM) and electrochemical AFM (EC-AFM) investigation were used to investigate localized corrosion phenomena. SKPFM shows clearly a high Volta potential difference between the precipitates and the matrix, indicating that the precipitates act as local anodes during corrosion. EC-AFM shows that during exposure to NaCl solution the precipitates undergo a strong change in height, owing their oxidation with subsequent formation of an oxide or oxyhydride due to their low stability in NaCl solution.

A. Anthes, O. Harper, W. Fürbeth

Erzeugung Nanofaser-verstärkter Ceroxidschichten auf AZ31

*Jahrbuch Oberflächentechnik, Band 72, Eugen G. Leuze Verlag KG,
Bad Saulgau (2016) 60-69*

The automotive and aerospace industries demand on more lightweight materials to make their vehicles more energy efficient and environmentally friendly. Vehicle components made of steel or aluminum may be replaced in the future by parts made of magnesium alloys. A new surface preparation for the magnesium alloy AZ31 was developed, which can produce very clean, smooth and mirror like surfaces. The method outlined is also characterized by its simple application. The surfaces were investigated with AFM and SEM measurements. In addition, ultrasonically prepared aqueous cerium(III)nitrate dispersions containing nanoparticles were investigated by dynamic light scattering (DLS) for the subsequent conversion step. The prepared sample sheets have a nearly crack-free nanofiber reinforced cerium oxide layer generated by using ultrasound. The coatings were analyzed by XRD, SEM and Raman spectroscopy. In the focus of future work, the coatings are intended to be electrochemically characterized (electrochemical impedance spectroscopy) with addition of corrosion inhibitor loaded nanotubes, which release the inhibitor by a trigger.

V. Kuznetsov, S. Benfer, A. Tenié, W. Bleck, W. Fürbeth,
Mehrschichtiges Zunderschutzsystem für presshärtbare Stähle,
DE 10 2016 115 746.5, angemeldet am 24.08.2016
EP 17185771.7, angemeldet am 10.08.2017 mit Priorität 24.08.2016

Die vorliegende Erfindung bezieht sich auf ein mehrschichtiges Schutzschichtsystem für Stähle, das als Zunderschutzsystem bei Temperaturen unter 975°C dienen kann und aus verschiedenen nanopartikulären Oxidschichten besteht.

For further information, also to completed projects or about the DECHEMA-Forschungsinstitut, please visit: www.dechema-dfi.de

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