Materiale- og overfladeteknologi

Materials and Surface Engineering

Student projects Spring 2016

The section for Materials and Surface Engineering has expertise in many aspects of materials science and engineering and covers disciplines as materials synthesis, materials solutions, materials characterisation, materials performance and materials modelling. The section consists of 9 faculty staff and teaches and researches in topics covering fundamental materials science as well as innovative materials engineering solutions. Within the section three broad titles cover the many activities.

Surface engineering and materials design

Surface engineering is the major materials synthesis activity in the section and for this purpose electrochemical, thermochemical and PVD techniques are applied and further developed. The research activities in surface engineering cover the entire chain from basic research of generic importance to applied research, engineering and innovation.

Microstructure evolution and phase transformations

Materials microstructure evolution during processing as well as during application lies at the very essence of understanding the relations between process parameters, properties and performance. Understanding the occurring microstructure evolution and phase transformations in materials forms the basis for materials modelling activities.

Materials performance and degradation

Research in materials performance and materials degradation is concentrated on corrosion, tribology and high temperature performance (creep and corrosion), i.e. the chemical, biological, mechanical and thermal interaction (or combinations thereof) of materials with the environment. The strategy is to investigate, identify and understand the degradation mechanisms that affect the performance of materials and to use this understanding to predict the life expectancy and design of improved materials solutions.

Currently, we focus on materials for (sustainable) energy applications and materials in medical applications. We have a broad international network of collaboration within academia and industry.

Faculty staff:

Marcel A.J. Somers- head of section
Per Møller
John Hald
Rajan Ambat
Andy Horsewell
Seunghwan Lee
Karen Pantleon
Wolfgang Pantleon
Grethe Winther

Biophysics, biomechanics, and biotribology of mucins and mucus gels

High temperature exposure of superheater tubes for thermal power plants

Hydrogen in superheater tubes and its influence on steam oxidation in thermal power plants

Optimization of a dual phase model alloy

Refinement of Si containing ferritic alloys for applications in biomass fired power plants

Electropolishing failures in the pharma and biopharma industries

Nano-indentation of individual grains - to control strength and formability of metals

Improved materials for fusion reactors

Monitoring fatigue in fcc metals by X-rays

Intrinsic versus enforced anisotropy in plastic deformation of single crystals

Mapping the microstructural path

Corrosion of materials in oil and gas applications

Climatic reliability of electronic devices

Surface modification of aluminium alloys

Corrosion protection of electronic devices: Sulphur corrosion

Development of porosity in iron-nitrides

Application of cryo-treatment for a new generation of martensitic stainless steels

Investigation of reverse austenite formation in stainless steels

Effect of externally applied stress on layer growth kinetics during carburizing

Surface hardening of titanium alloys

Pack cementation aluminizing; co-deposition of active elements

Development of irregular white etching cracks in bearings for wind turbines

Long-term microstructure stability of 12%Cr steels in Danish power plants

High N martensitic steel for high temperature steam turbines

Coatings resistant against high temperature biomass induced corrosion

Microstructural evolution in centrifugally cast high temperature austenitic alloys

Development of anodic electrodes for alkaline electrolyzers

Development of cathodic electrodes for alkaline electrolyzers

Sol-Gel based dense silica-quartz coatings for the corrosion protection of aluminium

Liquid phase deposition of sililca-quartz for the corrosion protection of metallic substrates

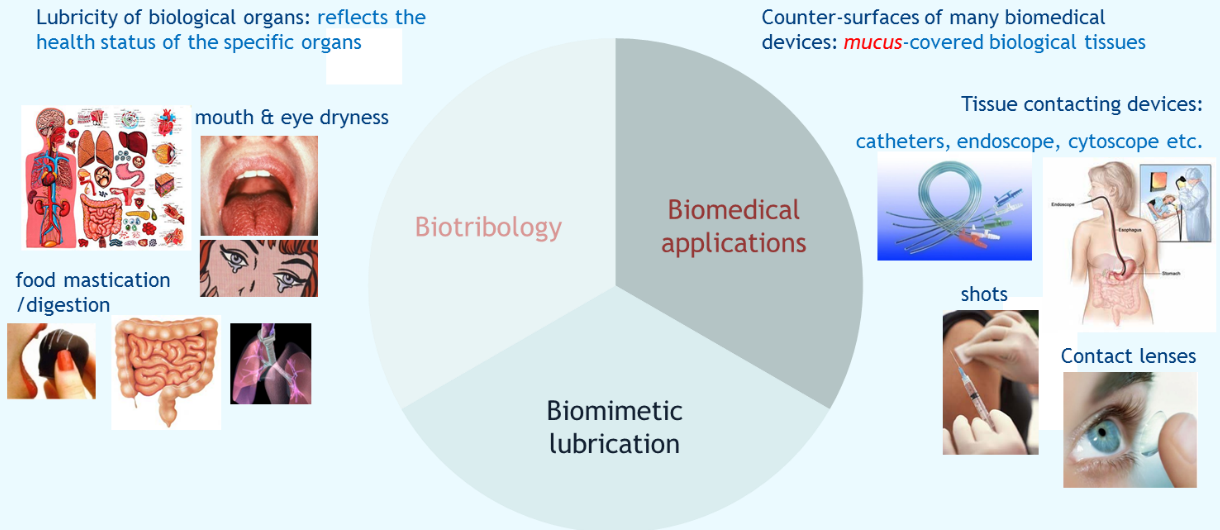
Materials and Surface Engineering
Department of Mechanical Engineering

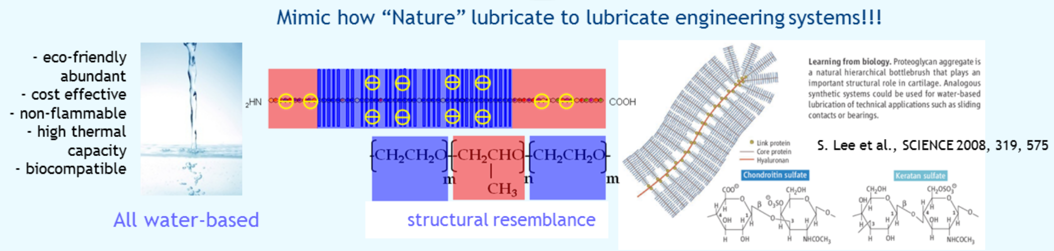
DTU

Biophysics, Biomechanics, and Biotribology of Mucins and Mucus Gels

Supervisor: Seunghwan Lee (seele@mek.dtu.dk, Tel: 4525 2193)

The lubricity of mucus gels/mucins are often considered granted. However, systematic scientific researches and understanding of this topic is surprisingly scarce to date. The significance of lubricity of mucin/mucus gels is mainly three-folded; (1) Biotribology: "good lubricity" by mucus layers often indicates the state of health in respective organs; for instance, impaired lubricity of mucus gels leads to discomfort in eye blinking, dryness in oral cavity and disturbed mastication, several airway diseases (asthma), digestion problems in stomach, etc. (2) Biomedical applications: in the application of various biomedical devices and personal care products, in particular, tubular tissue-contacting devices such as catheters, endoscopes, and cytoscopes, and contact lenses, counter surfaces that interact with them are mucus-gel-covered, soft biological tissues. Thus, it is of prime significance to understand the fundamental lubrication properties of mucus layers for optimum operation of such devices. In turn, it can provide many useful hints on how to tailor the surface properties of the medical devices for most favorable interaction with the biological tissues. (3) Biomimetic lubrication: efficacy of the lubrication by mucus gel layer is remarkable when it is considered that the base lubricant employed in biological systems is water; while many previous studies have shown that surface-adsorbing, brush-forming polymers behave as good aqueous lubricant additives, mucus gels can provide even more powerful approaches to utilize water as lubricant.





Multiple bachelor and master projects are currently available with diverse focuses on biophysics, biomechanics, and biotribological properties of mucins and mucus gels, depending on the specific interests of students.

various aspects of

High temperature exposure of superheater tubes for thermal power plants

Supervisors: **Karen Pantleon (kapa@mek.dtu.dk),**
Melanie Montgomery (mmon@mek.dtu.dk)

The lifetime of superheater tubes in thermal power plants depend on the materials long-term response to the high temperature exposure at the simultaneous presence of an (aggressive) chemical environment. High-temperature corrosion is of significant importance for both traditional coal-firing plants and for the changeover to (co-)firing of biomass, where the materials have to meet additional challenges.
For understanding the mechanisms of occurring surface modifications, systematic studies of high-temperature corrosion under well-controlled laboratory conditions mimicking real industrial exposure are required. Results from lab-scale experiments can be supplemented with industrial samples obtained after long-term exposure in Danish power plants.

Various BSc or MSc projects are offered, where each of the projects can address one or more of the following issues (specific content and corresponding time frame can be adapted as needed):

1. **The influence of thermal cycling on high-temperature corrosion**, mimicking conditions of shut-down and running-in periods as well as temperature variations during day and night.

2. **The influence of various gas atmospheres** (e.g. CO_2, C_2H_2, CO, chlorine containing gases as relevant for biomass firing and combinations of gasses).

3. **The effect of type and particle size of a synthetic deposit** applied on the surface for mimicking biomass firing in relevant gas atmospheres during high temperature exposure.

4. **In-situ analysis of oxide growth and phase transformations during high-temperature exposure** by means of in-situ microscopy and in-situ X-ray diffraction techniques.

5. **Depth-resolved analysis of corrosion products** including microstructure and phase analysis by successive layer removal of the exposed steel tube.

All projects require literature study and a lot of experimental work, including high-temperature corrosion experiments and materials characterization (microscopy, diffraction, spectroscopy).

Hydrogen in superheater tubes and its influence on steam oxidation in thermal power plants

Supervisors: **Karen Pantleon (kapa@mek.dtu.dk),**

Melanie Montgomery (mmon@mek.dtu.dk)

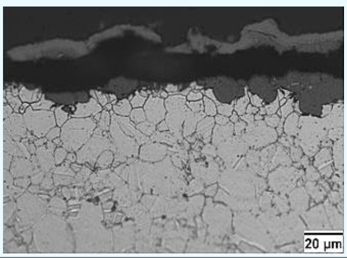
Steamside oxidation of superheater tubes applied in thermal power plants can cause serious problems, because oxide spallation can result in blockage of the loops and cause insufficient steam flow through the superheater and, consequently, overheating and failure of the tube.
It is anticipated that the presence of hydrogen in steel, originating from hydrogen dissolution during service conditions in the power plant, affects the rate of oxidation on the steamside of the superheater tubes.

The effect of hydrogen in steel is often directly related to the loss of ductility, i.e. hydrogen induced embrittlement. However, the role of hydrogen can be manifold and includes, for example, the initiation of phase transformations, changes of crack growth, localization of plastic deformation, weakening of interatomic bonds, changes in the type, number and interaction of lattice defects. All these hydrogen induced changes, indeed affect the mechanical properties and enhance embrittlement, but simultaneous influences by a certain chemical and thermal environment may further explain the effect of hydrogen on the lifetime of steel in these conditions.

A student project (MSc or BSc) aims to contribute to understanding the mechanisms of steam oxidation in hydrogen containing austenitic superheater tubes. The project requires thorough literature study and comprehensive experimental work including various aspects, as for example:

- systematic hydrogen-charging of austenitic steel (electrochemical treatment compared to thermal treatment in a furnace)
- stability over time as a function of thermal and/or mechanical influences
- testing of hydrogen loaded samples (mechanical tests, chemical analysis),
- high-temperature exposure of samples with and without hydrogen to steam oxidation conditions in laboratory furnaces at industrial relevant conditions,
- microstructure characterization of the near-surface region applying microscopic, spectroscopic and diffraction techniques, with particular focus on hydrogen-induced phase transformations and the evolution of internal stresses.

(note: the content will be agreed according to the type and time frame of projects):



Optimization of a dual phase model alloy

Supervisor: Karen Pantleon (kapa@mek.dtu.dk)

The development of advanced methods for materials characterization often requires well defined, simplified materials both for testing purposes and fundamental materials investigations.
For example, for understanding the elastic and plastic deformation behaviour of multiphase materials on the sub-micron scale, a copper-iron alloy is considered a suitable model system.

As copper and iron are practically immiscible at room temperature, the resulting microstructure of the iron-copper alloy will consist of well-separated regions of copper and iron. These two single phases with their specific crystal structure (FCC copper and BCC iron) represent an interesting combination of essentially different mechanical properties within the multiphase material.

The project aims at

– the **synthesis of such a model alloy** consisting of 50wt% Cu and 50wt% Fe

and

– the **optimization of the internal structure** of the alloy with special focus on a homogeneous distribution of the two phases and uniform grain sizes in the range of only a few micrometers up to several tenths of micrometers.

The practical work involves, in addition to appropriate heat treatment procedures, thorough analysis of the microstructure applying various microscopic techniques (light and electron microscopy) and X-ray diffraction for the phase-specific determination of preferred crystallographic orientations of grains and internal lattice strain.

The project is meant to be a MSc project, but parts of it can be formulated as a BSc project, if requested.

Refinement of Si containing ferritic alloys for applications in biomass fired power plants

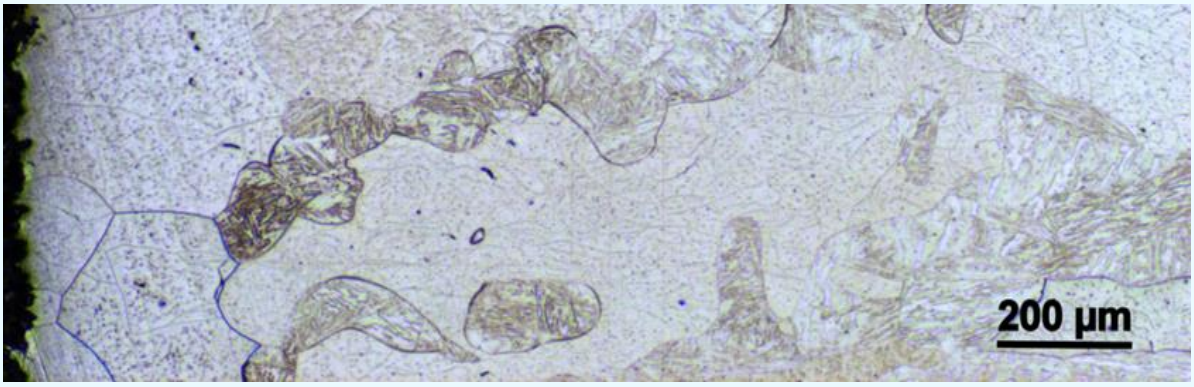
Supervisors: **Karen Pantleon (kapa@mek.dtu.dk),**

Matteo Villa (matv@mek.dtu.dk)

As renewable energy source, biomass becomes more and more attractive for replacing traditional coal firing in thermal power plants. However, during combustion of biomass, superheater tubes are exposed to oxidizing atmospheres containing aggressive solid and gaseous species, e.g. KCl, HCl and SO_2. The resulting more severe corrosion attack when (co-)firing biomass compared to traditional fossil fuels is currently limited by reducing the steam temperature in the plant, which, however, also reduces its efficiency. For full exploitation of biomass combustion with increased plant efficiency and lifetime despite the aggressive conditions, new materials solutions solving the tremendous high temperature corrosion problem are required.

Recent research indicates Si containing ferritic stainless steels as possible candidates for extending the service temperature of metallic materials in oxidizing atmospheres containing aggressive chemicals.
In Fe-Cr-Si alloys, passivation against high temperature corrosion under biomass firing conditions can be obtained by the formation of a continuous silica SiO_2 healing layer underneath the typical chromia layer Cr_2O_3 at the surface. Formation of such protective double oxide layers requires diffusion of the alloying elements from the bulk towards the surface, which strongly depends on the microstructure.
Present alloys obtained by casting reveal an extremely coarse microstructure, which is particularly unfavorable to promote diffusion of alloying elements to the surface. Classical routes for obtaining grain refinement recently revealed, at least, local SiO_2 formation, but a continuous protective oxide layer is not obtained yet.

In the present project (MSc or BSc), refinement of the microstructure near the surface should be obtained by an unconventional route, consisting of promoting a series of phase transformations in the material by changing its chemistry during heat treatment. The proposed process consists in high temperature solution nitriding/denitriding and carburizing/decarburizing of the material, which is expected to promote continuous grain refinement by alternatively stabilizing (and forming) different phases. Final exposure of the refined microstructure to conditions mimicking biomass firing will be used to evaluate applicability of the alloy as superheater in thermal power plants.



Electropolishing failures in the pharma and biopharma industries

collaboration with the Innovation Factory

IPU

Supervisors: Mikkel Østergaard Hansen (moh@ipu.dk),
Karen Pantleon (kapa@mek.dtu.dk)

Background:

In the pharma and biopharma industries, high requirements are made for both cleanliness and no cross-contamination from process equipment. Hence, electropolished austenitic stainless steel is often the material of choice for such equipment. The benefits of the electropolishing surface treatment are primarily reduced/smoothed surface topography, iron depletion and chromium enrichment of the surface, dissolution of surface contaminants and detrimental inclusions, increased corrosion resistance etc.

Problem:

Normally electropolishing is a robust and well tried process yielding good and consistent results on most austenitic steels. This is however not always the case, and sometimes the electropolishing process results in surface defects. These defects are usually manifested as hazy or streaky marks on an otherwise reflective finish and can typically be related to unwanted microstructural features in the steel such as banding of delta ferrite due to segregation, inclusions, carbides etc.
In some occasions, however, the observed defects manifest themselves as large macro-scale roughness. The reason for this phenomenon has not been explained yet and is almost exclusively observed on hot rolled sheets.

Project aim:

The project aims at identifying the underlying mechanism responsible for the observed surface appearance.
The practical work involves thorough analysis of the microstructure applying various microscopic techniques (light and electron microscopy) and X-ray diffraction for the phase-specific determination of preferred crystallographic orientations of grains and internal lattice strain.

The project can be formulated according to the education (BSc / MSc) and timeframe of the involved student(s).

Nanoindentation of individual grains - to control strength and formability of metals

Supervisor: Grethe Winther (grwi@mek.dtu.dk)

Background:

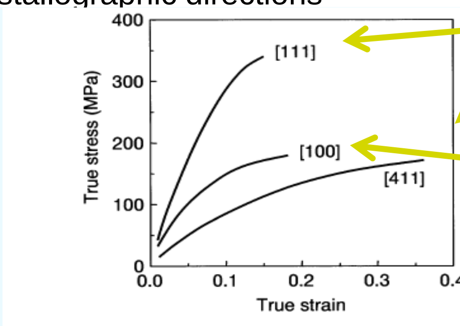
The strength of crystals depends strongly on the deformation direction with respect to the crystallographic lattice. Most metals consist of grains with differently oriented lattices. Hardness, elastic modulus and yield stress of individual grains can be determined by means of nanoindentation: A diamond tip is pressed into the metal surface and the force-displacement curve recorded for subsequent analysis. Plastic deformation (cold-working) of metals makes them stronger but also less ductile. The response of each grain is, however, different. Knowledge of the behaviour of individual grains is a key tool to tailor the polycrystalline metal for specific applications.

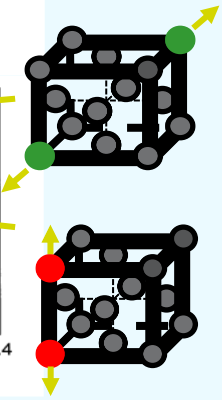
The project:

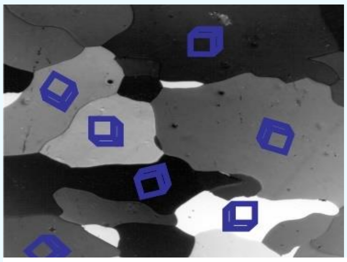
Mechanical differences between individual grains in deformed metals should be probed and correlated with the crystal orientation and the plastic strain. The aim is to establish hardening laws at the grain scale and to explain the mechanical behaviour of large samples consisting of thousands of grains.

The project can be adapted according to the study type (diploma, BSc, MSc) and the number of students by the choice of samples and inclusion of modelling.

Tensile properties along specific crystallographic directions



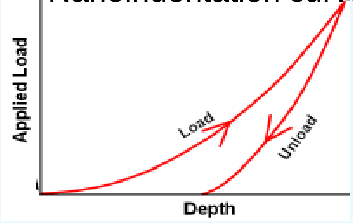


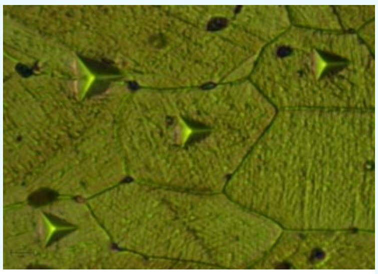


Optical micrograph of grains with differently oriented crystal lattices

Nanoindentation equipment

Nanoindentation curve



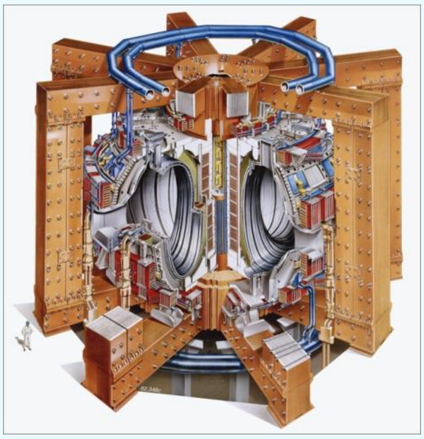


Indents in individual grains

Improved materials for Fusion Reactors

Supervisor: Wolfgang Pantleon (pawo@dtu.dk)

One of the key issues in building fusion reactors is the selection and development of materials being able to withstand high temperatures as well as high mechanical and radiation load which alter the microstructures of the materials during service. The suggested projects will focus on the microstructural property relationships of materials relevant for fusion reactors.



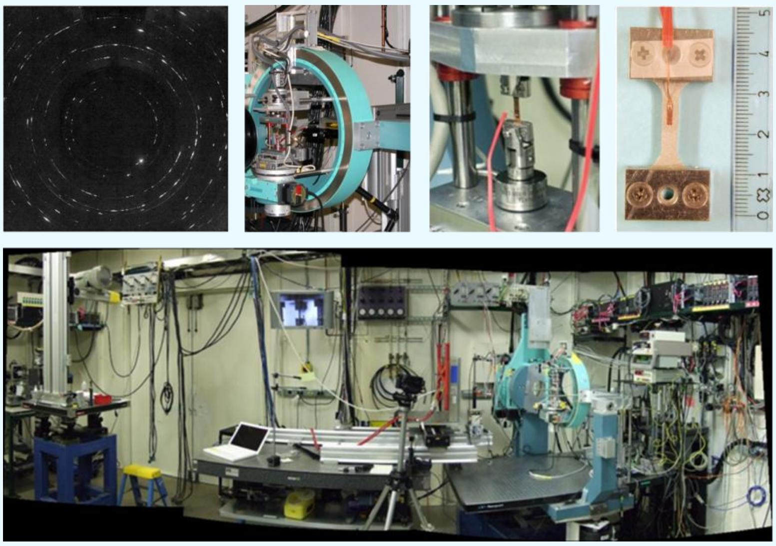
Tungsten and tungsten alloys are considered as preferred candidate for the plasma facing first wall material of fusion reactors. In service, the materials have to withstand high temperature (and radiation loads) altering their microstructure. The replacement of the instable microstructure leads to degradation of the mechanical properties as a loss in strength. The aim of the project is to investigate the thermal stability of differently processed tungsten with focus on the mechanisms (recovery and recrystallization) relevant for property degradation. Additionally, the mechanical properties of the as-processed material as well as after heat treatment will be analyzed.

Monitoring fatigue in fcc metals by x-rays

Supervisor: Wolfgang Pantleon (pawo@dtu.dk)

During plastic deformation of metals, the defects carrying plastic deformation are stored in dislocation walls separating dislocation-free subgrains. These emerging structures require applying higher and higher loads for continuing deformation (work-hardening) and, eventually, cause failure. A peculiar type of deformation occurs during fatigue when the sense of the deformation is reversed repeatedly. Even small plastic strains applied repeatedly e.g. in tension compression cycles cause formation of ordered dislocation structures which after a large number of cycles eventually lead to failure.

The evolution of dislocation structures during cyclic deformation can be monitored *in-situ* by X-ray diffraction. High-energy x-rays available at synchrotron sources provide bulk penetration and the opportunity of *in-situ* monitoring microstructural evolution under realistic conditions. Individual subgrains can be identified in high resolution reciprocal space maps from their characteristic high-intensity peaks and followed during repeated cycles.



Aim of the project is to analyze and quantify the microstructural changes occurring during fatigue of fcc metals. Preliminary data on copper have been taken already during 80.000 loading unloading cycles. Revealing the microstructure evolution by tracing individual subgrains during cyclic loading from the maps will shed light on their formation mechanism and further the insight in the initiation of failure.

DTU Mechanical Engineering
Department of Mechanical Engineering

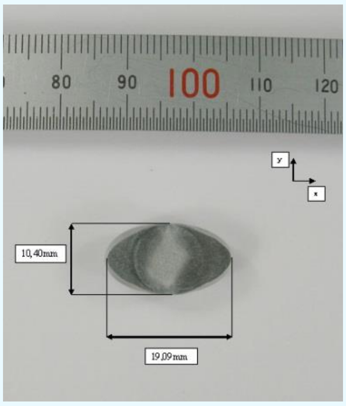
DTU

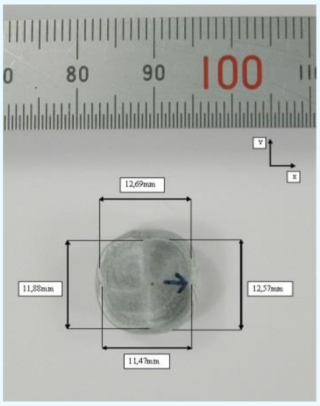
Intrinsic versus enforced anisotropy in plastic deformation of single crystals

Supervisor: Wolfgang Pantleon (pawo@dtu.dk)

Plastic deformation of polycrystals occurs by activation of multiple slip on five or more crystallographic slip systems in each grain. In this manner each grain can follow the imposed shape change.

In single crystals and very coarse grained materials, the individual crystals are not restricted in their shape change in a similar manner. In this way, the crystallites are able to deform by activating a lower number of slip systems. This leads to curios consequences as deviations from the original shape. For example, round cylindrical specimens of aluminum single crystals developed into elliptical cylinders or even more complicated geometries:





The development of shapes with lower symmetries is a result of a very specific selection of slip systems. The specific selection is an intrinsic feature not caused by boundary conditions. It is also reflected in the deformation structure as revealed by electron backscatter diffraction. Establishing of an intrinsic pattern of activated slip systems in individual grains has also consequences for the behavior of polycrystals and the understanding of their texture formation.

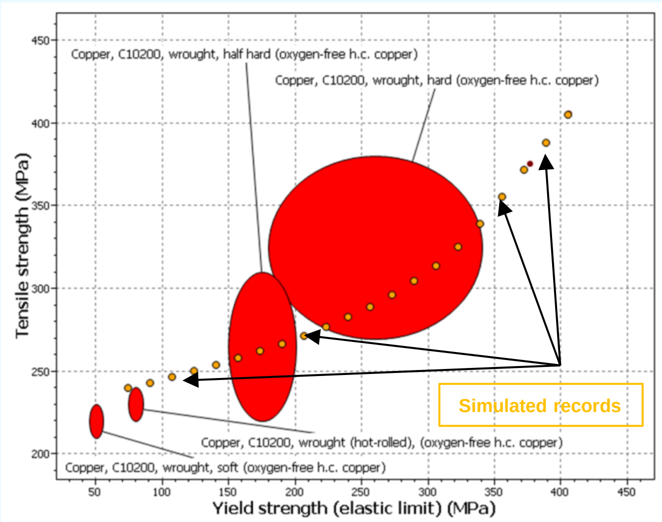
Aim of the project is to study the interplay of the intrinsic activation pattern with opposing boundary conditions. For that it is intended to build a setup allowing the performance of plain strain compression tests and performing such tests with single crystals of particular orientation.

Mapping the microstructural path

Supervisor: Wolfgang Pantleon (pawo@dtu.dk)

Materials selection for structural applications can be conveniently rationalized by means of material property maps reflecting mechanical, e.g. yield and tensile strength. Such maps can be constructed using the Cambridge Engineering Selector. For any given material, specific properties may vary within a certain range, but neither the physical origin of the variation, nor the influence of processing of a material on its properties is revealed. In this manner, insight in the enormous potential for tailoring properties is hindered.

In order to overcome this limitation, a composite-based approach has been developed to simulate the property changes due to thermo-mechanical treatment. As a first application, annealing of deformed metals is considered. During annealing, the hard material representing the deformed state is replaced by softer material representing the recrystallized state. Material resulting from any chosen annealing treatment leading to partial recrystallization of the metal can be simulated using the hybrid synthesizer as composite of material in the two states with respective properties. This approach cannot only be used to simulate the yield strength, under appropriate assumption, ultimate tensile strength and maximum uniform elongation of the partially recrystallized metal can be defined as well.



Such a modeling of microstructural changes in terms of a composite will be applied to other thermo-mechanical treatments leading to precipitation hardening, solid solution strengthening or grain refinement. Aim is to illustrate changes in the mechanical properties due to the microstructural evolution and trace their path in materials property maps.

Corrosion of materials in oil and gas applications

Supervisor: Rajan Ambat, DTU MEK

Co-supervisor: Magdalena Rogowska, DHRTC

Background:

Large number of materials are used in oil and gas applications. These materials should withstand highly corrosive conditions, which are observed in the topside and downhole conditions. The environment can be extremely aggressive, i.e. high pressures and temperatures, with CO_2 and/or H_2S and vigorous flow of fluids. Corrosion of materials is undesired as it risks the integrity of the pipes. Consequently, understanding of corrosion behaviour of various materials under extreme conditions with or without static or cyclic stresses is important.

Project aim:

A number of master level projects can be defined in this area based on the expertise of the student focusing on various aspects related corrosion and corrosion prevention. Key aspects are understanding the corrosion mechanisms of materials, corrosion scale formation, and the impact of chemistry on their corrosion behavior using lab scale experiments and simulated test rigs.

Internal corrosion in a crude oil pipeline

Practical experiences gained:

- Material use in oil and gas, and corrosion requirements
- Corrosion testing in general and specific to oil and gas conditions
- Experimental methods used for corrosion investigation and material analysis

The project is in collaboration with Danish Hydrocarbon Research and Technology Centre (DHRTC)

A number of Master/Bachelor project themes are available in this area in collaboration with DHRTC. Exact nature of the project and theme will be formulated in discussion with the interested students. Interested candidates, please contact:

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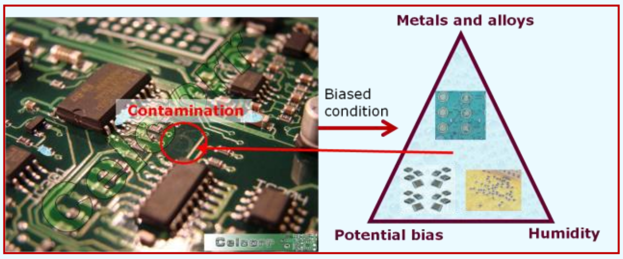
Magdalena Rogowska, mrog@dtu.dk

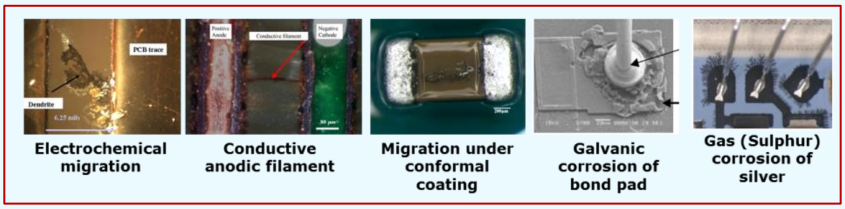
Climatic reliability of electronic devices

Supervisors: Rajan Ambat and Morten S Jellesen

Description

Climatic reliability of electronic devices has become an important issue due to the use of multimaterial combinations, potential bias, miniaturized devices, production practices, and wide spread use. At DTU-MEK, the "Centre for electronic corrosion (CELCORR, www.celcorr.com)" investigates various aspects of electronic reliability issues in collaboration with Vestas Windsystems, Danfoss, Grundfos, Velux, Widex, Bosch, etc. and many other electronic industries.





Schematic showing factors causing electronic corrosion and failure modes

A number of Master/Bachelor project themes are available in this area in collaboration with the industries mentioned above. Presently many master students are carrying out their proejct investigating various issues of climatic realibility in collaboration with above mentioned industries. Broadly the subject for the projects belongs to:

- **Climatic reliability issues of electronics in harsh environments**
- **Semi-emperical modelling of humidity inside electronic enclosures**
- **Climatic reliability issues of automotive electronics**
- **Corrosion prevention of electronic devices using conformal coatings**
- **Climatic Reliability modelling of circuit board design for early prediction**

Exact nature of the project and theme will be formulated in discussion with the students who are interested. Interested candidates, please contact:

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Morten S Jellesen, msj@mek.dtu.dk
Vadimas Verdingovas, vaver@mek.dtu.dk

Surface modification of aluminium alloys

Rajan Ambat, Morten Jellesen, V.C. Gudla

Description

Demand for light weight aluminium alloys are increasing due to the possibility of translating light weight into higher efficiency, fuel saving in transportation, and for envrionmental protection. However, efficient use of aluminium alloys for various applications requires high performance surfaces with various functionalities. These include ability to withstand corrosive environmental conditions, optical quality surfaces, wear resistant surfaces, anti-bacterial surfaces to name a few. Materials and Surface Engineering Division works on a number projects in this areas in collaboration with industries such as Sapa, Bang and Olufsen, Velux, research institutions namely DTI, TU Delft, VUB Brussels, and many other partners. The aim of the work is to produce aluminium surfaces with more functionalities, which could replace a number heavy structural materails used in various technological applications.

A kilo of aluminium, used as a substitute for heavier metals in car industry, reduces gas consumption by 8.5 liters and produces 20 kg less CO_2 emissions

A number of Master/Bachelor project themes are available in this area in collaboration with industries. Broadly the topics for project belongs to the following subjects:

- Optical quality surfaces on aluminium alloys (B&O)
- Microstructure and corrosion of aluminium alloys and painted profiles (Velux, Denmark)
- Microstructure and corrosion of heat exchanger components (SAPA, Denmark, Aluventa, Denmark)
- Surface modification of aluminium using steam (DTI, Denmark)

Exact nature of the project and theme will be formulated in discussion with the students who are interested. Interested candidates, please contact:

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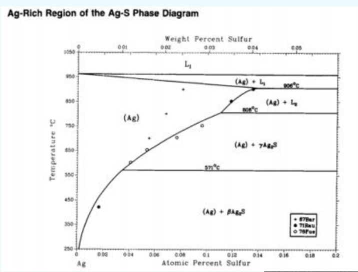
Morten Jellsen, msj@mek.dtu.dk or
V.C. Gudla, vichg@mek.dtu.dk

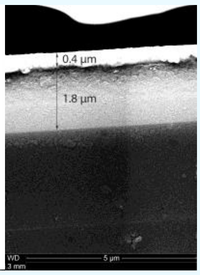
Corrosion protection of electronic devices: Sulphur corrosion

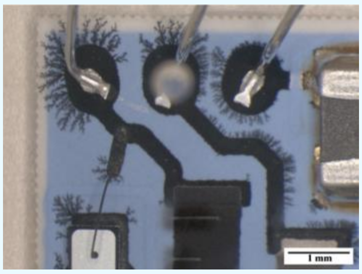
Supervisors: Morten S Jellesen, Rajan Ambat, Vadimas, Verdingovas, Svava Davíðsdóttir

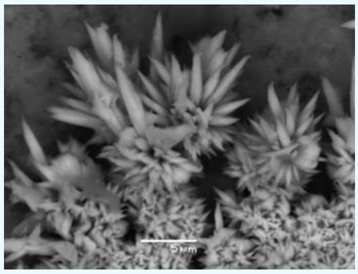
Background:

Environmental conditions such as humidity, temperature, contamination and gases affect the reliability and lifetime of electronic products. Sulphur polluted environments include regions near volcanic activity, pig farms, rubber manufacturing plants, oil refineries, coal-generation power plants, paper and pulp industry. Failure analysis of electronic products exposed to an environment containing sulphur gas typically show uniform corrosion and/or migration of silver and copper. The available coating is not always the adequate countermeasure against sulphur induced corrosion since gases can permeate through currently used coatings and react with metals at the printed circuit board especially silver, copper and alloys hereof.









Project aim:

To incorporate sulphur -sink /-degrations nano particles into new silicone based coating, and thereby to reduce the permeability of corrosive gases and water through the coating.

The project aims to design and characterize new coatings for Sulphur corrosion protection, and test the coatings in actual applications.

Practical experiences gained:

- Electronic corrosion; especially Sulphur corrosion related failure mechanisms and countermeasures
- Test methods employing use of climatic/gas chambers relevant to electronic corrosion testing
- Use electrochemical methods to characterize water/corrosive gas uptake into the coatings
- Sample characterization using scanning electron microscope (SEM) and X-ray Diffraction (XRD)

The project is in collaboration with HEMPEL.

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Development of porosity in iron-nitrides

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Description

Porosity in iron-based nitrides is a well known by-product during nitriding and nitrocarburirizing of steels. The driving force for such porosity has been recognized to be the thermodynamic meta-stability of iron nitrides with respect to pure iron and pure nitrogen gas. In this sense porosity could be interpreted as the precipitation of nitrogen gas in the solid state. So far, the actual scientific evidence for N_2 filled pores is missing; all evidence is circumstantial. The present project focuses on proving that N_2 formation is the origin of porosity. Furthermore the kinetics of the precipitation of N_2 will be investigated.

Theoretical work

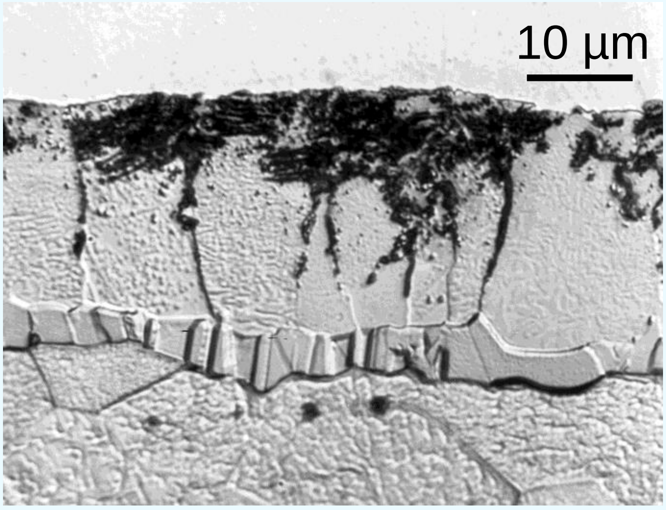
Literature study on porosity and critical evaluation of the various hypotheses put forward to explain this phenomenon. Thermodynamic calculations of the driving force for N_2 development in relation to composition of iron (carbo)nitrides.

Practical work

Synthesis of homogeneous iron nitrides with different nitrogen (and carbon) contents.

Kinetic analysis of decomposition of the (carbo)nitrides with thermogravimetry and differential scanning calorimetry.

Identification of N_2 as precipitates in the solid state with diffraction and or spectroscopic techniques.



Application of cryo-treatment for a new generation of martensitic stainless steel

Marcel A.J. Somers (somers@mek.dtu.dk)

Thomas L. Christiansen (tch@mek.dtu.dk)

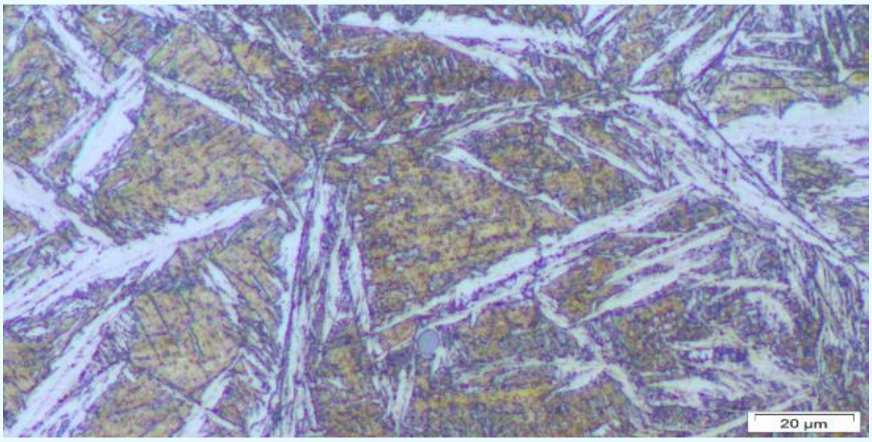
Matteo Villa (matv@mek.dtu.dk)

Description

When commercially available martensitic stainless steel were developed, their chemical composition was tailored to obtain a fully martensitic structure at room temperature. Martensite formation occurs at a lower temperature the higher the content of alloying element. In stainless steels, the requirement of martensite formation limits the alloying possibilities to a relatively low content other then the 12%Cr necessary to reach stainless characteristic. The scope of the research activity in our group is to investigate how cryo-treatments, i.e. heat treatment performed well below zero degrees Celsius, can be applied to develop new alloys with superior performance in aggressive conditions requiring high mechanical performances. In particular, this project will focus on alloying commercially available stainless steel with additional C in order to obtain particularly hard stainless steel grades.

Practical work

- **addition of C by thermo-chemical treatment of 3 commercially available martensitic stainless steel containing 13%Cr, 15%Cr and 17%Cr, respectively.**
- **application of different cryogenic treatments to form martensite (ex. storage in dry ice / boiling nitrogen / at -40C);**
- **investigation of material microstructure and properties (hardness measurements, XRD, microscopy) also in connection with additional heat treating (i.e. tempering).**



Investigation of reverse austenite formation in stainless steels

Marcel A.J. Somers (somers@mek.dtu.dk)

John Hald (jhald@mek.dtu.dk)

Matteo Villa (matv@mek.dtu.dk)

Description

Dual phase stainless steels containing ferrite and austenite, i.e. duplex stainless steels, are extremely resistant to corrosion. Their chemical composition is tailored to obtain a dual phase microstructure in equilibrium conditions at high temperatures. Good mechanical properties are obtained by work hardening. The applicability of such steel grades is in the temperature range -50˚C to 300˚C.

The aim of the present project is to consider a different approach to the preparation of dual phase microstructures. Commercially available martensitic stainless steels will be austenitized at high temperatures. Thereafter, austenite will be transformed into martensite by cooling. Finally, dual phase microstructure is obtained by partially reverse formation of austenite and simultaneous tempering of the martensite and partition of the chemical elements upon reheating and isothermal holding at intermediate temperatures.

This approach is expected to yield materials with mechanical properties which are superior to currently available duplex stainless steels and with long term applicability at temperatures as high as 400˚C. On the other hand, at present nothing can be said on their resistance to corrosion in different environments.

Practical work

- preparation of the material and decarburization in hydrogen;
- austenitization at high temperature and following formation of martensite on cooling to room temperature;
- reverse austenite formation. In situ investigation of reverse austenite formation by Magnetometry (DTU nanotech) will be considered;
- investigation of the microstructure by SEM and XRD. Additional investigation by EBSD (DTU-CEN) will be considered;
- investigation of hardness and corrosion resistance in different environments.

Effect of externally applied stress on layer growth kinetics during carburizing

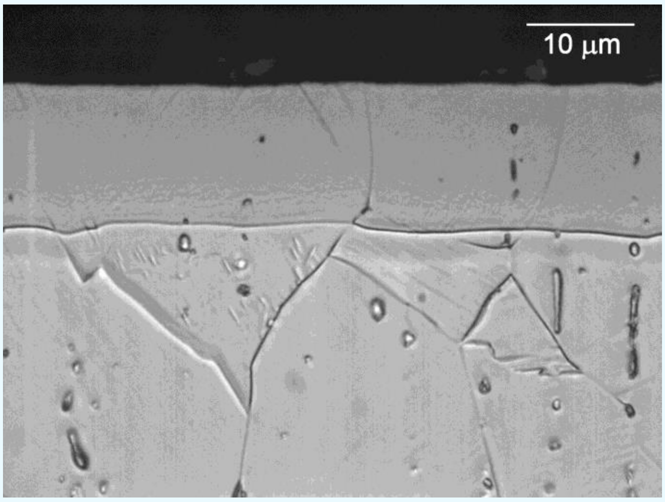
Supervisors: Marcel A.J. Somers (somers@mek.dtu.dk)

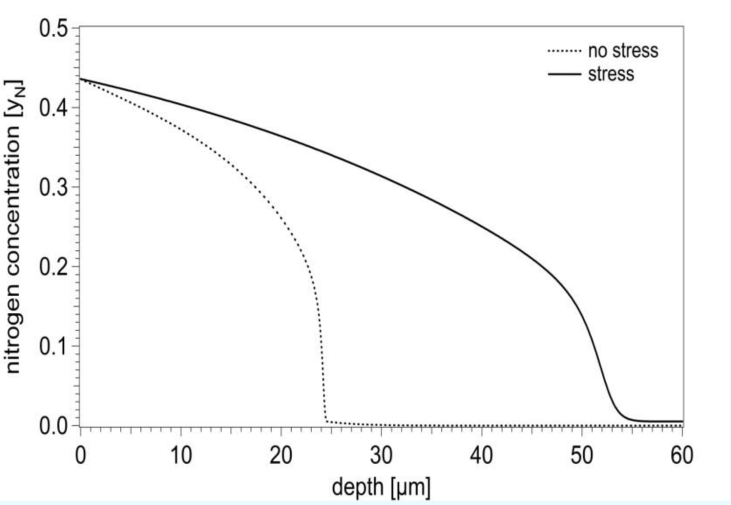
Carburizing is a thermochemical surface engineering process, where the composition of an alloy is deliberately modified in the surface region through the reaction of components from the workpiece with components from an external source at enhanced temperature. It is a widely applied surface treatment of in particular ferrous materials, to improve materials performance with respect to wear, corrosion and/or fatigue.

Carburizing causes compressive stresses in the treated zone, which arise from the volume changes that accompany the dissolution of carbon in the solid state or the occurring transformations. These stresses influence the diffusion of carbon by which the carburized zone is developing. It is the purpose of the present project to investigate the influence of externally applied stress on the growth rate of the carburized zone by experimental work. The data will be compared with a numerical model that is currently under development.

The experimental work consists of:

- **designing a device to apply an external load**
- **gaseous carburizing experiments on stainless steel**
- **metallographic characterization of the microstructure with microscopy and hardness indentation**
- **determination of carbon concentration profiles with Glow Discharge Optical Emission Spectroscopy**
- **Stress measurement with X-ray diffraction.**





Surface hardening of titanium alloys

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Morten S. Jellesen (msj@mek.dtu.dk)

Description and motivation

The increasing number of implants, joint replacements and revisions due to adverse body reactions represent an enormous socioeconomic challenge. Up to 20% of the patients undergoing a hip-joint replacement develop peri-implant bone destruction within 10 years after surgery, necessitating revision and replacement surgery. Such implant failure is considered to be strongly correlated with metal release from the implant by corrosion and wear and metal-allergy towards implant components. Longer implant durability and longer lifespan are needed without the risk of rejection of the artificial joint implants. Tailored surface engineering of implants is expected to be an effective means of combating metal release due to corrosion and wear.

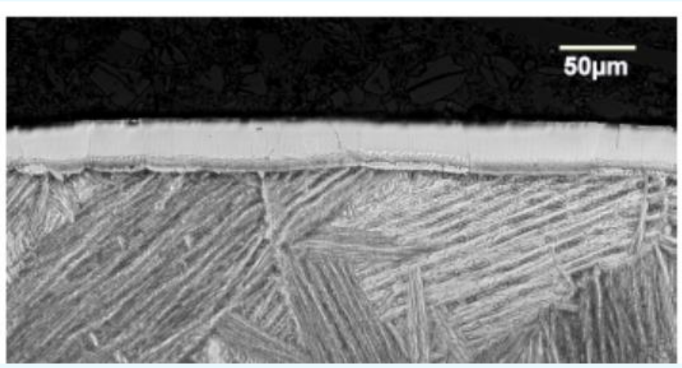
To this end newly developed thermochemical methods for surface hardening of titanium can be applied for improving the performance of such light-weight materials. Very high hardness and thick surface layers can be obtained by these new methods.

Theoretical work

Literature study on existing surface modification technologies used for titanium and titanium alloys.

Practical work

Gaseous thermochemical treatment of titanium and titanium alloys will be carried out various temperatures and in different gas mixtures. The hardened surfaces will be characterized by light optical microscopy, X-ray diffraction, microhardness and scanning electron microscopy. The corrosion resistance of the surface engineered materials will be tested by electrochemical characterization techniques (open circuit potential monitoring and polarization curves). Wear resistance will be investigated using a pin on disc sliding wear setup.



Pack cementation aluminizing; co-deposition of active elements

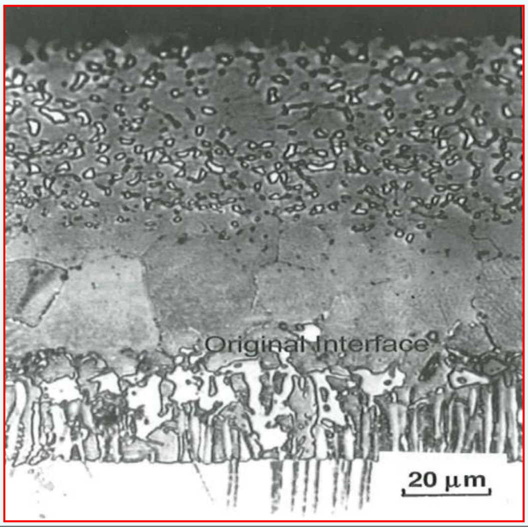
Supervisors: Thomas L. Christiansen (tch@mek.dtu.dk), Duoli Wu (duoliw@mek.dtu.dk) & Kristian V. Dahl (kvd@mek.dtu.dk)

Pack cementation is a versatile method to 'add' different metallic elements to the surface of steel components. The (powder) pack consists of an activator (e.g. halide containing compound), a metal source and a filler. Upon heating volatile metal-containing gaseous species of the active metal element are formed in the pack and the active metal can be diffused into the surface of the component to be treated. In the present project pack aluminizing will be investigated for protection of steels against high temperature corrosion in salt-containing environments. In-diffusion of aluminum gives rise to formation of various aluminides depending on the composition of the steel to be treated and the pack activity (chemical composition).

It is anticipated that improved high temperature corrosion resistance and enhanced thermal stability of aluminides can be obtained *by co-deposition of active elements*. The present project seeks to develop new powder pack aluminizing treatments for enhanced high temperature corrosion resistance. The project can/will contain the following /tasks:

- Tailoring of powder pack chemistry; this can entail use of thermodynamic modeling tools.
- Co-deposition aluminizing experiments in dedicated tube furnace.
- Investigation of process parameters
- Characterization of pack cementation treated steel components with light optical microscopy, scanning electron microscopy and x-ray diffraction
- Testing of treated components against alkali induced corrosion

FIGURE Aluminizing of a Ni-base alloy at low temperature and high Al-activity pack and subsequently heat treated. This has resulted in a layer of NiAl aluminide



Materials and Surface Engineering
Department of Mechanical Engineering

DTU

Development of irregular white etching cracks in bearings for wind turbines

The project is done in collaboration with Siemens Wind Power A/S

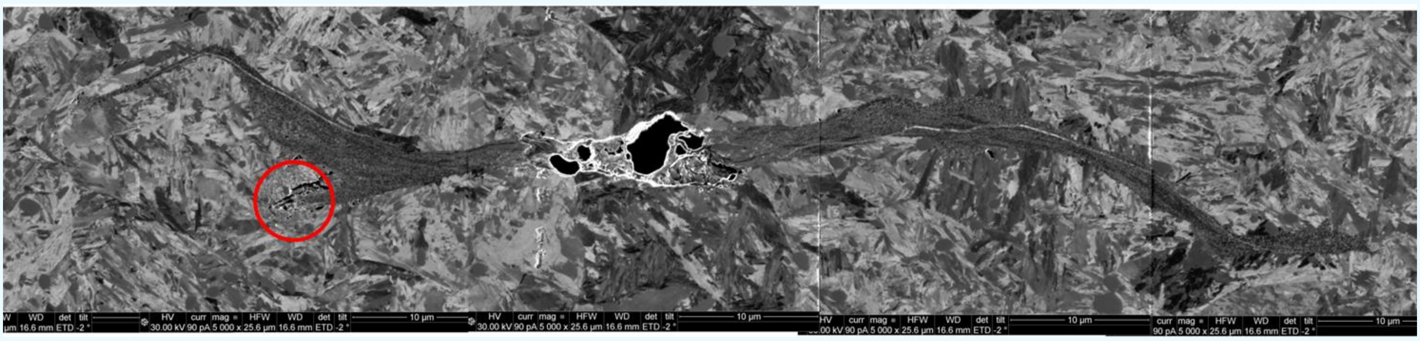
John Hald (jhald@mek.dtu.dk), **Kristian V. Dahl** (kvd@mek.dtu.dk)

One of the major failure manifestations found during metallographic inspections of bearings in wind turbine gears (WTG) is flaking associated with irregular cracks that are always accompanied by white etching areas; hence the name irregular white etching cracks (IrWEC). Such failures have been found to appear long before the predicted life of WTG bearings. There is no common consensus about the root cause for IrWEC formation in WTG bearings, but it is suspected that hydrogen entrance into the bearing steel plays a major role.

Recently IrWEC has been found to form in carburized martensitic bearings containing a high amount of non-martensitic transformation products. It has been hypothesized that the (unfavorable?) heat treatment leading to presence of the non-martensitic regions also has an influence on the kinetics of the IrWEC formation.

In the present project bearing steels containing both non-martensitic transformation products and large IrWEC networks will be investigated using state of the art microscopy techniques to investigate formation mechanism of IrWEC and if possible find a relation to the presence of the non-martensitic regions.

The microscopy techniques to be employed are scanning electron microscopy, ICCI and ECCI (Ion and Electron Channeling Contrast) combined with EBSD as well as transmission electron microscopy on thin foils prepared by lift out done using focused ion beam milling.



ICCI image of a branching "butterfly" in a martensitic bearing steel. A crack bordered by white etching regions has formed from a non-metallic inclusion. Is the branching the start of network crack formation?

Long-term microstructure stability of 12%Cr steels in Danish power plants

Supervisors: John Hald (jhald@mek.dtu.dk)

High temperature components in steam power plants are normally designed for a creep life of 200,000 hours (more than 20 years).

The 12%CrMoV martensitic steel known as X20CrMoV121 has been used for steam pipes in power plants since the mid 1960ies. A number of Danish power plants using this steel are now approaching the creep design life of 200,000 hours, but due to the energy transition there is a desire to maintain the steam pipes in operation for up to 300,000 hours.

This raises fundamental questions about the long-term stability of the microstructure, since long-term creep testing has only been performed up to 200,000 hours.

The project will address these questions by microstructure investigations of steel samples removed from steam pipes in Danish power plants after long-term service. The microstructure degradation of the steels will be investigated by light microscopy and electron microscopy (SEM and TEM) as well as assessment of the chemical compositions of the steels with thermodynamic equilibrium calculations.

The project is carried out in collaboration with the power companies DONG Energy and Vattenfall.

High N martensitic steel for high temperature steam turbines

John Hald (jhald@mek.dtu.dk)

Due to their high creep strength martensitic steels with 9-12%Cr are used for pipes, casings and rotors in steam turbines operating at temperatures up to 600ºC in thermal power plants.

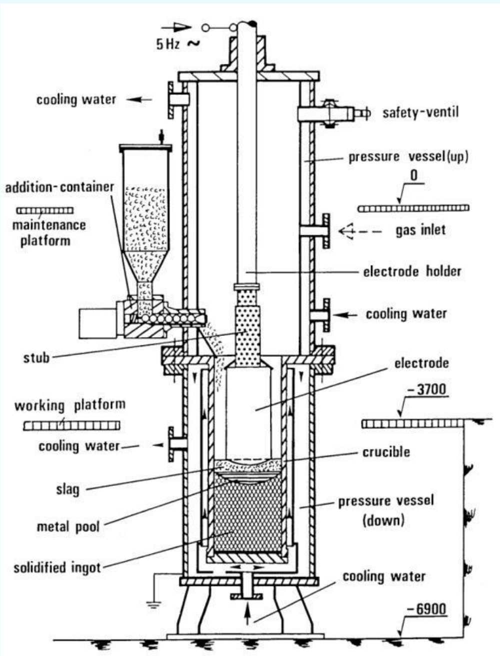
Ongoing research aims at improving the creep and oxidation resistances of such steels in order to increase operating temperatures up to 650ºC for better efficiency.

The high creep strength of the 9-12%Cr steels is to large extent achieved by precipitation hardening from a fine dispersion of nano sized nitrides in the martensitic microstructure. However, the amount of strengthening nitrides is limited by the solubility of Nitrogen in the steel melt. For N contents above some 0.08 wt % gas bubbles will form in the melt.

The present project explores the possiblities to increase the amount of nitrides by melting the steels under pressure. This allows N contents up to more than 0.2 wt %, and a similar increase of the amount of Nitrides in the steel.

The project will include investigations of the evolution of microstructure and hardness in high N steels during long-term exposure to high temperatures between 600 and 700ºC. Various microscope techniques can be applied including light microscopy and electron microscopy (SEM and TEM). Microstructure modeling of phase equilibria with Thermocalc can be included.

Steel samples will be delivered by Energietechnik Essen, who has equipment for pressurised casting of steels.



Materials and Surface Engineering
Department of Mechanical Engineering

DTU

Coatings resistant against high temperature biomass induced corrosion

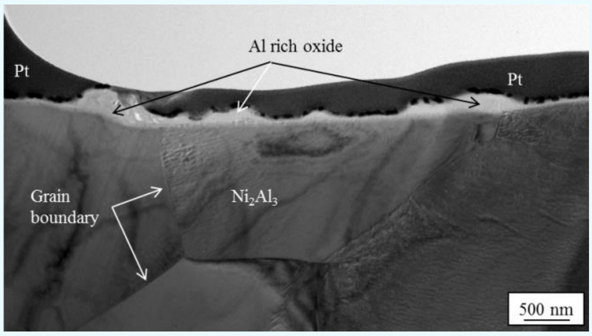
Thomas L. Christiansen (tch@mek.dtu.dk)& Kristian V. Dahl (kvd@mek.dtu.dk)

Alkali chloride induced corrosion is a key obstacle that must be overcome in order to improve the efficiency of biomass fired boilers. The goal is to increase the steam temperature from today's 540°C to 600°C. In order to obtain such an increase it is necessary to identify new materials since existing state-of-the art steels experience excessive corrosion rates above 540°C, severely limiting the life time of components such as superheater tubes.

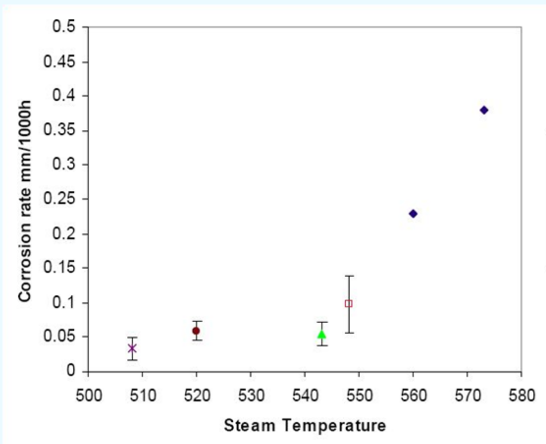
When firing with biomass, alkali chloride released during the combustion directly interacts with the otherwise protective Cr_2O_3 oxide, resulting in breakdown and non-protective behavior. Laboratory experiments indicate that Al_2O_3 shows a better protective behavior in the combustion environment, but very high Al contents are needed to facilitate the formation and stability of the Al_2O_3 oxide. Recently intermetallic Ni-Al coatings (i.e. Ni_2Al_3, NiAl) have been shown to have very low corrosion rates in laboratory tests but further tests are still needed.

The present project aims to develop the promising coatings and further explore their suitability towards alkali induced corrosion. The project will contain the following elements:

- Production of coatings by low temperature pack aluminizing
- Testing of coatings against alkali induced corrosion
- Introduction of a third chemical element to improve mechanical properties and/or further improve corrosion properties of the coatings
- Use of thermodynamic modeling tools to optimize pack chemistry, especially for Co-deposition
- Characterization before and after exposures, using light optical microscopy, scanning electron microscopy and x-ray diffraction



TEM image of thin Al-rich oxide formed on Ni2Al3 intermetalic during lab exposure at 600ºC. For the same exposure times, breakaway occurs for tested steels.



Corrosion rate of steel TP347HFG superheater tubes inserted in Danish biomass fired power plants as a function of steam temperature, cf. Montgomery et al. Materials and Corrosion, 2011.

Microstructural Evolution in Centrifugally Cast High Temperature Austenitic Alloys

The project is in collaboration with Haldor Topsøe A/S

John Hald (jhald@mek.dtu.dk), Kristian V. Dahl (kvd@mek.dtu.dk),&

Anette N. Hansson (annh@topsoe.dk)

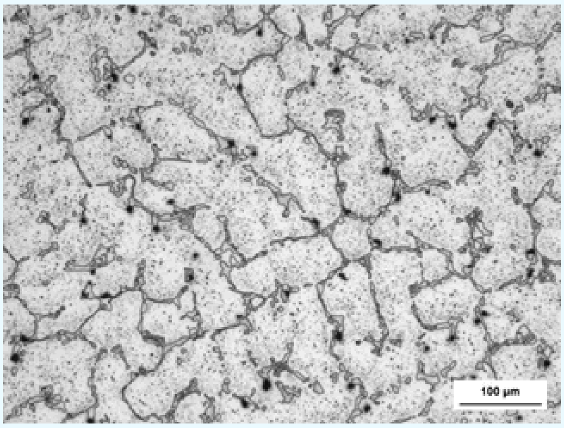
Centrifugally cast pipes made from high temperature austenitic alloys are widely used in steam reformers in petrochemical industries. The tubes are exposed to high temperatures (up to ~ 980 °C) and high pressure (up to ~ 40 bar) over a long period of time (10-15 years), therefore creep and thermal damage can be expected.

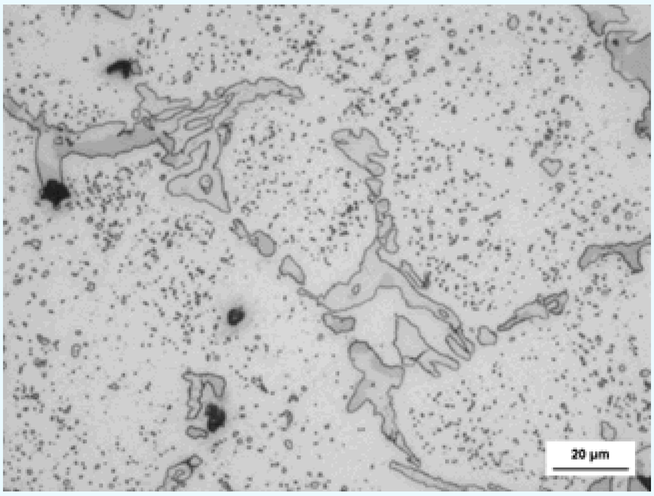
The alloys contain high amounts of Ni and Cr in order to ensure austenitic microstructure, high creep and corrosion resistance. Great improvement of the high temperature properties of the alloys has been achieved by small additions of other elements such as Nb, Si, Ti or Zr.

The as-cast alloy contains primary precipitates of Cr carbide that coarsen during the exposure at high temperatures. Furthermore, various types of strengthening precipitates in the as-cast alloy are dissolved and other larger precipitates are formed. This has a negative influence on the mechanical and creep properties of the alloys.

The aim of the project will be to study the evolution in microstructure of the high temperature centrifugally cast austenitic alloys. The study could include:

- **Literature survey on the microstructure evolution**
- **Thermodynamic simulation of stable precipitates**
- **Microstructure characterization of service exposed material by Light Optical Microscopy (LOM), Hardness measurements, Scanning Electron Microscopy (SEM) and possibly Transmission Electron Microscopy (TEM)**





DTU

Development of anodic electrodes for alkaline electrolyzers (M.Sc.)

Supervisor: Per Møller (pm@mek.dtu.dk)

During the last years the interest for environmentally friendly production of hydrogen has increased. Alkaline electrolysis is considered as one of the few promising near-term techniques suitable for commercialization.
The purpose of your work is to determine suitable material combinations and find processes for manufacturing of oxygen evolving electrodes for alkaline electrolysis. Often the technical focus is only put on the hydrogen overvoltage at the cathode surface. If the overall electrolysis efficiency has to be high, it is also important to reduce the oxygen overvoltage at the anode surface. The final solution has to be a compromise between stability, activity and price.

Project contents (suggested):

1. State-of-the-art literature study with focus on anodic electrodes

2. Deposition of low-overpotential materials

3. Investigate the influence of different anode deposition solutions

4. Electrochemical characterisation

The project is part of a partnership consortium between DTU mekanik, DTU Kemi, Siemens and Green Hydrogen.

Development of cathodic electrodes for alkaline electrolyzers (M.Sc.)

Supervisor: Per Møller (pm@mek.dtu.dk)

During the last years the interest for environmentally friendly production of hydrogen has increased. Alkaline electrolysis is considered as one of the few promising near-term techniques suitable for commercialization.
The purpose of your work is to determine suitable material combinations and find processes for manufacturing of oxygen evolving electrodes for alkaline electrolysis. Often the technical focus is only put on the hydrogen overvoltage at the cathode surface, which is the subject of this projectThe final solution has to be a compromise between stability, activity and price.

Project contents (suggested):

1. State-of-the-art literature study with focus on anodic electrodes

2. Deposition of low-overpotential materials

3. Investigate the influence of different anode deposition solutions

4. Electrochemical characterisation

The project is part of a partnership consortium between DTU mekanik, DTU Kemi, Siemens and Green Hydrogen.

Sol-Gel based dense silica-quartz coatings for the corrosion protection of Aluminium

Supervisors: Per Møller (pm@mek.dtu.dk); Felix Lampert (felamp@mek.dtu.dk)

Glass coatings made by vitreous enameling are well known in industry due to the inertness of the coating and the excellent barrier properties of the glass. However, the thick glass layers that are applied by this process are very brittle and as a consequence their applicability to protect metallic substrates are only limited to certain applications. Glass layers with thicknesses in the dimension of approximately 1 µm have shown to overcome the brittle issues associated with traditional enameling and are subject of current industrial research.
In sol-gel surface-processes a liquid precursor solution is applied to a substrate – usually by spinning or dipping – and cured on the surface. By this routine a ceramic film can be applied to the surface at temperatures considerably lower than for conventional ceramics processes. Films produced by sol-gel methods are porous in their nature, however the porosity can be precisely tailored by the processing conditions.
Aim of this thesis is the development of a sol-gel routine and curing method for silica-coatings on metallic substrates such as Aluminum. Since the coating is meant to act as a barrier between the substrate and the environment, the porosity of the coating needs to be minimized, while the processing temperature is limited to maximum temperatures of ca. 150 °C due to the deterioration of the substrate at higher temperatures.
The project will involve the development of a coating routine for dense silica layers on Al-substrates and the characterization of these. The coatings will need to be tested for their protective properties, i.e. the project will involve corrosion testing of the coatings and the characterization of the coatings by microscopy.

Liquid phase deposition of sililca-quartz for the corrosion protection of metallic substrates

Supervisors: Per Møller (pm@mek.dtu.dk); Felix Lampert (felamp@mek.dtu.dk)

Glass coatings made by vitreous enameling are well known in industry due to the inertness of the coating and the excellent barrier properties of the glass. However, the thick glass layers that are applied by this process are very brittle and as a consequence their applicability to protect metallic substrates are only limited to certain applications. Glass layers with thicknesses in the dimension of approximately 1 µm have shown to overcome the brittle issues associated with traditional enameling and are subject of current industrial research. Liquid phase deposition (LPD) is a process that has recently come into interest for the deposition of silica films on a variety of substrates. In this project LPD will be applied to form dense silica films on metallic substrates to create corrosion resistant barrier coatings.

In LPD, a substrate is immersed in a solution that is supersaturated with a precursor chemical and subsequently silica precipitates directly on the surface of the substrate. The overall advantage of the process is the low process temperature and the independence of the deposition on the substrate shape.

The project aims at the development of a suitable setup for laboratory-scale LPD and the successful deposition of stable and defect free silica layers on a metallic substrate. Since the stability and the defect ratio of the surface is highly dependent on the deposition conditions, different conditions have to be tested and evaluated.

The coatings will need to be tested for their corrosion protective properties and furthermore characterized by microscopy.