DECHEMA
FORSCHUNGSINSTITUT
Stiftung bürgerlichen Rechts

High Temperature Materials

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

Contents

High Temperature Materials Group – Overview

The demand for environmentally and resources-friendly processes as well as higher efficiency in thermal plants and machinery requires an increase of operating temperatures. However, processes conducted at high temperatures and often in complex atmospheres lead to increasing demands on the high temperature corrosion resistance of the materials used. The main research objectives of the "high temperature materials" group at DFI are material analysis and development in the field of aggressive, high temperature environments. Within this research field, we focus on the development of metallic and ceramic protective coatings and innovative material systems appropriate for extremely aggressive service conditions (e.g. chlorine, sulphur, bromine, vanadium, and carbon-rich environments) and operation temperatures up to 1800 °C.

Diffusion Coatings

In order to produce such coatings, the material surface is enriched with protective elements by diffusion, which later prevent substrate corrosion during high temperature exposure

- Methods: Pack cementation (in-pack, out-of-pack, slurry)
- Protective coatings for a better oxidation resistance of materials at high temperature in environments rich in water vapour, typical for gasification and combustion atmospheres
- Slurry-based coatings for application on-site in plants or on machine parts

Computational modelling of coatings and their lifetime

Computer simulation tools are used to predict the material behaviour during manufacturing as well as their lifetime during their operation at high temperatures

- Modelling of layer growth and phase formation in the pack cementation process
- Computer modelling of the influence of defects on the mechanical properties of thermal barrier coatings and oxide layers

High temperature light weight metals

The replacement of Ni-based alloys by lighter materials in aviation turbines can decrease the CO_2 emissions

- Determination and extension of the existing operation limits of intermetallic systems such as titanium aluminides
- Thermal barrier coatings for intermetallic titanium aluminides
- New materials for a "Beyond Nickel-based Superalloys" approach: Chromium-based alloys

"Minimally-invasive" high temperature corrosion protection

New developments show that a slight change in the chemical composition near the surface region of different materials induces a change in the reaction mechanisms and hence in their corrosion behaviour as well

- Development of stable and protective alumina layers by using the halogen effect
- Sn-modified surfaces for catalytic poisoning in metal dusting environments
- Controlling chlorine corrosion by selective doping of coatings

Research for industry

The work group also shares its methods and experience with industry and offers professional support and advice regarding industrial material problems and their explanation

- Materials selection for complex conditions
- Characterization of high temperature oxidation and corrosion resistance
- Development and testing of high temperature corrosion protection measures
- Investigation of damage cases specific to high temperature processes

Characterisation and investigation methods

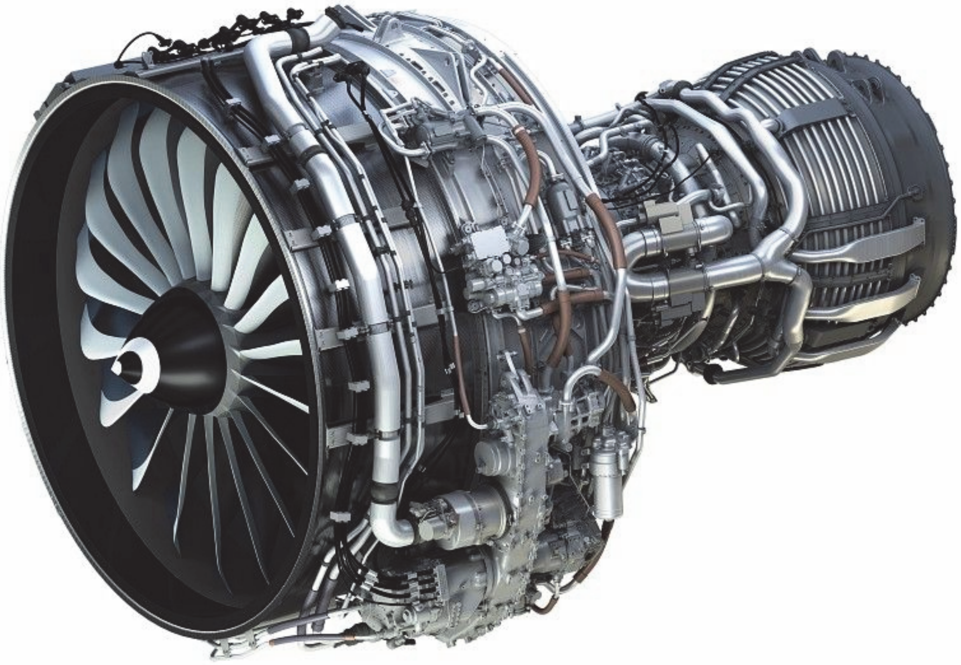
(to download further information, please visit www.dechema-dfi.de)

- Isothermal and cyclic exposure in different environments
  (e.g. air, water vapour, O_2, H_2, CO, H_2S, SO_2, HCl)
- Mechanical testing under tension, compression and four-point-bending
- Metallographic and microanalytical characterization
  (including water-free sample preparation)
- Melting furnaces for metals
- Contact angle measurements
- Dilatometer
- Combined creep and corrosion tests
- Thermogravimetric methods
- Acoustic emission testing
- Optical emission spectrometer
- Scanning electron microscope with EDX
- Transmission electron microscope with EDX
- Atomic force microscope
- Electron probe microanalysis (EPMA, WDX)
- X-ray diffraction (XRD)
- Raman spectrometer
- Nanoindentation and micro-hardness

Research Projects 2017

High temperature light weight materials

Development of high-temperature oxidation resistant coatings for titanium aluminides alloys



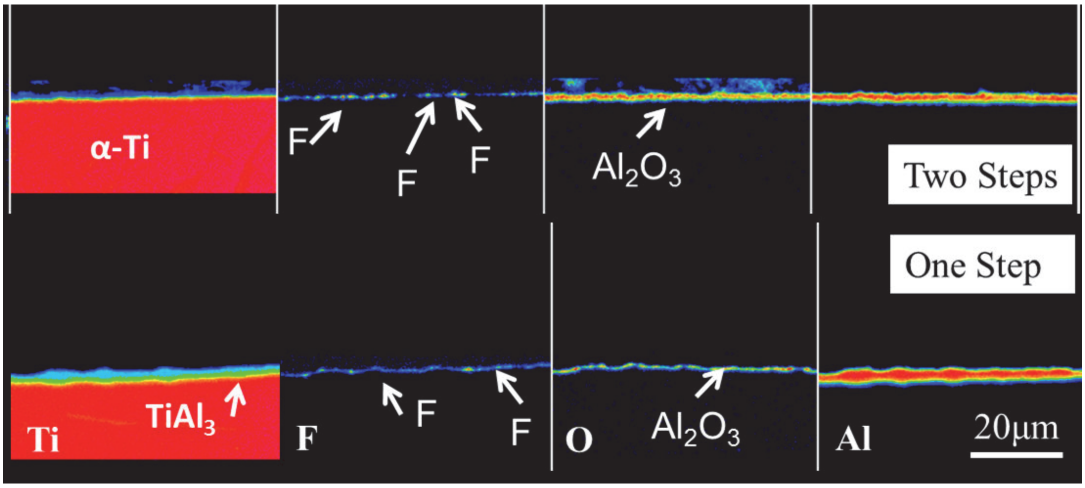
Period: 18.01.2017 - 17.01.2020
Partner: Safran Group, CIRIMAT
Funder: Safran Group

Titanium aluminide alloys have attractive properties for structural applications at high-temperatures. Therefore research has been focused on the improvement of intermetallic TiAl alloys for a few decades. The use of such alloys in aircraft engines allows the reduction of fuel consumption as well as the reduction of noise and NOx emissions. Engine manufacturers aim at improving the efficiency of the next generation engines. Although TiAl alloys look promising for reducing the weight in the low pressure turbine, the use of TiAl alloys remains limited to the coldest stages (up to 700°C) due to mechanical and environmental limitations of this type of material above this temperature. TiAl alloys suffer from ductility loss at room temperature after an exposure at high temperature.

This seems to be linked to the up-take of oxygen and nitrogen into the substrate subsurface zone which changes the mechanical properties. The aims of the current development are to extend the use of TiAl alloys to areas with higher temperatures in the engine. For this purpose the high-temperature resistance of TiAl alloys for low pressure blades has to be improved.

This project is a collaborative work between DECHEMA-Forschungsinstitut, Safran Group, and the French laboratory CIRIMAT. The aim of the project is the development of protective coatings that will allow the use of intermetallic TiAl components at elevated temperatures (up to 800°C) by providing improved oxidation resistance. The concept is based on the application of a pre-coating, serving as a reservoir for controlled surface enrichment. As a second step the halogen effect will be applied to the coated surface in order to achieve maximum oxidation resistance.

High temperature oxidation protection for technical titanium and nickel alloys via combined aluminizing and fluorination in a one-step process



Period: 01.12.2015 - 31.05.2018

Funder: AiF

Ti and Ni alloys are widely used structural materials due to their beneficial properties. Ti forms a passive rutile layer (TiO2) in oxidizing environments which is protective at ambient temperatures but gets deteriorated at higher temperatures (>600°C) and therefore loses its protective barrier effect. Hence, the oxygen inward diffusion becomes the rate-determining step and oxygen is enriched in the subsurface zone. This causes embrittlement which leads to failure of Ti components under cycling conditions (mechanical and thermal).

Technical Ni alloys usually form a chromia layer in oxidizing high temperature environments. This chromia layer has some disadvantages compared to alumina due to its evaporation in water vapor-containing atmospheres above 600°C and at temperatures above 900°C in dry air.

To overcome such problems the surfaces of Ti or Ni compounds have been modified. Single Al enrichment of the surface by coatings has been reported in the literature already, but these attempts were only slightly beneficial. An Al enrichment plus additional fluorine treatment proved to be much more beneficial which was shown already, but the two step treatment is more elaborate. A one step treatment will reduce the costs and save resources. The fluorine effect known from TiAl alloys with an Al content above 40 at.% will be transferred to Ti and Ni alloys with a much lower Al content.

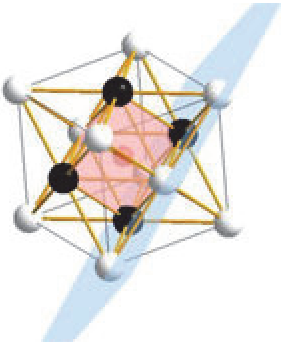
The formation of an Al_2O_3 scale is promoted by a defined amount of fluorine (fluorine effect), and this layer is protective against environmental attack even under thermocyclic conditions and in wet environments.

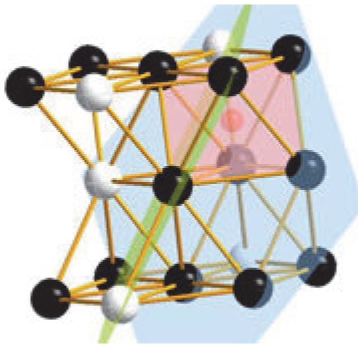
The parameters for the simultaneous Al enrichment and fluorination have to be evaluated and optimized. The subsequent investigations of the protective effect will prove the effectiveness of the treatment.

Supported by:
Federal Ministry for Economic Affairs and Energy
on the basis of a decision by the German Bundestag

Das IGF-Vorhaben Nr. 18947 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.

Understanding the HighTemperature Embrittlement of Titanium Aluminides and its Prevention





Period: 01.09.2015 - 28.02.2019

Partners: DLR, TUD

Funder: DFG

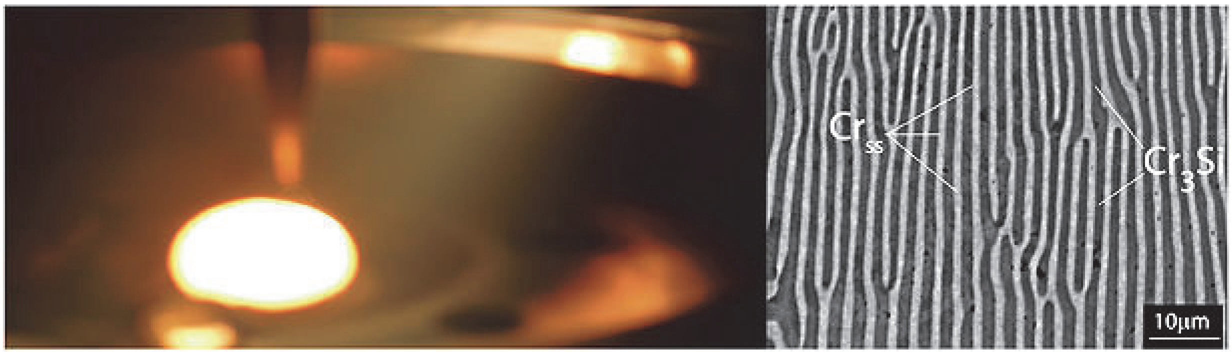
Intermetallic titan aluminide (TiAl)-based alloys represent an important class of high temperature structural materials for applications such as turbine blades. Due to their low densities TiAl-based alloys offer the potential to substitute Ni-based superalloys and increase the efficiency of high temperature applications. Their operating temperature is currently limited to 750°C due to insufficient oxidation resistance and embrittlement. In previous projects a thermal barrier coating (TBC) concept was developed to protect the TiAl material from oxidation. However, the base material and its mechanical properties are affected by the coating deposition process. This project aims at understanding the impact of coating deposition on the subsurface zone and thus the mechanism of subsurface embrittlement. Based on this research the coating concept is optimized to maintain the mechanical properties for long term applications.

The coating manufacturing and mechanical analysis is done in cooperation between DECHEMA-Forschungsinstitut (DFI), Deutsches Zentrum für Luft- und Raumfahrt (DLR), and Technische Universität Dresden (TUD). The coating comprises a 7 wt.% yttrium-stabilized zirconia TBC layer, a thermally grown oxide (Al_2O_3), an Al-rich diffusion coating, and a fluorine treatment of the surface including a pre-oxidation step. The TBC layer, deposited at DLR, has a low thermal conductivity resulting in a steep temperature drop between the hot gas and the metal temperature of a turbine blade.

The oxide grown on the diffusion coating is formed by selective oxidation of aluminum during exposure to air, providing an effective oxygen diffusion barrier and protecting the underlying metal from destructive oxidation. The selectivity of aluminum oxidation is enhanced by the halogen effect of fluorine treatment in conjunction with aluminum enrichment of the surface area. For the Al-rich diffusion coating two processes are used, the pack cementation process (DFI) and magnetron sputtering (DLR). The microstructure and chemical composition of the subsurface area are analyzed after each deposition step. In addition the influence on the mechanical properties is investigated via 4-point bending, nanoindentation, tensile testing, and fatigue testing (TUD). Finally, the effect of each single layer and of the whole coating system on the oxidation behavior of the TiAl alloys will be examined under isothermal and thermocyclic conditions (900°C) in air.

Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation – SCHU 729/27-1)

Heat-Treatable Cr-Alloys for Ultra-High Temperature Applications



Period: 01.03.2016 - 28.02.2019
Partner: Chair of Metals and Alloys, University Bayreuth
Funder: DFG

Recently, refractory alloys have received increasing attention for the purpose of substituting Ni-based single crystal superalloys in high temperature applications. Cr-based alloys are promising candidates next to other refractory alloys such as Mo-Si-B, Co-Re, and Nb-Si alloys. They offer higher melting points (T› 1700°C), and have densities lower than those of Ni-based superalloys. However, challenges such as nitrogen embrittlement at high temperatures, reduced oxidation resistances at ultra-high temperatures (T› 1000°C), and lack of room temperature ductility have hindered the development of Cr-based alloys.

In our earlier DFG-supported project, oxidation and nitridation resistance of chromium was improved by addition of Si and Ge leading to higher oxidation resistance and suppressed nitridation at high temperatures.

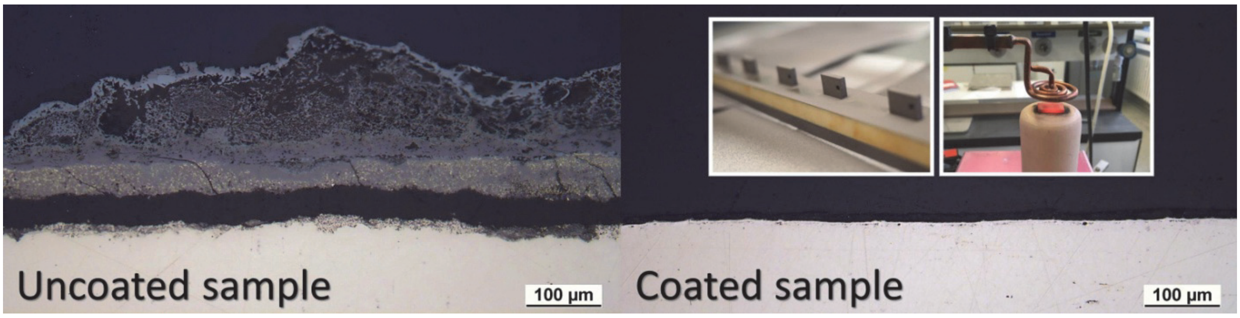
This project is a cooperation between DECHEMA-Forschungsinstitut (DFI) and the Chair of Metals and Alloys at University of Bayreuth (MW). It is aimed to develop heat treatable Cr-alloys with Cr contents higher than 90 at.% and to optimize their microstructure via intermetallic precipitations. The influence of a heat treatment process on microstructural evolution, mechanical properties, and oxidation behavior of alloys will be studied.

Mechanical testing such as creep tests and fracture toughness measurement will be carried out. Furthermore the alloying capacity of the system is investigated by adding molybdenum and platinum to the Cr-Si-Ge system.

Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation – SCHU 181/45-1)

Materials for Aggressive Environments

Development of a lifetime model for superheater tubes with combustion of refined biomass fuels in power plants, industrial furnaces (co-combustion), and local applications (biomass combustion)



Period: 01.06.2016 - 30.11.2018

Partner: Institute of Combustion and Power Plant Technology (IFK)

Funder: AiF

In the course of energy transition the use of existing power plants for co-firing of biomass has become more and more substantial in terms of base load supply. However, while co-firing reduces the CO_2 footprint of the plant, it also introduces higher amounts of corrosive species such as chlorine and sulfur into the system. Consequently, higher corrosion rates and material loss are observed in the firing chamber components. Especially superheater tubes are subjected to increased corrosive attack and are prone to early replacement. Thus, co-firing is commonly limited to temperatures below 500°C and small biomass-to-coal ratios (10%).

This project is a collaboration between DECHEMA-Forschungsinstitut (DFI) and the Institute of Combustion and Power Plant Technology (IFK). Supported by different industrial partners it aims at developing a lifetime model for selected steels used as superheater tube material. IFK focuses on the characterization of the biomass and its ash arising from co-firing in the institute's 500 kW pulverised fuel combustion rig. The main emphasis at DFI is on the evaluation of protective diffusion coatings applied via the slurry route (Al, Cr, Si) in order to protect the metal surfaces against high temperature corrosion. These coatings are very promising as they are cost-effective and may be applied on-site as well. Furthermore, testing at DFI is performed in fire-side-simulating atmosphere containing SO_2 and HCl and with the specimens embedded in ash originating from biomass (co-)firing at IFK. Finally, experimental results will be combined with thermodynamic calculations in order to develop a lifetime model and to maximize service life of superheater tubes. Eventually an increasing demand for biofuels can be achieved and, subsequently, local biomass refiners might benefit from the development of new business areas.

Supported by:

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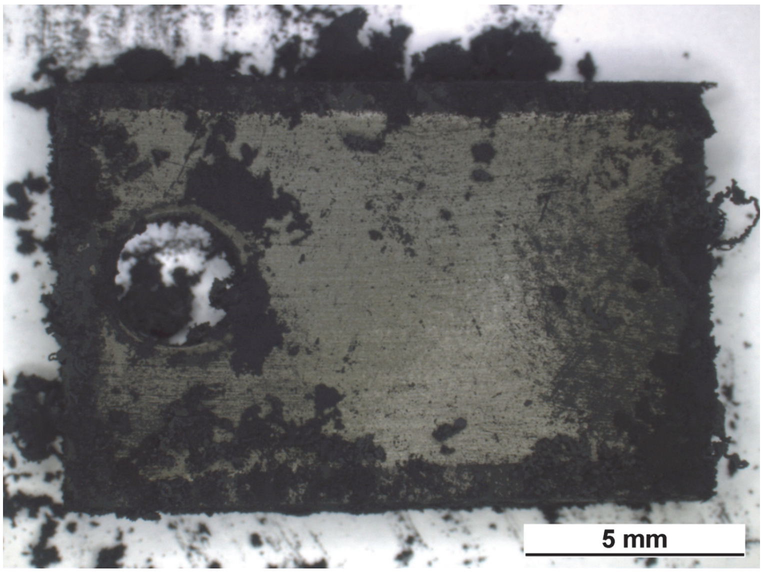
and Energy

on the basis of a decision
by the German Bundestag

Das IGF-Vorhaben Nr. 18370 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.

DryRef2: Energy-efficient production of synthesis gas by dry reforming at industrial scale subproject: Metal Dusting



Period: 01.04.2015 - 31.03.2018

Partners: Linde AG, BASF SE, hte GmbH, Karlsruhe Institute of Technology (KIT)

Funder: BMWi

DRYREF 2 is a corporate project funded by the BMWi, in which the industry partners BASF SE, Linde AG, and hte GmbH as well as the research centers DECHEMA-Forschungsinstitut and Karlsruher Institut für Technologie (KIT) work together. The motivation of the project is to bring a newly identified catalyst to technical maturity. Using the catalyst, carbon monoxide (CO)-rich syngas with a H_2/CO-ratio of 2:1 to 1:1 can be produced via the so called dry reforming process. CO-rich syngas is of great importance for chemical industries since it is a feedstock for several chemical syntheses such as the Fischer-Tropsch process. Dry reforming provides technical progress of resource-friendly technologies since the process consumes carbon dioxide (CO_2). The dry reforming process is conducted under high pressure so that further compression steps are not necessary, but the high pressure also increases the requirements for the plant components. Especially in the down streaming section the high carbon-containing gases pass through a temperature range that bears high risk of a special form of high temperature corrosion, the so-called Metal Dusting. High carbon ingress in the material produces graphite precipitations in the micro structure which is accompanied by volume increase and high stresses in the material. In the end the metal part disintegrates into fine dust of metal particles, graphite, and amorphous coke. Since in practice it is hardly possible to predict the time and location of a metal dusting attack, tests under process-related conditions are carried out at DFI. The performance of several alloys is investigated by isothermal exposure tests at high temperature and pressure in syngas atmosphere. Additionally alloy specimens are exposed to thermocyclic conditions since this provides a way to accelerate the attack on oxide scale-forming materials. From the results materials recommendations can be developed to ensure safe operation of the plant.

Supported by:

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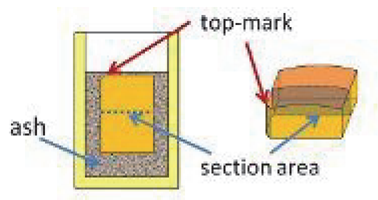
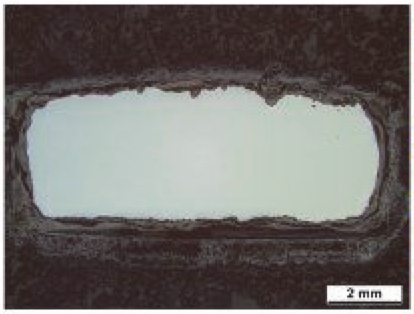
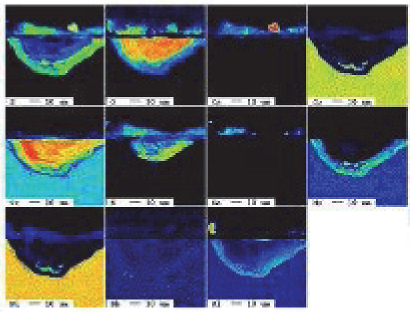
by the German Bundestag

Lübkorr: Accelerated hotcorrosion through cofiring of “green fuels” in conventional coal-fired power plants







Period: 01.01.2014 - 31.12.2018

Funder: BMWi

Conventional coal-fired power plants are still an important pillar in energy industry to supply the base-load energy when wind and solar power are not sufficiently available. In an effort to reduce consumption of limited fossil fuels, co-firing of biomass has become more and more common. While co-firing reduces the CO_2 footprint of the plant, it also introduces higher amounts of corrosive species such as chlorine and sulfur into the system. Consequently, higher corrosion rates and material loss are observed in the firing chamber components. Especially superheater tubes are subjected to increased corrosive attack and are prone to early replacement.

Several materials are selected for exposure experiments in order to clarify the role of sulfur- and chlorine-containing salts on the hot corrosion attack. The investigated materials cover a broad range of commercially available alloys, from nickel-based to iron-based materials. Testing is performed with the specimens embedded in artificial ash and in fire-side simulating atmosphere containing SO_2 and HCl.

Supported by:

Federal Ministry
for Economic Affairs
and Energy

on the basis of a decision
by the German Bundestag

VOKos: Raising the efficiency of waste-to-energy plants by procedural optimization of corrosion protection concepts

Period: 01.11.2013 - 30.04.2017

Funder: BMBF

Waste-to-energy (WTE) plants offer a possibility of municipal waste disposal with the additional benefit of energy generation. Unfortunately the combustion gas contains aggressive species, which leads to fast corrosion on important components such as superheater tubes in boilers. Most critical species of the process gas are alkaline chlorides and HCl, which can form molten salts or volatile corrosion products, respectively.

Damages in boilers caused by high temperature corrosion account for 500,000 Euros per year and plant due to high material wastage and downtime. Additionally incinerators are run below their possible efficiency in order to increase service life of the superheaters. For an average plant this fact leads to further yearly costs amounting to 750,000 €. The total economic loss of 200 incineration plants in Germany accounts for 250 million Euros per year.

Chlorine-induced high temperature corrosion has been investigated since the early 1990s, but the underlying corrosion kinetics and mechanisms especially in complex atmospheres are still under debate.

The goal of the VOKos project is to finally elucidate the mechanism and kinetics of chloride corrosion under high temperature conditions such as those in WTE boilers. For this purpose the operating condition used in plants will be simulated in the laboratory in order to study the corrosion process systematically. Furthermore the impact of corrosive particles on high temperature corrosion will be investigated. Based on the results a corrosion model will be developed which can be used to predict the lifetime of the critical components in boilers.

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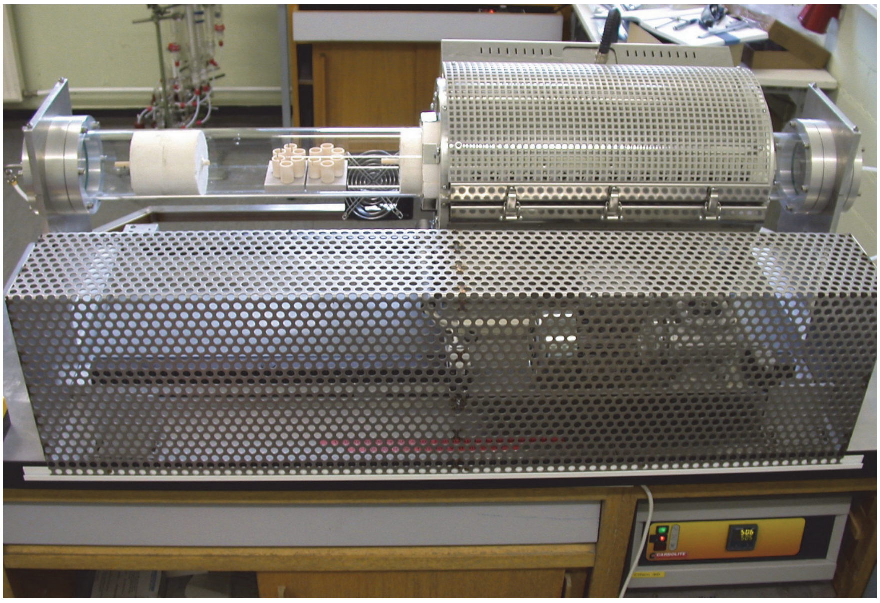
Coatings for high temperature

Development of coatings with advanced catalytic properties and improved life-time



Period: 01.09.2017 - 31.08.2019

Funder: BASF SE

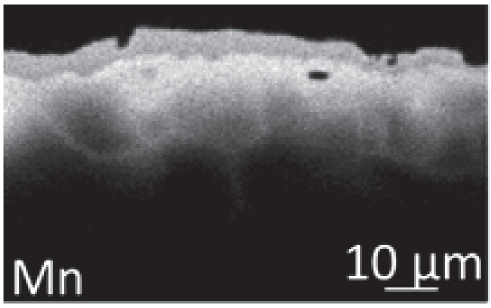
Crackers are utilized to convert the hydrocarbon feedstock with the aid of water vapor into higher-value products such as ethylene or propylene, which are preliminary products for plastics, paints, solvents, pesticides, and many other things. As a side product, coke is formed, which deposits on the inner wall of the tubular coils, affecting the cracker process negatively. Major drawbacks are the diminished heat transfer from the furnace to the reactor due to the highly insulating coke layer and the reduced cross-sectional area of the tubular reactor. The former leads to an increased furnace temperature and, thus, to reduced coil life time.
The latter results in a high pressure drop over the reactor and therefore to a change in product selectivity. Hence, coke formation has a significant impact on the energy efficiency and profitability of the steam cracking process.

A good amount of research has been conducted in recent years to reduce coke formation. The main focus has been on coatings, which can be distinguished in barrier coatings - passivating the inner coil wall - and catalytic coatings - converting coke to carbon oxides. All coatings have in common that they prevent the formation of catalytic coke by passivating the catalytically-active sites of the metallic reactor alloy. However, the formation of pyrolytic coke, which is formed non-catalytically, is thereby not impeded. Catalytic coatings gasify the deposited coke forming carbon dioxide.

For this purpose, catalytic coatings reveal a promising opportunity to prolong the cracking process to a longer run length, making the process greener and more cost-effective.

The aim of the current project is to develop coatings with advanced catalytic properties and improved life-time.

Raiselife:
Raising the Lifetime of Functional Materials for Concentrated Solar Power Technology



manganese-enrichment

Period: 01.04.2016 - 31.03.2020
Funder: European Union
Project Homepage: https://www.raiselife.eu

RAISELIFE is a project funded by the European Union's Horizon 2020 research and innovation programme coordinated by Deutsches Zentrum für Luft- und Raumfahrt at Cologne, Germany.

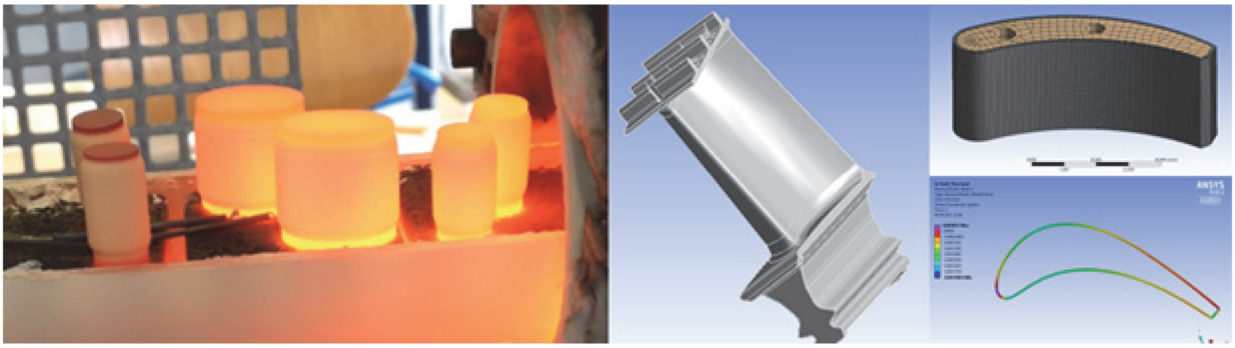
RAISELIFE addresses the challenges of materials for CSP technology focusing on the 2020 targets stated in the Materials Roadmap (SEC(2011)1609). For this purpose the project brings together a broad consortium formed of leading industry partners, SMEs, and research institutes in the concentrated solar thermal and materials science sector. The project scope has been significantly shaped by the leading Engineering, Procurement and Construction (EPC) of ST technology BSII. This unique constellation permits a direct transfer of the results obtained in RAISELIFE to new commercial CSP plants within less than 5 years.

This project focuses on raising the lifetime of five key functional materials for concentrated solar power (CSP) technologies: 1) protective and anti-soiling coatings for primary reflectors, 2) very high-reflective surfaces for heliostats, 3) high-temperature secondary reflectors, 4) receiver coatings, and 5) corrosion-resistant high-temperature metals and coatings for molten salts.

At DFI new coatings for different applications will be developed. On the one hand new high absorptivity diffusion coatings based on manganese and chromium will be applied on different steels and nickel-based alloys as material for receivers. The formed black oxide scales must exhibit high absorptivity, low emissivity, and good resistance against corrosion and thermal shock. The coated materials will be tested in different laboratories of the project partners for high temperature and water-based corrosion. On the other hand the solar energy has to be transferred to a medium such as steam of molten salts. Therefore diffusion coatings for the inside of the absorber tubes on the base of chromium and nickel will be applied on the same materials. The coatings will be investigated in static and dynamic molten salt conditions at different temperatures and impurity levels in order to understand the corrosion and failure mechanisms precisely.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 686008.

Development of a mechanism-based lifetime model for bi-layer thermal barrier coatings, part 2



Period: 01.07.2015 - 31.03.2018

Partners: TU Darmstadt, Forschungszentrum Jülich

Funders: DFG, FVV

Ceramic bi-layer thermal barrier coatings with a top layer of Gadoliniumzirconate (GZO) and a bottom layer of partially yttria stabilized zirconia (YSZ) allow a significant increase of surface temperature in comparison with conventional monolayer coatings, thus achieving a higher energy efficiency. In the first project period the following main objectives were pursued: (i) establishing a reliable production route for GZO coatings, (ii) determination of the basic physical properties, (iii) identification of the relevant damage mechanisms, (iv) characterization of the damage evolution and mechanical properties acting as input parameter for lifetime modelling as well as (v) development of a life time model.

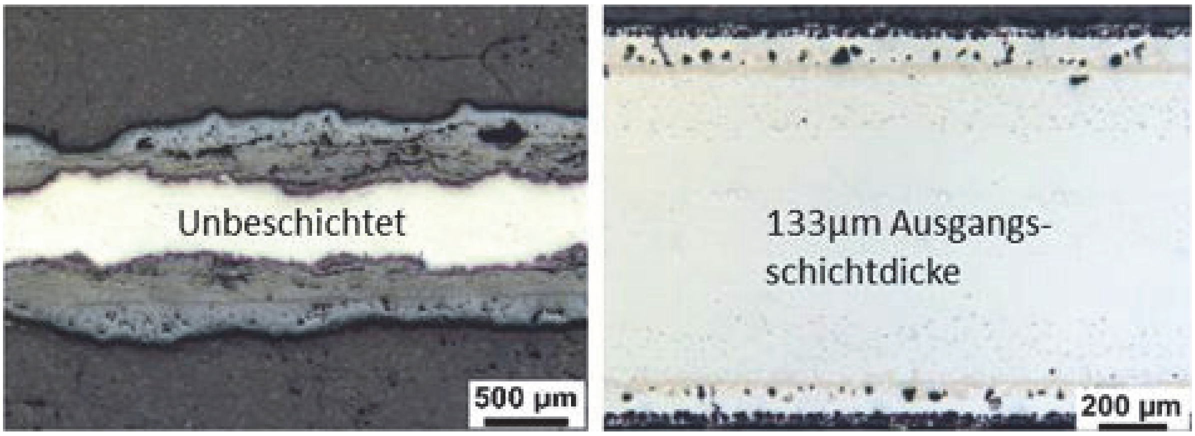
Following a systematic parametric study, stoichiometric coatings with a tailored microstructure were produced which showed a significant increase in thermo cyclic performance in comparison with standard YSZ coatings. Nevertheless the coating properties are highly dependent on the initial and process conditions. Consequently, one main objective of the follow-up project is to develop a process tool to produce reliable coatings with properties in a specific property range. Moreover, the influence of thermal gradient loading conditions and the influence of constraint sintering on coating properties will be investigated in detail. Especially the development of residual stress state is one main issue which can have a significant influence on damage evolution and lifetime.

With the knowledge of the relevant damage mechanisms the lifetime model was modified and successfully adapted to the bi-layer. The developed lifetime model enables a prediction of the critical strain to failure and a lifetime assessment by comparing the critical strain with component loading cycles. However, up to now, the influence of complex geometric boundary conditions, which can significantly affect the stress distribution in the layer system and the damage evolution, on lifetime is not considered in the lifetime model. Consequently, in the second project period, cylindrical specimens with varied diameter and more complex specimens with concave and convex shape will be studied. Using this kind of specimens, the influence of geometric boundary conditions on layer properties and lifetime can be investigated systematically. Moreover a statistical sensitivity analysis of input parameters on critical strain and lifetime will be performed, to quantify the influence of the scattering of coating properties. On the basis of the results the lifetime model will be extended with a geometry factor. The critical strain, acting as a macroscopic damage parameter, is then a function of loading and geometric boundary conditions. Finally, the determined mechanical stability limits of the coating system will be integrated in a finite element model to enable a prediction of the failure location as well as the time to failure of the coating system.

Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation – SCHU 729/25-2)

FVV-Nr. 1195

Analyzing creep performance and corrosion resistance of thin-walled aluminized austenitic steels



Left: uncoated 1mm sample of 1.4828 after exposure in $5CO_2$, $9O_2$, $12H_2O$, rest N_2 for 2000h at 1000°C.
Right: coated 1mm sample of 1.4828 after exposure in $5CO_2$, $9O_2$, $12H_2O$, rest N_2 for 2000h at 1000°C

Period:	01.12.2014 - 31.12.2017
Partner:	Oel-Wärme-Institut (OWI), Aachen
Funder:	AiF

Metallic components in industrial furnaces and oil burners are exposed to high temperatures and aggressive atmospheres. In general for mechanically low stressed sheets relatively cheap and heat-resistant steels are used up to temperatures of 900°C. Above such temperatures currently cost intensive Ni-based-alloys have to be used.

In this project cheap, heat resistant steels (1.4828 and 1.4841) are aluminized in order to enhance their high temperature corrosion resistance. Before such coatings can be industrially used, the influence of Al diffusion coatings on the mechanical properties (especially creep properties) has to be investigated. In thin-walled sheets (1-3 mm) the interdiffusion zone in which the microstructure of the alloy is changed cannot be neglected as it is commonly done with thick-walled components. In order to study this influence the following investigations are performed at a temperature of 1000°C:

- Creep tests in burner atmosphere
- Thermocyclic tests
- Tensile tests at RT
- Exposure tests
- Characterization of the coatings and sheets via metallographic examination, EPMA and phase analysis.

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Das IGF-Vorhaben Nr. 18496 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.

Antiadhesion surfaces for high temperature Applications

Period: 01.10.2014 - 28.02.2017

Partners: Fraunhofer Institute for Environmental, Safety, and Energy Technology UMSICHT (Germany) and MateriaNOVA (Belgium)

Funder: AiF

Corrosion, erosion, sticking, and caking are widespread problems in power plants, caused by aggressive flue ashes with corrosive components such as sulfur, chlorine, and alkali-based low-melting salts. Furthermore, the use/co-firing of a diversity of biomass or alternative fuels with lower quality enhance the problems arising from adhesion (caking, sticking) and the corrosion and erosion issues. As a result, the efficiency of the power plant decreases (lower heat transfer) and periodically service maintenance shutdowns have to be planned in order to clean the facilities and to change damaged parts, generating costs from 100,000 to €1 Million/day.

The innovative concept proposed in this research project combines thermally sprayed coatings functionalized with a sol-gel layer providing low wettability/sticking. FeCrAl alloy-based thermally sprayed coatings including targeted hard materials, such as Cr-carbides, will provide a suitable corrosion and erosion protection. The thin sol-gel layer, in combination with the thermally sprayed coatings, will reduce the sticking ability of aggressive liquid phases or solid flue ash particles.

The project is a collaboration between DECHEMA-Forschungsinstitut (Germany), Fraunhofer Institute for Environmental, Safety, and Energy Technology UMSICHT (Germany), and MateriaNOVA (Belgium).

Supported by:

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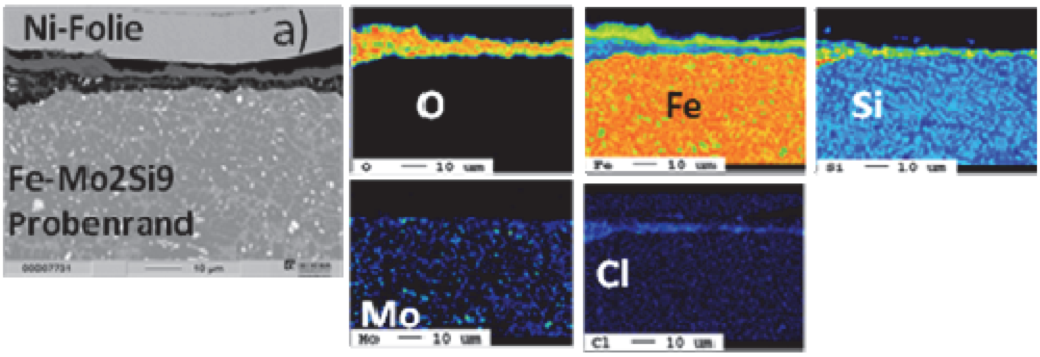
Development of corrosion- and erosion-resistant coatings for chloride-rich high temperature thermo-chemical processes



Period: 01.04.2014 - 31.03.2017

Partner: Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany

Funder: AiF

The most severe corrosion problems in biomass-fired systems are caused by chlorine-rich species released during the combustion process. Erosion occurs due to the high content of solid particles in the flue gas characteristic to the fluidised bed technology often used in energy production with biomass as fuel. Such particles are solid reaction products from biomass combustion (i.e. fly ash) as well as gaseous components (i.e. KCl) which condensate, for example on superheaters. Their influence on the corrosion mechanisms is controlled by their hardness and concentration in the gas flow as well as by the force of the overall turbulence specific to each firing technology. Presently studies on the combined mechanisms of corrosion and erosion are rather few.

Biomass fuel can have various characteristics influenced by its type, the region where and the season when it is produced. Most important criteria for the corrosion behaviour are the potassium and chlorine content. The potassium content of the energy plant Miscanthus for example can vary between 0.7 and 7.2%, its chlorine content between 0.2 and 2.2%. Such variations in potassium and chlorine content demand the use of materials with a tailored composition to guarantee a good resistance against corrosion and erosion. Unfortunately, the use of carbides to counteract erosion damage of these materials is not an acceptable alternative due to their poor resistance against high temperature corrosion in Cl-rich environments.

The best solution currently available is the use of Ni-based material systems with high amounts of Cr and Mo, such as Inconel 625. However, the success of such materials has been based on empirical results and not on a profound knowledge of the beneficial influence of different elements such as refractory metals or silicon on their performance. Our aim is to reduce the gap between practical experience and material knowledge by studying the positive effects of the above mentioned elements.

Therefore we present results related first to the corrosion mechanism of different model alloys in a gaseous chlorine-rich atmosphere and second to the combined corrosion-erosion mechanism in ashes retrieved from a real biomass combustion process. The composition of the investigated model alloys is based on a Fe, Ni or a combined FeNi matrix with additions of Nb, Mo, W, and Si. The reference material chosen for this study is In 625/Alloy 625. Particular attention is given to the influence of each element on the corrosion-erosion mechanisms. The development of a metal matrix rich in refractory metals and silicon, able to form hard silicides, is an innovative approach in reducing the combined corrosion-erosion damage at temperatures between 450 and 550°C in alkali- and chlorine-rich oxidizing environments related to biomass firing processes.

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Das IGF-Vorhaben Nr. 18118 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.

Selected publications

X. Montero, I. Demler, V. Kuznetsov, M.C. Galetz
Factors governing slurry aluminization of steels
Surface and Coatings Technology 309 (2017) 179-186

Slurry aluminization has been used for a long time. This work presents the study of several important parameters affecting the formation of aluminum diffusion coatings onto iron base alloys via slurry application. The study concentrates on the formation mechanism of aluminides using the coating surface coverage and the coating thickness of different steels as evaluation method. Steel composition, heat treatment atmosphere, and steel surface finishes were the studied parameters. These three parameters have to be in accordance in order to obtain aluminum in the melted phase, avoid excessive substrate oxidation, promote fast diffusion of elements forming aluminides, and avoid diffusion of elements blocking the exothermic reaction that forms aluminides during the heat treatment.

L. Krumm, M.C. Galetz
Chlorine Attack of Carbon Steel Between 350 and 500 °C and Its Importance Regarding Corrosion in Waste Incineration
Oxidation of Metals 87 (2017) 757-766

Corrosion in waste to energy (WTE) plants is an extremely interesting issue, involving complex atmosphere and deposit interactions. In this work, the influence of the complex WTE atmosphere and its various constituents was simulated between 350 and 500 °C in order to obtain a better understanding of the corrosion mechanisms occurring in such atmospheres. For this purpose, the typical flue gas mixture of WTE plants was reduced to simpler systems, and the impact of gaseous species typically contained in WTE plants atmospheres on the corrosion rate of the carbon steel 16Mo3 was investigated. Four different atmospheres were used in this work: "full" WTE atmosphere 0.1%HCl + 0.01%SO2 + 8%O2 + 17H2O + 10%CO2 + N2, 0.1%HCl + 15 ppmO2 + 0.01%SO2 + N2, 0.1%HCl + 15 ppmO2 + N2, and 0.1%HCl + 450 ppmO2 + N2. All exposures were carried out in the temperature range between 350 and 500 °C (30 °C steps) for up to 900 h. Parabolic, paralinear, and linear mass change dependent on time, temperature, and atmosphere was observed, the metal consumption as a function of temperature was determined, and the corrosion scales were analyzed and compared with results of field tests. Finally it is shown that the test results obtained from low-oxygen atmospheres match best the corrosive scales observed in field-tested samples.

X. Montero, M.C. Galetz

Coatings for Boiler Components Exposed to Vanadium-Containing Oil Ash in Oxidizing Atmosphere

Oxidation of Metals 87 (2017) 717-727

Corrosion in oil-fired boilers is accelerated in the presence of vanadium, sodium, and sulfur from low-grade fuels. In order to avoid sulfate—–vanadate-induced corrosion of boilers made from 10CrMo9-10 steel, several diffusion coatings (Cr, Al, and AlSi) were investigated together with additional model alloys which could potentially be applied as coatings, such as TiAl, Cr, and CrSi16. All samples were immersed for an exposure time of 100 h in 60 mol% V2O5–40 mol% Na2SO4 salt at 600 and 650 °C. Materials performance was analyzed using substrate recession rate and metallographic characterization of the corrosion scales and of the metal subsurface zones to characterize the extent of corrosion and mechanism. Thus, the present results provide deep insight into materials resistance and degradation in vanadium-containing environments under simulated boiler conditions. The corrosive attack follows a combined effect of sulfidation and acceleration of metal loss by dissolution of the formed scale under such vanadate salts.

S. Madloch, M.C. Galetz

Microstructural evolution of germanium modified AlSi-slurry coatings on alloy 600 at 620 °C in metal dusting environment

Surface and Coatings Technology 315 (2017) 335-341

Germanium-modified AlSi-slurry coatings were produced via airbrush spraying of two different suspensions on the conventional Ni-base alloy 600, followed by a heat-treatment in Ar at 800 °C. The resulting coatings exhibit a thickness of approximately 130 μm and mainly consist of outer Al-rich β-Ni(Al,Ge) phase followed by inner Ni-rich β-Ni(Al,Ge). In the interdiffusion zone, a continuous layer of (Cr,Ni)3Ge phase formed. Long term exposure tests in carbonaceous atmosphere at 620 °C showed excellent metal dusting protection. Furthermore, the exposure tests revealed that the (Cr,Ni)3Ge layer acts as a diffusion barrier, preventing the diffusion of the major coating element aluminum into the substrate. Depletion of aluminum would be detrimental for the lifetime of the coating and consequentially for that of the structural component. Microstructural evolution of the coating during exposure showed inward diffusion of nickel into the coating, resulting in fine Ge3Ni5 precipitates, whose formation will be discussed based on the ternary phase diagram of Al-Ge-Ni.

M. Rudolphi, M. Schütze

Extracting oxide scale cracking data from acoustic emission data using the example of oxidized cobalt

Materials and Corrosion 68 (2017) 249-255

4-point bending with in situ acoustic emission measurement has proven to be a successful route for determining the critical strain values for various oxide scales. In combination with metallographic investigations, such critical strain data can be used to establish mechanical stability diagrams for an assessment of the maximum tolerable strain before scale failure becomes imminent. The use of the acoustic emission technique enables to detect micro-cracking in the oxide scale without metallographic inspection, thereby, providing access to the critical strain required to initiate oxide cracking. However, in some cases, acoustic emission is generated not only by oxide cracking but also from plastic deformation processes within the metal substrate. In this work, a tailored analysis procedure is developed for discriminating the signals generated by oxide scale cracking from those generated by plastic deformation in the cobalt substrate. From the resulting critical strain data, the above-mentioned failure diagrams were deduced for cobalt oxide scales grown on high-purity cobalt at 650°C in dry synthetic air, and synthetic air with 10vol% H_2O, respectively.

M. Schütze, W.J. Quadakkers

Future Directions in the Field of High-Temperature Corrosion Research

Oxidation of Metals 87 (2017) 681-704

High-temperature corrosion research will face a significant change in the near future. Up until now, this research area was dominated by materials issues related to the use of fossil fuels in energy conversion and transportation. Recent political decisions in many of the industrialized countries resulted in a paradigm shift towards the preference of non-fossil renewable energy and CO_2 neutral or CO_2-free technologies. These political constraints driving the development of new energy conversion technologies in combination with new materials and new manufacturing methods lead to new challenges in high-temperature corrosion research. The availability of advanced investigation techniques as well as increased IT power provides significant potential for the improved in-depth understanding of corrosion mechanisms and the development of comprehensive and reliable lifetime models. The present overview addresses all these aspects and attempts to sketch an outlook, although incomplete, on expected future developments in high-temperature corrosion research.

A. Soleimani Dorcheh, M.C. Galetz

Oxidation-Nitridation Mechanism in Eutectic Cr-Silicide Alloy and Its Mitigation by Germanium Alloying

Oxidation of Metals (2017) DOI: 10.1007/s11085-016-9685-1

The oxidation and nitridation of the eutectic Cr–Cr_3Si alloys during exposures in air was investigated with focus on the detailed mechanism of the attack. Exposures in synthetic air (N_2-21%O_2), and nitrogen (N_2-5%H_2) atmospheres revealed inward diffusion of nitrogen as the key mechanism for the nitridation process which was markedly higher in nitrogen compared to that in air. Post-exposure investigations proved selective nitridation of the Cr-solid solution phase in both synthetic air and N_2-5%H_2 atmosphere. During oxidation in air, a continuous A15 silicide layer (Cr_3Si) formed at the oxide-alloy interface inhibiting the internal nitridation. This layer formed exclusively in oxidizing atmosphere as a result of the primary oxidation and outward diffusion of chromium, and dissolution of the Cr-solid solution phase. The barrier character of the A15 phase against nitridation was evident based on microstructural and chemical investigations as well as on thermodynamic considerations. Long-term oxidation results indicated that overtime the protective A15 layer was damaged by the formation porosities and internal oxidation during exposure which led to internal selective nitridation. Additions of germanium (Ge) was found beneficial by supporting the formation of the self-protecting A15 layer with long-term protective behavior against internal nitridation for more than 1000 h.

A. Soleimani Dorcheh, R.N. Durham, M.C. Galetz

High temperature corrosion in molten solar salt: The role of chloride impurities

Materials and Corrosion 68 (2017) 943-951

The role of chloride impurities in nitrate mixture $NaNO_3$-KNO_3 (solar salt) on corrosion behavior at 600°C was studied on a low-chromium ferritic-martensitic X20MoV11-1 steel (X20) and a stainless steel 316 (SS316). Gravimetric and metallographic methods were employed to characterize the kinetics of oxidation and the resulting corrosion products. Steel X20 showed non-protective character in both low- (up to 0.02 wt% Cl^-) and high- (up to 0.25 wt% Cl^-) chloride salts by forming a thick and non-compact oxide scale. A significant increase in weight gain was observed when X20 steel was immersed in the high-chloride containing salt. Furthermore, the scale underwent severe deformation. SS316 showed superior corrosion resistance in both low- and high-chloride salts. Oxide scales formed on both steels included two zones: an outer Na-rich oxide and an inner mixed oxide based on Fe_2O_3 and Fe_3O_4 structures.

The morphology and composition of these zones were significantly different on X20 and SS316 steels. A passive Cr-rich oxide layer at the metal/oxide interface was characterized as a protective layer. In the case of stainless steel 316 this layer showed even higher continuity when tested in the high-chloride salt resulting in better protection during the isothermal test.

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

Contact:

PD Dr. Mathias Galetz
Head of High Temperature Materials
+49 69 7564 397 – galetz@dechema.de

Prof. Dr. Michael Schütze
Scientific Advisor to the Executive Board
+49 69 7564 361 – schuetze@dechema.de

DFI Secretariat
+49 69 7564 252 or 337
dfi@dechema.de

DECHEMA-Forschungsinstitut

Theodor-Heuss-Allee 25
60486 Frankfurt am Main