

## Fundamental Aspects of Material Degradation Focus Topic Room A212 - Session DM+BI+SS-ThM

### Material Stabilities and Technology for Degradation Protection

**Moderators:** Markus Valtiner, Vienna University of Technology, Austria, Gareth S. Parkinson, TU Wien, Austria

8:00am **DM+BI+SS-ThM-1 Extremely Thin Protective Oxide Layer for Reflective Silver Thin Films**, *Midori Kawamura, E Kudo, Y Sasaki, T Kiba, Y Abe, K Kim*, Kitami Institute of Technology, Japan; *H Murotani*, Tokai University, Japan

Silver (Ag) thin films possess high electrical and optical properties, but their low stability should be resolved. We have developed a highly stable Ag thin film where thermal agglomeration can be suppressed, by utilizing nanometer thick surface Al layers. Then we have confirmed that Al surface nanolayer deposited Ag films show a high optical reflectance as well as Ag single film. Here, the Al nanolayer was oxidized to be Al oxide nanolayer, being transparent in visible region, by natural oxidation in air. In the present study, we investigate durability of the Ag films with surface nanolayers under high humidity condition.

We prepared Ag single layer (150 nm), Ti (1, 3 -nm) / Ag films and Al (1, 3 -nm) / Ag films on glass substrate by rf magnetron sputtering in Ar discharge. In addition, vacuum evaporation method was also used for the preparation of Al (1, 3 -nm) / Ag films. A difference on degradation of the films by different fabrication methods was investigated. The samples were kept for 16 hrs in a chamber where temperature and humidity was set to 55°C and 90%RH, respectively.

After the test, agglomeration occurred in Ag single layer and optical reflectance was decreased. On the other hand, Ti or Al nanolayer covered Ag films kept smooth surface even after the test. The surface roughness observed using AFM was as small as 1.0 nm. As a result, we have found that both Al and Ti surface nanolayers can play significant role as protective layer under high humidity condition. However, Ti / Ag films showed a lower reflectance due to light absorption by TiO<sub>2</sub> layer formed on the surface, and the samples with Al surface nanolayer showed a higher optical reflectance.

By XPS analysis, very thin Ag sulfide formation was observed in Ag single film after the humidity test, but not in Ti or Al covered Ag films. This suggests very thin Al oxide or Ti oxide nanolayer prevented contact of Ag atoms and SO<sub>2</sub> gas in air. However, Ag signal was detected in the surface oxide layers, which indicates onset of outward diffusion of Ag atoms.

8:20am **DM+BI+SS-ThM-2 Influence of the Electric Double Layer on Degradation of Materials**, *Dominik Dworschak, M Valtiner*, Vienna University of Technology, Austria

Corrosion and adhesion science usually focuses on the solid side of a liquid/solid or solid/adhesive interface. However, the only some nanometer thick interface itself is the complex transition region which drives many important processes in corrosion and delamination. The electric double layer (EDL) is a key part of the interfacial region but remains mostly neglected as a potential key player in degradation processes. Here, we will demonstrate that the EDL has an important influence on the corrosion mechanism of passivating materials in the transpassive region (material dissolution at potentials where the passive film breaks down).

We utilize an electrochemical flow cell combined with an inductively coupled mass spectrometer (ICP-MS) to enable the in-situ study of the time-resolved release of elements into solution. This provides detailed insights into the nature of the passive and transpassive condition. As model systems, we use nickel based alloys. These are essential to modern industry and uniquely tailored for a wide range of applications, which rely on high corrosion and heat resistance. In particular, we polarized a series of Ni<sub>75</sub>Cr<sub>16</sub>Fe<sub>9</sub>, Ni<sub>86</sub>Cr<sub>5</sub>Fe<sub>9</sub> as well as Ni<sub>74</sub>Cr<sub>16</sub>Fe<sub>9</sub>Mo<sub>1</sub> model alloys in order to understand the effect of chromium concentration and molybdenum on transpassive dissolution

In the transpassive regime we can detect the presence of protective species of chromium and molybdenum on the surface. Unexpectedly, we can demonstrate significant corrosion resistance above a critical potential where the passive film breaks down. This is traditionally known as trans passive region with bulk dissolution of metal alloys. However, we find that the EDL forms a transient passivating solution side protective layer in the transpassive region – i.e. we characterize an electric double layer induced corrosion resistance, which solely – and surprisingly – lies in the structure of

the solution side. This finding has general important implications for designing degradation resistance in highly corrosive environments.

8:40am **DM+BI+SS-ThM-3 Key Issues for the Stability of Protective Surface Oxides**, *Philippe Marcus*, CNRS - Chimie ParisTech, France **INVITED**

This lecture will focus on a surface science approach of corrosion and protection of metals and alloys, with emphasis on the structure and growth of surface oxide layers, a central theme in corrosion science.

Understanding early stage oxidation of metal surfaces at atomic or nanometric scale is a key to a better design and an improved control of engineering metals.

The following topics will be addressed:

- Nanostructure of ultra-thin oxide layers (passive films) on metals,
- Early stage oxidation of stainless steels,
- Local electronic properties of passive films,
- Mechanisms of initiation of localized corrosion, with emphasis on the role of surface defects in localized attack leading to corrosion,

The data that will be presented are obtained by using *in situ* Scanning Tunneling Microscopy (STM), Scanning Tunneling Spectroscopy (STS), X-Ray Photoelectron Spectroscopy (XPS), Time-of-Flight Secondary Ions Mass Spectrometry (ToF-SIMS) combined with electrochemical techniques and DFT calculations.

9:20am **DM+BI+SS-ThM-5 Controlling and Observing Localized Dealloying Corrosion and Dissolution via Lateral Modification of Surfactant Inhibitor Layers**, *S Neupane*, Hasselt University, Belgium; *Frank Uwe Renner*, IMEC vzw. Division IMOME, Belgium

Corrosion processes on metals and alloys may result in substantial degradation and loss of functionality. Mitigation strategies include alloy design, to allow for passivation, or the application of inhibitors to protect materials but they are often causing irreversible damage and potential catastrophic failure at more severe corrosion conditions. The ultimate understanding of the involved fundamental processes including the initial stages of corrosion attacks is still lacking, in particular on the important atomic and molecular scale. Surfactant inhibitors protect surfaces from corrosion by forming molecular layers or so-called self-assembled monolayers separating the material from the corrosive environment. Yet, with inhibitors *localized dealloying* takes place at higher electrochemical potentials [1]. To address the fundamental nature of the site of initiation of dealloying corrosion we have recently introduced different strategies for novel surface-science approaches [2]. On the one hand the inhibitor layer can be laterally modified by using a sequential application combining different steps of micro-contact printing and solution backfilling [3]. In consequence an array of artificial defects such as patch boundaries or displacements by overprinting using foreign impurity molecules can be obtained in a well-controlled way. On the other hand the molecular stability may be locally probed by molecular-scale force measurements employing AFM techniques. In the retract force curve molecular fishing events are eventually visible which can be correlated to the inhibition efficiency. We here exemplify both aspects on noble metal model systems such as Cu-Au and more reactive surfaces including Cu-Zn and pure Cu. On Cu-Au surfaces initial dealloying pits are occurring along patch boundaries formed by sequential application of thiol inhibitors [4]. On Cu surfaces we applied different mercapto-benzimidazoles and could indeed link the observed layer stability with the actual corrosion behavior.

[1] A. Pareek et al., J. Am. Chem. Soc.133 (2011) 18264–18271. [2] B. Shresta et al., Faraday Discuss. 180 (2015), 191. [3] S. Neupane et al., Langmuir. 34 (2018) 66–72. [4] S. Neupane et al., submitted.

9:40am **DM+BI+SS-ThM-6 In Situ Characterization of Interactions at Polymer/Metal Oxide Interfaces Under Aqueous Conditions by a Spectro-electrochemical Approach**, *Sven Pletincx*, Vrije Universiteit Brussel, Belgium; *L Fockaert, A Mol*, Delft University of Technology, Netherlands; *H Terryn, T Hauffman*, Vrije Universiteit Brussel, Belgium

The mechanisms governing coating/metal oxide delamination are not yet fully understood, although strong and durable adhesive interactions at the interface are considered to be an important prerequisite for good coating durability. Achieving adequate adhesion strengths between an organic and inorganic system in various operating conditions is one of the complex challenges of interface engineering. However, obtaining local chemical information at this solid/solid interface is challenging, since common surface sensitive analysis techniques only operate under vacuum conditions, making it impossible to probe environmental effects *in situ*.<sup>1</sup>

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The analysis of this so-called buried interfaces is achieved by characterizing ultrathin polymer films onto a metal oxide substrate by ambient-pressure photoelectron spectroscopy (APXPS).<sup>2</sup> Here, we show that APXPS with a conventional X-ray source can be used to study the effects of water exposure on the interaction of acrylic coatings with aluminum oxide. This is done by making the polymer layer sufficiently thin to probe the interface non-destructively.

A *spectroelectrochemical* setup of *in situ* ATR-FTIR Kretschmann and Odd Random Phase Electrochemical Impedance Spectroscopy (ORP-EIS) on a complementary model system is used to characterize and monitor the formed bonds at the metal oxide/polymer interface.<sup>3</sup> A nanometer thin aluminum layer is sputtered on an IR transparent crystal, such that the IR signal reaches the oxide/polymer interface, obtaining a near-interface spectrum. This way, we have direct access to the interface, and the influence of an above-the-polymer electrolyte (i.e. H<sub>2</sub>O) is probed. Simultaneously the protective properties and corrosion processes of the overall hybrid system are monitored by ORP-EIS.

This work shows that by using ultrathin films in combination with a set of recently developed techniques, it is possible to non-destructively and *in situ* probe interfacial changes in hybrid systems.

1. Watts, J. F. The Interfacial Chemistry of Adhesion: Novel Routes to the Holy Grail? *Adhes. Curr. Res. Appl.* 1–16 (2006). doi:10.1002/3527607307.ch1

2. Pletincx, S. *et al.* In Situ Characterization of the Initial Effect of Water on Molecular Interactions at the Interface of Organic/Inorganic Hybrid Systems. *Sci. Rep.* **7**, 45123 (2017).

3. Pletincx, S. *et al.* In Situ Methanol Adsorption on Aluminum Oxide Monitored by a Combined ORP-EIS and ATR-FTIR Kretschmann Setup. *J. Phys. Chem. C* **122**, 21963–21973 (2018).

11:00am **DM+BI+SS-ThM-10 Design of Corrosion Resistant High Entropy Alloys**, *Gerald Frankel*, *C Taylor*, *W Windl*, The Ohio State University; *J Scully*, University of Virginia; *J Locke*, The Ohio State University; *P Lu*, Questek Innovations

**INVITED**

The corrosion resistance of a metal alloy is dictated by the exposure environment as well as the alloy structure, composition, and details of the surface condition such as the presence of a passive film. The design of new alloys with improved corrosion resistance must take all of these factors into account. As a result, the degrees of freedom in alloy design are so numerous that the standard process of trial and error is extremely lengthy, even using high throughput methods. This is particularly true for emerging materials such as high entropy alloys (HEAs) and bulk metallic glasses. The complexity of the corrosion process makes integrated computational materials engineering (ICME) for corrosion resistance very challenging. In this work we describe an approach for design of corrosion resistant alloys (CRAs) using ICME. The work has focused on HEAs because of the vast, multidimensional compositional and processing space associated with HEAs. The ultimate goal of CRA design is a combination of multiscale, multiphysics models that accurately describe the details of each of the controlling mechanisms and chemical/physical interactions in the degradation process. However, progress can be made using computational approaches coupled with empiricism. Calculation of Phase Diagrams (CalPhaD) methods are extremely useful in this regard. Furthermore, a number of relevant calculable parameters, such as metal-metal and metal-oxygen bond strength or chloride ion adsorption energies, can be used to create correlations with corrosion metrics that enable prediction of corrosion properties of alloys in previously unexplored compositional space. We will present the methodology used for the design of an extremely corrosion resistant HEA as well as a series of HEAs that are less resistant, but allow for the assessment of critical parameters controlling corrosion resistance in HEAs.

11:40am **DM+BI+SS-ThM-12 Determination of Hydrogen in High Strength Steels using Scanning Kelvin Probe Force Microscopy**, *Ines Traxler*, *G Schimo-Aichhorn*, CEST Competence Centre for Electrochemical Surface Technology, Austria; *A Muhr*, *G Luckeneder*, *H Duchaczek*, *K Stellnberger*, voestalpine Stahl GmbH, Austria; *D Rudomilova*, *T Prosek*, University of Chemistry and Technology Prague, Czech Republic; *B Lutzer*, CEST Competence Centre for Electrochemical Surface Technology, Austria; *D Stifter*, *S Hild*, Johannes Kepler University Linz, Austria

High-strength steels are important materials for the automotive industry. Due to their good formability and high strength they are used for the manufacture of light weight and fuel-efficient automotive parts. A disadvantage of high strength steels is their proneness to hydrogen

embrittlement. Even small amounts of hydrogen can cause a deterioration of mechanical properties. Therefore, the effect of hydrogen on the steel microstructure is of great interest and it is important to study and visualize the effects and mechanisms of hydrogen in steels. For this purpose, Scanning Kelvin Probe Force Microscopy (SKPFM) is a promising technique for the investigation of hydrogen in the steel microstructure with a very good spatial resolution.

Hydrogen diffusion in different high-strength steels was investigated using SKPFM. Hydrogen entry at cut edges and coating defects was studied as well as the influence in the individual steel grains. The measurements were carried out with different salt solutions on the backside of CP1000 (complex phase), DP1000 (dual phase) and zinc coated DP1000 steels to induce corrosion and promote hydrogen entry into the steel. The permeating hydrogen was measured on the upper side of the sample by repeated surface scans and the effect on the contact potential difference (CPD) was studied. Furthermore, SKPFM measurements with different relative humidity were carried out, monitoring the effects of corrosion. Additionally, Scanning Kelvin Probe (SKP) measurements were done for comparison.

With SKPFM, the preferred diffusion pathways of hydrogen through the steel microstructure could be visualized as well as the effect of zinc coatings on hydrogen permeation.

12:00pm **DM+BI+SS-ThM-13 Reflection Mode Interferometry for studying interfacial processes**, *Kai Schwenzfeier*, *P Bilotto*, *M Lengauer*, *C Merola*, *H Cheng*, *M Valtiner*, TU Wien, Austria

Molecular level processes at electrified solid|liquid interfaces play a critical role in corrosion and degradation processes. These include adsorption of ions, evolution of electrochemical double layers, oxidation/dissolution of metals, screening effects as well as liquid properties at an interface. However those processes/effects are notoriously hard to measure due to long integration times or too small probe with many available analysis techniques.

We refined Multiple Beam Interferometry (MBI) to enable time resolved *in situ* and *operando* measurement of processes at solid|liquid interfaces in both transmission and reflection geometry. In this presentation dynamic interfacial processes such as changes of refractive indices in small (nanometer sized gaps), a micro-to-angstrom scale view into corrosion processes and surface oxidation, as well as specific and non-specific potential driven ion adsorption in aqueous solutions will be discussed in detail. We will relate these measurements to molecular resolution AFM imaging and force spectroscopy at solid|liquid interfaces.

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