|  |
| --- |
| **Monday 6th September** |
| **10:30** | **Refreshments and registration** |
| 10:45 | Welcome to the conference / safety briefing*Stuart Lyon, University of Manchester* |
| 11:00 | “The oxidation and carburisation behaviour of type 316H austenitic stainless steel in a simulated advanced gas-cooled reactor environment”*Fabio Scenini, University of Manchester* |
| 11:30 | “The carburisation and oxidation of 9Cr-1Mo steel exposed to CO2”*Lawrence Coghlan, University of Loughborough* |
| 12:00 | “Next generation of ceramic coatings for active protection of light alloys”*Beatriz Mingo, University of Manchester* |
| **12:30** | **Lunch** |
| 13:30 | “Corrosion performance of a wire arc additive manufacture deposited 316L alloy”*Corentin Penot, University of Southampton* |
| 14:00 | “A 2D cellular automata model for understanding the leaching of corrosion inhibitors from primer coatings”*Simon Gibbon, AkzoNobel* |
| **14:30** | **Break** |
| 14:45 | “Microstructural evolution of polyester powder coating exposed to neutral salt spray (NSS) and cyclic corrosion test (CCT)”*Reza Emad, University of Manchester* |
| 15:15 | “Investigation of “green” corrosion inhibitors and comparison with conventional inhibitors using the electrochemical noise method”*Tianyan Lan, University of Nottingham* |
| 15:45 | **Close** |

|  |
| --- |
| **Tuesday 7th September** |
| **10:00** | **Refreshments** |
| 10:15 | “3D characterisation of corrosion and coatings”*Tim Burnett, University of Manchester* |
| 10:45 | “Electrochemical tests for assessment of anti-corrosive organic coatings: a short review”*Douglas Mills, University of Northampton* |
| **11:15** | **Break** |
| 11:30 | “Atomic Force Microscopy: a tool to study early-stage corrosion”*Dominic Craske, University of Manchester* |
| 12:00 | “A career in corrosion and its importance in the future of energy including renewables”*Bill Hedges, President of the Institute of Corrosion*  |
| **12:30** | **Lunch** |
| 13:30 | “Exploring the use of machine learning for interpretation of electrochemical impedance spectra after corrosion testing”*Vincenzo Bongiorno, University of Manchester* |
| 14:00 | “Understanding water diffusion through organic corrosion protection coatings: insights from computer simulations”*Charlie Wand, University of Manchester* |
| 14:30 | **Break** |
| **U.R. Evans Award Ceremony** |
| 14:45 | Presentation of the U.R Evans Awards to Bob Cottis (2020) and Mary Ryan (2021)*Bill Hedges, President of the Institute of Corrosion* |
| 15:00 | U.R. Evans award lecture: “Corrosion at the nanoscale” *Mary Ryan, Imperial College London* |
| **16:00** | **Close** |
|  |  |
| **18:00** | **Conference dinner YANG SING restaurant (confirm booking with Jane Deakin)** |

|  |
| --- |
| **Wednesday 8th September** |
| **10:00** | **Refreshments** |
| 10:15 | “X-ray computed tomographic/focused ion beam investigation of defects in a niobium coated copper radio frequency cavity”*Sepidah Aliasghari, University of Manchester* |
| 10:45 | “High-resolution NanoSIMS mapping of deuterium at microstructurally relevant scales in stainless steel, precipitation hardened nickel alloys and zirconium alloys”*Katie Moore, University of Manchester* |
| **11:15** | **Break** |
| 11:15 | “Chemical gradients and polymer dynamics in the epoxy-amine/iron oxide interphase”*Suzanne Morsch, University of Manchester* |
| 11:45 | “Methods for measuring network heterogeneity in crosslinked polymer networks and implications for corrosion performance”*Andy Parnell, University of Sheffield* |
| **12:30** | **Lunch** |
| 13:30 | “Marine atmospheric corrosion of carbon steel in the tropical microclimates of Mauritius”*Yashwantraj Seechurna, University of Mauritius and Southampton* |
| 14:00 | “Role of barrier pigments and free volumes in degradation of water ballast tank coating after long term service of water ballast tank in ship vessel”*Yanwen Liu, University of Manchester* |
| 14:30 | **Break** |
| 14:45 | “Some outstanding issues and anomalies in mobility and transport near polymer/solid interfaces”*Richard Jones, University of Manchester and Sheffield* |
| 15:15 | ““Challenges in prediction of corrosion by FEM modelling”*Herman Terryn, Vrije Universiteit Brussel* |
| **15:45** | **Close** |

|  |
| --- |
| **Thursday 9th September** |
| **10:00** | **Refreshments** |
| 10:15 | “Anti-corrosive paints: diffusion and dissolution through a pore network”*Josef Giddings, University of Manchester* |
| 10:45 | “Electrochemical Investigation of novel zinc-rich organic coatings”*Isehaq Al-Nafai, University of Manchester* |
| **11:15** | **Break** |
| 11:30 | “Corrosion testing under variable pH: experimental setup and preliminary results”*Michele Curioni, University of Manchester* |
| 12:00 | “The influence of zinc loading on the efficiency in the transfer of galvanic current during cathodic protection mode by the zinc dust in epoxy zinc primers on steel”*Katarzyna Rzeszutek, University of Manchester* |
| **12:30** | **Lunch** |
|  **“Prosperity Partnership”: Sustainable coatings by rational design (SusCoRD)***EPSRC and AkzoNobel, with the Universities of Manchester, Sheffield, and Liverpool* |
| 13:30 | What is SusCoRD?*Simon Gibbon, AkzoNobel* |
| 13:40 | SusCoRD: programme vision*Stuart Lyon, University of Manchester* |
| 13:50 | Work package 4: “Modelling and simulation”*Flor Siperstein (Manchester), Peter Visser (AzkoNobel) and researchers* |
| 14:10 | Work package 2: “Polymers and interfaces”*Richard Jones (Manchester), Mark Irwen (AkzoNobel) and researchers* |
| **14:30** | **Break** |
| 14:45 | Work package 1: “Predictive design”*Douglas Kell (Liverpool), Bob Luigjes (AzkoNobel) and researchers* |
| 15:05 | Work package 3: “Coatings and substrates”*Xiaorong Zhou (Manchester), Niek Hijnen (AkzoNobel) and researchers* |
| 15:25 | SusCord’s place in AkzoNobel’s research portfolio*Claudio di Lullo, AkzoNobel* |
| 15:40 | “Corrosion protection in a sustainable world”*Open discussion* |
| 16:00 | **Close** |

**The oxidation and carburisation behaviour of type 316H austenitic stainless steel in a simulated advanced gas-cooled reactor environment**

*Gredis A.1, 2,Palkó S. 1, 3 , Connolly B. 1, 2, Ainsworth R. A. 3, Scenini F. 1, 2*

*1 Materials Performance Centre, The University of Manchester, UK*

*2Department of Materials, The University of Manchester, UK*

*3School of Mechanical, Aerospace & Civil Engineering, The University of Manchester, UK*

Austenitic stainless steels are widely used in the primary circuit of advanced gas-cooled reactors (AGR) where they operate in a CO2/CO gaseous environment at temperatures in the creep regime. Recent findings suggest that type 316 SS is affected by the pressurised CO2-based coolant which increases the surface hardness of the steels due to a carburisation process. This also affects the near surface creep properties. Therefore, the effect of the microstructure, applied load and dynamic deformation (creep) on the oxide evolution as well as the effect of the operational parameters (i.e. exposure time and temperature) on the materials needs to be understood. In this work, the behaviour of 316H Austenitic SS in a simulated AGR environment has been investigated in order to enhance the understanding of the effects of stress, strain and their combined effect as creep on oxide evolution and carburisation depending on the surface finish. The results are discussed in terms of CO2/CO metal interactions and subsequent oxide formation and carburisation; the effects of grinding/machining on the passive film formation, and carbon ingress, and ultimately carburisation-induced hardening, have been elucidated.

**The carburisation and oxidation of 9Cr-1Mo steel exposed to CO2**

*Lawrence Coghlan1, Rebecca Higginson1, Mark A.E. Jepson1,*

*Aya Shin2, Jonathan Pearson2*

*1Department of Materials, University of Loughborough*

*2EDF Energy*

Due to its high creep strength and oxidation resistance at high temperatures, 9Cr-1Mo steel is used within Advance Gas Cooled Reactors (AGRs) for the pipework This oxidation resistance is provided through the growth of a duplex oxide scale consisting of a protective Cr rich inner spinel and an outer Fe rich layer of magnetite. Under the operating conditions of the plant 9Cr-1Mo is exposed to CO2 rich gas at high temperatures leading to complex interactions taking place. CO2 reacts to form CO, C and O via the Boudouard reaction leading to carburization and oxidation taking place.

Breakaway oxidation is a rapid-oxidation phenomena associated with failure of the once protective scale and is linked with component failure. Due to the importance of better understanding breakaway oxidation multiple aspects of the steel were investigated. The characterization of carbides within the substrate using transmission electron microscopy has identified chemical variations between carbides which form at different stages of oxidation Complex multiphase, multi element cored carbides have been identified and characterized.

Characterization at the interface between oxide and substrate has identified an oxide growth mechanism through preferential oxidation of carbides within the substrate. In pre-breakaway samples an internal oxidation zone develops at this interface due to this preferential oxidation ahead of the oxidation front. This internal oxidation zone is not present on samples which have suffered breakaway.

**Next generation of ceramic coatings for active protection of light alloys**

Beatriz Mingo

*Department of Materials, University of Manchester, Oxford Road, Manchester, M13 9PL*

*beatriz.mingo@manchester.ac.uk*

Smart coatings are defined as materials capable of interacting with the environment, responding selectively to certain triggers, such as mechanical fracture, temperature or pH variations. Depending on the incorporated functionality, different properties can be achieved, e.g. specific corrosion inhibition or self-healing. Up to now, this technology has primarily been implemented in organic coatings, but their applicability is limited to mild environments.

The scientific question proposed in this work is whether incorporating smart functionality is feasible in ceramic-based coatings, produced by Plasma Electrolytic Oxidation (PEO) and Aerosol Deposition (AD). Such coatings present excellent performance in demanding conditions, but active functionalisation is highly challenging given the rigid and inert nature of inorganic matrices compared to organic materials. The novelty of this research lies in the incorporation of nanocontainers loaded with corrosion inhibitors, which are released in response to pH changes arising from electrochemical activity. Upon emerging from their nanocontainers, they will act locally at the anodic and/or cathodic sites inhibiting corrosion propagation.

**Corrosion performance of a wire arc additive manufacture deposited 316L alloy**

Corentin Penot1, Julian Wharton2, Adrian Addison3, Yikun Wang4, Qing Lu5

1nCATS, University of Southampton; NSIRC, Granta Park, Great Abington, Cambridge, UK; email: c.penot@soton.ac.uk\*

2nCATS, University of Southampton; j.wharton@soton.ac.uk

3TWI Ltd, Granta Park, Great Abington, Cambridge, UK; email: adrian.addison@twi.co.uk

4Fluid Structure Interactions group, University of Southampton, Lloyd’s Register, Bolderwood Campus, Southampton, UK; email: y.wang@soton.ac.uk

5TWI Ltd, Granta Park, Great Abington, Cambridge, UK; email: Qing.lu@twi.co.uk

Material properties resulting from additive manufacturing builds are currently under intensive research, driven by the possible economic gains these techniques may offer. Wire and Arc Additive Manufacturing (WAAM), a Direct Energy Deposition process, is particularly suitable for the manufacturing of large metallic structures of several metres in size. However, the corrosion performance of WAAM deposited parts has received only limited attention and needs further investigation. WAAM walls of 180 mm × 90 mm × 40 mm were deposited using conventional 316L welding wire and multi-axis MIG/MAG arc welding equipment. Disc specimens were extracted from the WAAM wall (diameter: 15 mm). Potentiodynamic polarizations, critical pitting temperature and pitting test by 24 h immersion in 6% ferric chloride were carried out. The WAAM specimens had higher pitting potentials and critical pitting temperatures compared to a conventional wrought 316L (see *Figure 1*), which can be attributed to the absence of MnS inclusions within the microstructure. However, WAAM specimens suffered high mass losses during immersion in ferric chloride compared to its wrought counterpart revealing a weaker passivity. The microstructure consisted of an austenite matrix with inter-dendritic ferrite and sigma phase. Evidence of Cr and Mo de-alloying was found by EDX analysis where the austenite matrix was depleted at interphase regions (austenite/ferrite or austenite sigma). The de-alloying is believed to be responsible for the weaker passivity of the WAAM specimens.



Figure : **a)** potentiodynamic polarization scans obtained in a 3.5% NaCl solution at room temperature, **b)** current density (black) and temperature (red) profiles obtained during the CPT tests (1M NaCl solution, +700 mV vs SCE).

A 2D cellular automata model for understanding the leaching of corrosion inhibitors from primer coatings

Simon R Gibbon, AkzoNobel, Newcastle, UK

Organic primer coatings provide the primary corrosion protection for metal assets, incorporation of soluble corrosion inhibitors allows the primer to provide protection against corrosion even when the coating is damaged. The corrosion inhibitor is present in primer coatings as pigment particles, so that when the coating is damaged the corrosive environment causes some of the corrosion inhibitor to leach from the coating into the damaged area where it causes the formation of a protective layer on the metal surface. Experimental evidence has shown that the primary mechanism of leaching is through voids left following the dissolution of corrosion inhibitor particles and this residual pore structure determines the inhibitor leaching rate. Thus, sufficient inhibitor must be released to prevent early corrosion and sufficient corrosion inhibitor must remain to provide long term corrosion protection. Bonetti et al., through a 3D Cellular Automata, simulation investigated the relationship between the microstructure of a coating and the release of corrosion inhibitor. Their simulation showed good agreement with experimental observations, giving comparable quantitative results. However, it was computationally intensive and caused challenges in visualisation.

The aim of this work was to develop a flexible responsive multi-parameter visual 2D simulation which could be run from any computer using JavaScript within a web browser to aid understanding of the leaching process. The 2D Cellular Automata model simulates the process of dissolution and diffusion of the inhibitor through the 2D coating structure. The 2D model is not tied to any microstructure generation methods allowing a range of different structures to be selected by the user and physical parameters of the model can be varied across multiple runs. However, agreement with experimental studies is qualitative, and as such quantitative studies require use of the 3D model.

The talk will focus on the insights which can be gained from the use of such a 2D simulation by master’s students, into the processes which occur within an active corrosion protection coating, the strengths/weaknesses of simplified computer modelling and the importance of validating any insights obtained from such a simplified model. Potential and value of any extensions to such a model will also be highlighted, from both educational and product development viewpoints.

**Microstructural evolution of polyester powder coating exposed to neutral salt spray (NSS) and cyclic corrosion test (CCT)**

S. Gh. R. Emada\*, K. Borwankara, T. L. Burnetta, b, X. Zhoua, S.B. Lyona, S. Morscha, Y. Liua, G. D'Ambrosioc, N. Hijnend, S.R. Gibbond

a Department of Materials, School of Natural Sciences, The University of Manchester, The Mill, Sackville St, Manchester, M13 9PL, UK

bHenry Royce Institute for Advanced Materials, Department of Materials, The University of Manchester, Manchester, M13 9PL, UK

c AkzoNobel, Viale Silvio Pellico 8, Como-Tavernola, 22100, Italy

d AkzoNobel, Research & Development, Stoneygate Lane, Felling, Gateshead, Tyne & Wear, NE10 0JY, UK

One layer pigmented polyester powder coatings were exposed to neutral salt spray (NSS) and cyclic corrosion test (CCT). The microstructure of organic coated panels are characterized in this study to identify key microstructural features comparing exposed and non-exposed coating to understand the performance of the coatings. All the panels exposed to CCT showed blister formation after 4 months (16 cycles) of exposure while more significant failure of the coating is evident after 6 months CCT (25 cycles). The failure of coatings exposed to CCT appears to be mainly associated with crack formation and development within the coating. On the other hand, performance of the coatings exposed to NSS appears to be dependent on the coating thickness in association with aluminium hydroxide pigment volume concentration (PVC), particle size and clustering that span the coating thickness.

Scanning electron microscopy (SEM) showed cracks form on the surface and within the coatings after exposure to CCT. Three types of initiation site are proposed based on the microstructural observations including: i) the interface between aluminium hydroxide particles and the polymeric binder, ii) relatively sharp variations and the rogue peaks on the substrate surface and iii) aluminium hydroxide particles that fracture within the coating. After crack initiation within the coating, cyclic exposure results in further propagation of the crack until it spans the entire thickness of the coating. After the coating failure, cracks also formed due to the stress of blister formation and growth and hence a stage of damage propagation rather than initiation. Energy dispersive X-ray spectroscopy (EDS) showed that corrosion product can penetrate and fill these cracks. On the other hand, corrosion product appear to decorate the interface of aluminium hydroxide particles in the absence of any visible cracks. It is proposed that the interface of aluminium hydroxide particles and the polymeric binder could be a weak point when the coating is under residual stresses generated during the coating application and film formation. The internal stresses may also increase further due to the exposure and interaction of the coating with the environment. This weak interface may act as an easy transport path that facilitates the transport of aggressive species into the coating and, hence, accelerate the failure of the organic coating when networks of aluminium hydroxide clusters span the entire coatings thickness. This is supported by the X-ray computed tomography data of a blister, which revealed presence of two clusters of connected aluminium hydroxide particles at the central regions of the blister, which almost span the entire thickness of the coating.

**Investigation of “green” corrosion inhibitors and comparison with conventional inhibitors using the Electrochemical Noise Method (ENM)**

*Tianyang Lan1, Eleanor Binner1, Douglas, Mills2*

1. Chemical and Environmental Engineering, The University of Nottingham NG7 2RD

2. Engineering and Technology, The University of Northampton NN1 5PH

Applying corrosion inhibitor in water-based environment is an efficient and economic method used by oil and gas companies for the protection of steel assets. It can largely reduce corrosion rate during production and transport which helps retain the physical properties of metal parts. Electrochemical Noise Method (ENM) is a non-invasive and quick technique that processes the natural signal fluctuations arising during the electrochemical reaction to calculate a parameter called Rn which can be related to corrosion current. In this work, ENM is employed as the main monitoring method. Two conventional inhibitors provided by Clariant Oil Services were tested in a 3% NaCl/CO2 environment at different temperatures. Also 1% propargyl alcohol was tested in different concentrations of HCl solution. Because the corrosion inhibitors currently used are toxic and harmful to environment, this work also used a standard method to extract solution from green plants (broccoli and sugar beet, mainly root section). These were then added in NaCl/CO2 or HCl environment as potential green inhibitors. In addition, ICP-OES as an accurate analytical technique was employed to confirm the iron mass loss calculated from the ENM results. The results obtained will be presented and discussed in this paper.

**3D characterisation of corrosion and coatings**

T L Burnett

Department of Materials, The University of Manchester, Manchester, M13 9PL

Corrosion processes, the resulting damage, coating systems and their behaviour all require an understanding of the 3D morphology and organisation to get the clearest insight into the microstructure and operating mechanisms. To quantify the volume of metal loss in a pit, the extent of an intergranular corrosion network, the organisation of a coating microstructure and the ionic pathways that form through it all require 3D characterisation. Many of these features and processes also require multiscale, multimodal and sometimes time-lapse information to understand the mechanisms controlling them.

In this talk I will present a range of 3D characterisation techniques and methodologies and how they can be linked together to provide a view rich in information to help understand the coatings and the corrosion processes. I will share examples showing the 3D characterisation of several different corrosion processes in steel and aluminium as well as characterisation and interaction with coating systems to illustrate the power of utilising 3D imaging techniques.

**Electrochemical Tests for Assessment of Anti-corrosive Organic Coatings – A Short Review**

Douglas J. Mills

*University of Northampton, Northampton, UK*

*e-mail: Douglas.Mills@Northampton.ac.uk*

This paper will focus on recent developments in test methods which are taking place both in the author’s laboratory and elsewhere with the aim of assisting in more effective development of anti-corrosive coatings, as well as for quality control, and for assessing coatings in the field. In much of the work electrochemical methods such as DC resistance, EIS (Electrochemical Impedance Spectroscopy) and ENM (Electrochemical Nosie Method) are used. These techniques are seen as complimentary in their application to anti-corrosion coatings. Two novel (and quick) ways of investigating heterogeneity in resistance behaviour (D and I areas) will be discussed. An electrochemical method of measuring adhesion has also been investigated as an alternative to the destructive pull-off test. Regarding inhibitor effectiveness the original method of pot tests is still of use. But it is now being supplemented by more modern electrochemical approaches like use of EIS to look at level of disbonding and the corrosion at the scribe. SVET (Scanning Vibrating Electrode Technique) also has a role to play here. These methods as they might be used in lab contex,t will all be discussed briefly. The latter part of the paper will put a strong emphasis on making measurements on structures in the field to assess the degree to which the organic coating is still protecting the metal substrate The method of choice here is ENM. Developments in ENM that have taken place, are currently taking place, and will need to take place in the future to make this method user friendly and universally applicable will be summarised. The practical side of is proving challenging and contributions from the many coatings experts at this conference will be welcomed!

**Atomic Force Microscopy: A Tool to Study Early-Stage Corrosion**

Dominic Craske, Christopher A. Muryn, Robert Lindsay

*The University of Manchester, Manchester, UK*

*In situ/operando* studies are key to gaining further insight into corrosion phenomena, including avoiding data artifacts generated through removal of a sample from the environment of interest. Many researchers are now active in this area, applying a range of spectroscopy, microscopy and scattering approaches. In this presentation, our endeavour in this field will be described, focusing on the application of atomic force microscopy (AFM) for the study of aqueous corrosion.

AFM is a scanning probe technique, which can produce high-resolution real-space images of surfaces, as well as gain spatially resolved details of other properties. Most pertinently, it can relatively easily image surfaces in liquid, and so is a good candidate for studying aqueous corrosion, although surface roughness can be a limitation. On this basis, we are using AFM to explore the evolution of polished substrates in the early stages of aqueous corrosion. Results of recent work will be discussed, namely the evolution of carbon steel in weak acid solutions, i.e. acetic acid and carbonic acid. For carbon steel in acetic acid, the substrate microstructure is rapidly revealed, and surface roughness initially increases linearly with time. Furthermore, it is found that roughening kinetics are grain dependent, suggesting different local corrosion rates during the period of immersion.

**A career in corrosion and its importance in the future of energy including renewables.**

Bill Hedges

President, Institute of Corrosion (corrosion guy@btinternet.com)

Bill Hedges has been working in electrochemistry and corrosion for almost 40 years with the last 30 in the oil and gas industry. In this talk he will describe some of the opportunities his work in corrosion has given him as well as some of the challenges he has faced – both technical and non-technical. He will illustrate his talk with some of the important scientific developments that have occurred during that time. Bill will finish with a look to the future and the critical need for corrosion scientists and engineers in the field of renewable energy.

**Exploring the use of machine learning for corrosion testing: interpretation of electrochemical impedance spectra**

V. Bongiorno1, S. Gibbon2, E.Michailidou3, M.Curioni1

1 Corrosion and Protection Group, Department of Materials, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK

2AkzoNobel, Northallerton, North Yorkshire, DL7 7BJ, UK

3 AkzoNobel, 31 Rijksstraatweg, Sassenheim, 2171 AJ, Netherlands

Electrochemical impedance spectroscopy is a powerful tool to evaluate the conditions of a corroding surface and it can be applied to corrosion testing of a variety of substrates. The interpretation of electrochemical impedance spectra (EIS) often requires modelling the response of the corroding system by an equivalent circuit. The approach is effective, but it requires a a-priori understanding of the processes occurring on the corroding surface. Machine Learning (ML) algorithms can solve complex tasks after a training process, without a-priori knowledge of the behavior of the system considered. This work explores the possibility of using ML to interpret EIS data. Using simulated EIS datasets, the number of interpreted EIS spectra required to train a ML algorithm is evaluated.Two scenarios are considered: classification, i.e. identifying which equivalent circuit is associated with an EIS spectrum, and fitting, i.e. estimating the numeric values of the components of an equivalent circuit. The results show that, on ideal EIS data, approximately 200 examples are sufficient for the training. Further, the impact of non-idealities in the EIS spectra (i.e. the effect of electrochemical noise) on the training requirements is considered. Finally, the approach is applied on a set of experimental EIS spectra.

**Understanding water diffusion through organic corrosion protection coatings: Insights from computer simulations**

Charlie Wand1, Simon Gibbon2 and Flor Siperstein1

*1 Department of Chemical Engineering and Analytical Science, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK*

*2 AkzoNobel Research & Development, Northallerton, North Yorkshire, DL7 7BJ, UK*

charlie.wand@manchester.ac.uk

The infrastructure of our modern society relies on large scale metal structures, which have a very large embedded carbon dioxide footprint. Protective organic coatings are key to sustainability as they extend the life of assets in aerospace, automotive, and freight by providing protection against corrosion. It has been considered that polymer coatings provide corrosion protection by forming a barrier to prevent mass transfer between the metal surface and the surroundings. However, it has been shown that water can permeate through these coatings and reach the metal surface [1]. Therefore the mechanism for corrosion protection is significantly more complex than originally assumed, with the transport of species through the coating playing a significant factor in corrosion protection properties of the coating.

Here we perform atomistic molecular dynamics simulations to investigate the diffusion of water through an epoxy-amine coating and investigate the effect of temperature, cross-linking (cure), and moisture content on the diffusion of water through the organic coating. We find that water diffusion is via a polymer-assisted hopping mechanism between isolated free volume nanoscale pores and that the polymer mobility is the determining factor for the speed of water diffusion [2].

 [1] C. Grave, I. Mcewan, and R. A. Pethrick, *Influence of Stoichiometric Ratio on Water Absorption in Epoxy Resins*, J. Appl. Polym. Sci. **69**, (1998).

[2] C. R. Wand, S. Gibbon, and F. R. Siperstein, *A Computational Study of Water Diffusion through an Epoxy-Amine Thermoset Polymer*, Prep. (n.d.).

**X-ray computed tomographic/focused ion beam investigation of the defect on niobium coated copper radio frequency cavity**

S. Aliasghari1, B. Mingo1, P. Skeldon1, A. Gholinia2, X. Zhang2, P.J. Withers2

1 Department of Materials, The University of Manchester, Manchester M13 9PL, UK.

2 Henry Moseley X-ray Imaging Facility, The University of Manchester, Manchester M13 9PL,

Defects in niobium coatings on superconducting radio frequency (SRF) cavities can have an important impact on the quality factor at low accelerating fields. However, the investigation of the location and nature of the defects can be difficult due to shape of cavity. In this work defect formed in a PVD niobium coating on a copper substrate are examined using high resolution X-ray computed tomography (X-ray CT). The observations are validated by comparisons with cross-sectional views of the features obtained using focus ion beam (FIB) scanning electron microscopy. The X-ray CT technique is shown to be capable of correlating the locations of defects in the niobium surface and ones in the copper substrate. Furthermore, the volumes of the defects are revealed on the niobium surface.

**High-resolution NanoSIMS mapping of deuterium at microstructurally relevant scales in stainless steel, precipitation hardened nickel alloys and zirconium alloys**

K. L. Moorea,b, Y. Abouraa, C. Jonesa, D.F. Marteloa, R. Moranac, R. Akida, M Preussa, d

a Department of Materials, University of Manchester, M13 9PL, UK

b Photon Science Institute, University of Manchester, M13 9PL, UK

c BP Exploration Operating Company Limited, Chertsey Road, Sunbury-on-Thames, TW16 7LN, UK

d Department of Materials Science & Engineering, Monash University, VIC 3800, Australia

Hydrogen mapping at the scale of the microstructure is analytically challenging but if overcome could provide important observations to understand the key mechanisms involved in hydrogen embrittlement. The Cameca NanoSIMS is one of the emerging analytical techniques capable of mapping hydrogen and deuterium at the microstructural scale with sensitivities in the ppm range. This presentation will demonstrate the successful implementation of NanoSIMS imaging of deuterium in a range of alloys which includes electrochemically deuterium charged 303 stainless steel, precipitation hardened 625+ nickel alloys and zircalloys. Deuterium was used as an isotopic tracer and mapped instead of hydrogen to avoid artefacts related to the detection of hydrogen. The high resolution (~ 200 nm lateral resolution) isotope ratio maps revealed deuterium localisation at sites of deformation bands (shear and dislocation slip bands), strain localised regions, strain-induced α' martensite and grain boundary secondary phases in steel and nickel alloys. In zircalloy, deuterium was found to be localised around secondary phase particles. This presentation will also show the potential of the NanoSIMS technique, how we have mitigated for NanoSIMS artefacts, and the best practice for hydrogen and deuterium mapping in engineering alloys.

**Chemical Gradients and Polymer Dynamics in the Epoxy-Amine/Iron Oxide Interphase**

Suzanne Morsch, Charlie R. Wand1, Seyedgholamreza Emad1, Stuart Lyon1, Flor Siperstein1 Mikhail Malanin2, Julia Muche2, Anja Caspari2, Astrid Drechsler2, Klaus-Jochen Eichhorn2 and Simon Gibbon3.

University, Institute, Country: 1.The University of Manchester, UK 2. Leibniz-Institut für Polymerforschung Dresden, Germany 3. AkzoNobel, Stoneygate Lane, Felling, Gateshead, NE10 0JY, UK

The physicochemical properties of network polymer / metal oxides interphase regions determine the performance of many advanced composites, adhesives and protective coatings. The nature and origins of the buried interphase structure have, however, remained elusive, since these regions are inaccessible to most organic analysis techniques. Here, a unique combination of nanocomposite specimens, conventional analysis techniques, nanospectroscopy and molecular dynamics simulations is applied to characterise the epoxy-amine/iron oxide interphase in detail, and identify the molecular interactions underpinning its formation.

First, ATR-FTIR and sub-diffraction resolution AFM-IR mapping are used to unambiguously confirm the presence of nanoscale off-stoichiometric interphase regions. Whilst extensive (up to 100 μm) chemical gradients have often been proposed on the basis of thin film studies, we have previously used cross-sectional AFM-IR, TEM (transmission electron microscopy) and EELS (electron energy loss spectroscopy) analysis to directly probe the buried interphase in thick films, and rule out chemical consumption of the epoxy or amine constituent molecules towards an iron interface. Instead, in composite samples, interfacial segregation of the molecular triethylenetetraamine (TETA) cross-linker is shown to result in a highly localised (<50 nm depth) excess of epoxy near synthetic hematite, (Fe2O3) magnetite (Fe3O4) and goethite (Fe(O)OH) particle surfaces. Under ambient cure conditions, this is found to occur independently of the amine-surface binding energy, and is considered to occur as a result of entropic segregation during the cure. The nature and extent of the epoxy-amine chemical interphase is therefore dependent on the relative mobility of the molecular constituents, i.e., the cure temperature and molecular weight.

Next, thermal analysis and molecular dynamics simulations demonstrate that restricted segmental motion of the cured polymer is, in contrast, only imparted by strong interfacial binding between surface Fe sites and electron rich heteroatoms in the polymer network, resulting in significantly raised Tg values. On goethite, the position of surface hydroxyl protons enables synergistic hydrogen bonding and electrostatic binding to Fe atoms at specific sites, providing a strong driving force for molecular orientation. For hematite, favourable electrostatic binding also results in raised Tg values, however detectable increases in Tg are strongly dependent on the thermal history of the specimen.

For protective coatings on steel, these results indicate that surface preparation, pre-treatments, cure schedules and the structure of molecular constituents all play significant roles in controlling the buried polymeric interphase properties.

**Methods for measuring network heterogeneity in crosslinked polymer networks and implications for corrosion performance**

Andrew Parnell, Dept. of Physics and Astronomy

University of Sheffield

One explanation for the enhanced water transport and subsequent failure in coating performance of polymer network-based coatings has been the paradigm of regions of high and low cross link density. As such the ongoing debate of nodules versus no-nodules has dogged our fundamental understanding of cured polymer networks for the last 40 years. In my talk I will discuss ways in which it is possible to probe these materials and understand them on the nanoscale and hopefully resolve some of these longstanding issues. Better insight into the cured network architecture will hopefully help us to have a more holistic understanding of what makes a coating achieve high performance.

**Marine atmospheric corrosion of carbon steel in the tropical microclimates of mauritius**

Yashwantraj Seechurna,b,\*, B. Yashwansingh R. Surnama, Julian A. Whartonb

aMechanical and Production Engineering Department, University of Mauritius, Reduit 80837, Mauritius

bNational Centre of Advanced Tribology at Southampton (nCATS), School of Engineering, University of Southampton, Southampton SO17 1BJ, UK

The atmospheric corrosion performance of S235 carbon steel was assessed when exposed to the tropical/marine aerosol pollutants of Port-Louis, Mauritius. Port-louis is situated on the northwest coast and has a distinct microclimate leading to major atmospheric corrosion concerns. In addition, sulphur dioxide emissions from three heavy oil-fired power stations complicate corrosion prediction within the region. Atmospheric exposures were carried out to determine the corrosion rates of S235 carbon steel subjected to the Mauritius/Port-Louis atmospheric conditions and a mass-loss analysis showed a marked difference among the corrosion rates obtained for the different sites investigated, linked to environmental and geographical variables. The formation of porous surface layers led to continuous increase in metal dissolution during the electrochemical process. Surface analysis using XRD and SEM revealed lepidocrocite (γ–$ FeOOH$) and goethite (α–$ FeOOH$) as the predominant rust phases, with low percentages of magnetite ($Fe\_{2}O\_{3}$), akageneite (β–$ FeOOH$) and jarosite $(KFe\_{3}(OH)\_{6}(SO\_{4})\_{2})$. A key insight in the S235 atmospheric corrosion indicates two stages: the early rapid corrosion stage, followed by a slow corrosion stage due to the formation of stable rust phases.

**Role of barrier pigments and free volumes in degradation of water ballast tank coating after long term service of water ballast tank in ship vessel**

1Paul Iannarelli, 1Douglas Beaumont, 2\*Yanwen Liu, 2Xiaorong Zhou, 2Timothy Burnett, 2Michele Curioni, 2Stuart Lyon, 1Simon Gibbon, 2Suzanne Morsh 2Reza Emad, 2Teruo Hashimoto, 1Niek Hijnen

1AkzoNobel, Stoneygate Lane, Felling, Gateshead, NE10 0JY England, UK

2School of Materials, The University of Manchester, Manchester, M13 9PL England, UK

\*Yanwen.Liu@Manchester.ac.uk

Water ballast tanks (WBTs) in cargo ships are used to maintain vessel stability. Sea water is pumped into the ballast tanks when the cargo is unloaded and it is discharged during cargo loading. This process creates a corrosive environment within ballast tanks due to cyclic variation between wet and high humidity conditions. The ballast tanks also experience cyclic heating when the adjacent cargo tanks are filled with hot crude oil and cooling when the ballast tank filled with sea water (25 to 10 ºC). Protective coatings used in water ballast tanks generally consist of an epoxy-based polymer binder containing barrier pigments or fillers. These coatings are sprayed onto the steel substrate to form 2 or 3 layers that provide a minimum dry film thickness of 300-400 µm with IMO PSPC requirements that water ballast tank coatings will achieve a service life of 15 years.

In order to effectively monitoring the coating degradation in water ballast tank after long term service of 18 years, in the present study, on board examination of degradation of water ballast tank coating was analysed by electrochemical impedance spectroscopy, dynamic vapour sorption (DVS) measurements, glass transition temperatures, and electron microscopic observation. Through the fitting of equivalent circuits of onsite EIS and compared with the fresh coating, it was found that not only the electric resistance of the coating was reduced, but also ionic resistance of the coating was reduced significantly. These reductions were accompanied by the increase of water uptake and glass transition temperatures. Electron microscopic analysis showed such changes are associated with the increase of flaws in the coating with increased free volume of the coating as well as associated with the structure of the barrier pigments in the coating, which is susceptible to the changes of service conditions, e.g. cyclic variation of between wet and high humidity and cyclic heating and cooling of environments.

**Some outstanding issues and anomalies in mobility and transport near polymer/solid interfaces**

Richard A.L. Jones1, A.J. Parnell2, S.L. Burg2

[1] Department of Materials Science, University of Manchester

[2] Department of Physics and Astronomy, University of Sheffield

The failure modes of polymeric anti-corrosion coatings necessarily involve transport of water and ions, not just through the bulk of the resin, but crucially in the vicinity of the coating/substrate interface. This transport is likely to be highly anomalous – there is growing evidence that within a region of a few nanometers or more from an interface, macromolecular dynamics are substantially perturbed from their bulk parameters, even in the absence of chemical heterogeneity. How polymer segmental motions on different length and time scales are affected by the interaction with the interface is not yet clear, nor is the way polymer chain motion is coupled with the transport of the diffusing species fully understood. Moreover, some key experimental probes of these effects – for example measurements of the thickness dependence of glass transition temperatures – look at collective phenomenon that may be confounded by other effects. In this talk, I will summarise progress so far and map out a route to a better understanding of these important effects.

**Challenges in prediction of corrosion by FEM modelling**

Herman Terryn1,2

*1 Vrije Universiteit Brussel, Research Group SURF Electrochemical Surface Engineering,*

*Materials and Chemistry Department MACH,*

*Pleinlaan 2, 1050 Brussels, Belgium*

*2 Delft University of Technology,*

*Corrosion Technology and Electrochemistry*

*Department of Materials Science and Engineering,*

*Mekelweg 2, 2628 CD Delft, The Netherland*

*herman.terryn@vub.be*

In the advanced materials industry, there is a clear trend towards more sustainable concepts, and this is certainly also the case for metals. Nowadays, metals are developed for providing components with a typical lifetime ranging from 10 to 25 years. The lifetime of a metal highly depends on its exposure to the environment inducing ageing processes. In the current state of the art, lifetime and ageing assessment are performed by means of experiments, combining accelerated and field testing. The limitation of the first is that the conditions of the accelerated tests are not representative for the real environmental conditions and that there is no proven relationship between accelerated laboratory tests and field performance data. The limitation of the second is that it takes several years (5 to 10 years).

The long term scientific motivation of our research is to build a knowledge and technology platform to enable the prediction of durability behaviour and the estimation of lifetime of (organic coated) metals under long-term environmental ageing and corrosion conditions. This requires advanced research because corrosion of a (organic coated) metal is the result of an intense interplay between several physical phenomena that need to be characterized in real conditions and modelled. Within VUB and TUDelft research we try to focus on both aspects bringing in new advanced combined electrochemical & in situ surface analysis, advanced finite element electrochemical modelling and more recently quantum chemical modelling.

Acknowledgements: all VUB-SURF and TUDELFT-CTE colleagues for the excellent collaborations

**Anti-corrosive paints: diffusion and dissolution through a pore network**

Josef Giddings, Claudio Pereira Da Fonte: Chemical Engineering, University of Manchester

Simon Gibbon, Peter Visser: AkzoNobel

Most of us think that coatings used to protect a metal from corrosion are perfect barriers that prevent water and ions from reaching the metal surface, limiting the extent of chemical reactions that lead to its corrosion. Nevertheless, a perfect barrier is hard to achieve on large surfaces, and coatings can get damaged when exposed to the elements or working environments. Therefore, many applications, from packaging of consumer goods to the aerospace sector, require complex formulations of coatings consisting of a polymer matrix loaded with corrosion inhibitor particles that can dissolve, leach out of the coating and create a protective layer on an exposed metal surface when the coating is damaged.

In this talk, we consider a simple diffusion model with a front-tracking moving mesh algorithm in order to capture moving interfaces corresponding to the dissolution of the leachable particles. This methodology will allow us to describe the dynamic evolution of the pore network structure and mass transfer from the coating to the defect area in a physically grounded way, which will represent a major breakthrough towards building a virtual twin of a coating.

**Novel zinc-rich organic coatings for infrastructure and offshore applications**

Isehaq Al-Nafaia, Stuart Lyona, Chris Jonesb, Douglas Beaumontb, Simon Gibbonb

aDepartment of Materials, The University of Manchester, Manchester, M13 9PL England, UK

bAkzoNobel, Stoneygate Lane, Felling, Gateshead, NE10 0JY England, UK

Novel zinc-rich organic coatings with different contents of zinc and aluminium have been made and tested for anti-corrosion performance. Electrochemical measurements, such as OCP vs time and electrochemical impedance spectroscopy, were carried out to investigate the cathodic protection and barrier effect. Furthermore, the investigation included standard corrosion test such as neutral salt spray. The characterisation and analysis of the new coatings, before and after electrochemical tests, involved SEM microscopy to study the morphology and structure, and XRD analysis to assign the phases and corrosion products. Results showed an enhanced anti-corrosion performance for the new Zn-Al formulations in all electrochemical tests and salt spray compared to commercial ZR epoxy coating. The better performance was reported for coatings with Al content of 10 -15 wt.%. The observed improvement in anti-corrosion properties can be attributed to increased structure compactness that caused by successful dispersion of Al flakes between Zn particles vacancies. In addition, the Al flakes improved the percolation path between Zn particles and extended the galvanic action. Besides, the corrosion products analysis revealed the presence of relatively high amounts of simonkolleite and Zn-Al layered doubled hydroxide (LDH). These corrosion products improved the barrier effect of the coatings. The presence of Zn-Al LDH proves that Al took place in galvanic action over longer immersion time when the local pH is high enough to cause Al dissolution. The new Zn-Al formulations showed promising alternatives to standard zinc-rich epoxy coatings.

**Corrosion testing under variable pH: experimental setup and preliminary results**

Michele Curioni, Meng Lyu, Fabio Scenini

*Department of Materials, School of Natural Sciences, University of*

*Manchester, Oxford Road, M13 9PL, Manchester, UK.*

*Michele.curioni@manchester.ac.uk*

A new experimental design is introduced to control the pH of a sodium chloride solution used for corrosion tests and simultaneous electrochemical measurements. An electrochemical cell, separated into two chambers with a porous material that allows ion exchange between the two chambers is used. Graphite electrodes are placed in each of the two chambers and connected to a computer-controlled variable voltage power supply. A pH probe is placed into one of the chambers (the test chamber) and connected to a controller that sends the pH value to the computer. In the same compartment where the pH electrode is placed, a counter electrode, an Ag / AgCl reference electrode and working electrode (ie the specimen under study) are placed. An automatic controller connects the two graphite electrodes in the two cells and provides sufficient potential to generate hydrogen from one electrode and oxygen from the other. As a result, the pH of the half-cell where hydrogen develops increases, while the pH of the half-cell where oxygen develops decreases. By measuring the pH of the test cell and applying the appropriate potential to the graphite electrodes, the pH value of the test cell can be adjusted, and pH scanning experiments performed. Furthermore, the same controller allows electrochemical measurements to be made on the working electrode placed in the test cell. As a result, information on changes in electrochemical behavior as a function of pH can be obtained with only one experiment. This paper introduces the experimental setup and provides some application examples on treated aluminum and magnesium.

**The influence of zinc loading on the efficiency in the transfer of galvanic current during cathodic protection mode by the zinc dust in epoxy zinc primers on steel**

Katarzyna Rzeszutek, Stuart Lyon (The University of Manchester),

Douglas Beaumont, Christopher Jones, Simon Gibbon (AkzoNobel)

Every year, around 4 million tonnes of zinc is used in the form of coatings to protect roughly 100 million tonnes of steel. It is assumed that zinc-rich coatings can only work similarly to metallic coatings, i.e. sacrificially. Nevertheless, environmental and cost pressures are strong factors encouraging the reduction in the quantity of zinc in such materials.

In the presented research work, the conventional zinc-rich primer, and the three primers with reduced zinc content have been tested in both intact and scribed forms. Open Circuit Potential measurement (OCP), Anodic Potentiostatic Polarisation (APP), Electrochemical Impedance Spectroscopy (EIS), and Scanning Electron Microscopy (SEM) have been employed to characterise and evaluate the performance of every zinc paint. The study shows the relationship between zinc loading in the analysed coatings and their efficiency in the transfer of galvanic current during accelerated corrosion testing. The analysis of the amount of dissolved zinc from all coatings indicates that the ratio of the anode and the cathode surface areas that are exposed to a corrosive medium affects the utilisation of the zinc for the galvanic protection.