

UNDERSTANDING AND PREDICTION OF SURFACE PROTECTION MATERIALS AND PROCESSES PROPERTIES

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Summary

In addition to experimental investigation numerical modelling and simulation is a well known and accepted method to describe, understand and predict the behaviour and performance of materials as well as of technical compounds. Depending from the technical questions various simulation techniques could be applicable. This paper gives an overview about the use of simulation methods to simulate materials and process behaviour in surface technology for typical aircraft applications.

1. INTRODUCTION

Modelling and simulation of material and process behaviour were identified as one key factor for requested development time reduction within aircraft industry. The aim of the here presented modelling and simulation activities is to provide stepwise mature simulation methods to predict behaviour of surface protection systems under in-service conditions. Understanding, modelling and simulation of surface protection relevant effects as e.g. (galvanic) corrosion in mix material assembly (e.g. CFRP-AL...) and its interaction with protection system as well as the environmental conditions will enable significant reduction in definition and development time for surface protection systems and the associated, necessary experimental test effort.

The presentation will give an overview about Airbus surface technology modelling and simulation work

- adhesion mechanism and behaviour of coatings and sealant materials,
- (galvanic) corrosion simulation
- simulation of wear and fretting behaviour

and the interdependencies of material/process behaviour from parameters as environmental condition, geometry, kind of surface protection, material or material combination will be shown. To obtain a sensible result to this wide range of investigation the suitable modelling methods has been used as FEM and BEM methods as well as quantum mechanical methods.

The presentation will be focused on aircraft relevant materials and material combination as well as surface protection systems.

2. MODELLING OF COATING BEHAVIOUR

2.1. Behaviour of poly sulfide sealants

Sealant materials are used in a wide range within aircraft industry. Polithioether are used as quick curing sealants with high adhesive properties. For most structural application polysulfide sealants are in use. The sealants combine different functions that are mandatory for aircraft

structural performance and durability. The sealants enable fuel tightness of the wings and other tank areas. In assembly the sealants avoid moisture access to cavities and gaps and are mandatory part of the corrosion protection system. For mixed material assembly (e.g. aluminium parts assembled with composite material or steel) the sealants result in electrical insulating between the different materials and avoid galvanic corrosion. On the outer surface of the aircraft sealants fill gaps and smooth so the structure what results in better aerodynamic behaviour. As shown in **Fehler! Verweisquelle konnte nicht gefunden werden.** the sealants are applied as interlay, fillet or overcoat sealant.

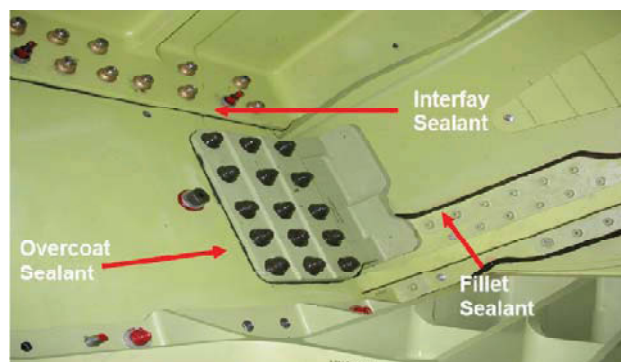


BILD 1. Different kind of sealant application

The bonding characteristics of self-bonding cured polysulfides can be determined experimentally. The properties of polysulfide sealants as well as polithioether sealants have been investigated with respect to self-bonding after compression under a variety of conditions. It was found that polithioether sealants have a limited self-bonding after pressure compared to polysulfide sealants what is caused by the different chemical composition. Using molecular dynamics and computational chemistry approaches simulation of physical and chemical mechanisms involved in the self-bonding of polysulfide- and polythioether based sealants has been done. Relevant aspects of the self-bonding process by providing insight into the physical and chemical mechanisms: The physical mechanisms of the self-bonding process

include polymer chain mobility which leads to chain entanglements for both types of sealants studied. As a result of the chain mobility, a nearly homogeneous distribution of polymer backbone atoms is found in the former gap region which enables chemical reactions involving functional groups of the polymer. An example of a computation based on molecular dynamics for a polythioether sealant is shown in BILD 2. Similar results have been obtained for polysulfide sealants.

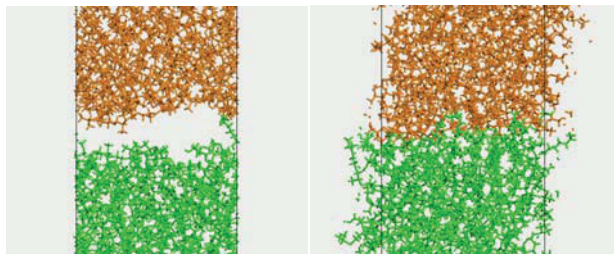


BILD 2. Structural development during the MD simulation shown for simulation times of 5 ps (left) and 500 ps (right) for typical polythioether sealant

In the case of polysulfides, the intimate contact of functional groups enables energetically favourable substitution reactions at disulfide linkages which is the most probable chemical mechanisms for self-bonding for this class of compounds. In the case of the polythioether-based sealants, chemical reactions leading to chain transfer and thus improved self-bonding performance are less likely.

Disulfide bridges encountered in polysulfide-based sealants are susceptible to nucleophilic attack which leads to dissociation of the bridge and initiates chain transfer which eventually leads to self-healing. In this report, we consider nucleophiles originating from polymer-terminating mercaptan groups (1) and also nucleophiles (2) which are present as impurities in the cured sealants.

- (1) $\text{RSH} \rightarrow \text{RS}^- + \text{H}^+$
- (2) $\text{RSSR} + \text{Nu}^- \rightarrow \text{RSNu} + \text{SR}^-$
- (3) $\text{RS}^- + \text{R'SSR}' \rightarrow \text{RSSR}' + \text{SR}'^-$

As an example the energy profile of the reaction of SH^- with the disulfide bridge present in the backbones of polysulfide based sealants is shown in BILD 3. The largest reaction barrier in this two stage reaction amounts to only 11 kcal mol⁻¹. This reaction represents step (2) of the mechanism in which the disulfide linkage is disrupted and a nucleophile (MeS^-) is formed. Based on this simulation and in comparison with other theoretically possible mechanisms, it can be concluded that chemical reactions between backbone functional groups can improve the self-bonding by generating new chemical bonds which cross the former gap between the polymeric surfaces. These backbone reactions are more likely in the case of polysulfides which contain reactive disulfide $-\text{SS}-$ linkages susceptible to nucleophilic attack at sulphur centres as compared to polythioethers which lack these groups. Polysulfide-based sealants are therefore expected to exhibit a greater tendency towards self-bonding.

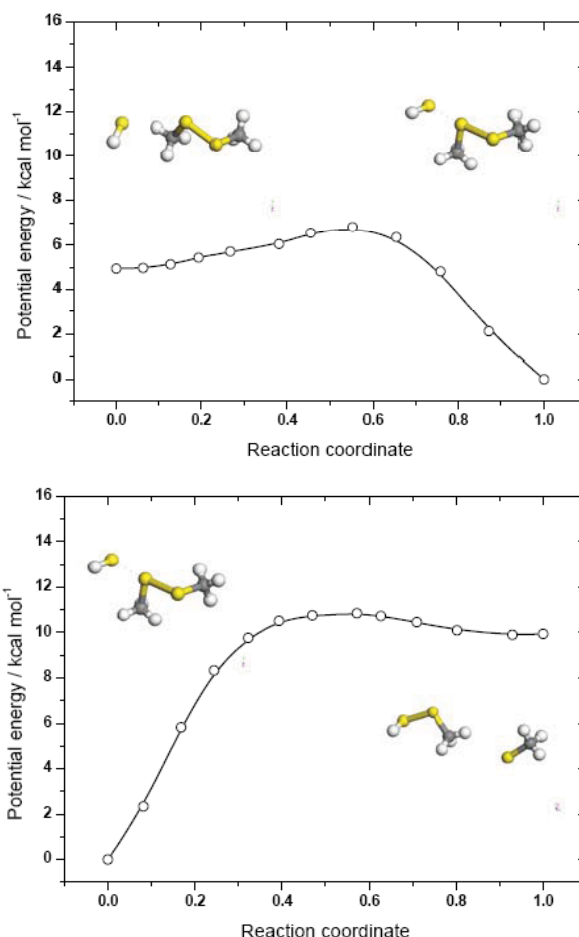


BILD 3. Energy profile of the reaction of SH^- with the disulfide bridge present in the backbones of polysulfide based sealants what represents step (2) of the mechanism.

2.2. Behaviour of sol-gel coatings

Sol-gel derived films are developed as potential alternatives for metal-surface pre-treatment methods. Inorganic sol-gel derived films cannot provide adequate corrosion protection, due to their high crack-forming potential. Introduction of an organic component to an inorganic sol-gel system leads to the formation of more flexible and functionalized films with enhanced compatibility to different organic top coatings. Previous analytical investigations using a commercial product (AC130) and one model sol-gel system reveal first indications regarding the chemical interaction between sol-gel systems and the surfaces of AA2024 alloys.

The bonding characteristics of the sol-gel layer to the surface of the amorphous aluminium oxide are investigated by means of molecular simulation techniques. Main focus was on the influence of Zirconium both on oxide stability and on the sol-gel layer bonding itself. Conceptually, the sol-gel layer to alumina interface can involve chemical bonding as proposed by various authors [1] and as indicated in BILD 4.

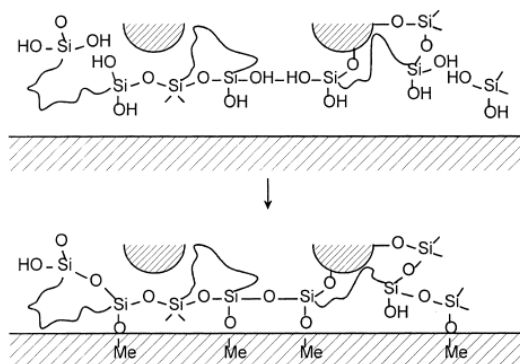


Figure 3 Concept of the interface design for corrosion-protective coatings on aluminium

BILD 4. Concept for the Sol-gel-Layer to Alumina surface bonding from [1]

Technically, molecular simulations can be conducted by means of molecular dynamics (MD) approaches which employ empirical potentials to represent the interatomic interactions. This approach is applicable to large scale models and can be used to gather statistical information on amorphous systems but is restricted in the sense that chemical bonding cannot be described.

Computational chemistry techniques including ab initio and Density Functional Theory (DFT) are used to study chemical reaction mechanisms and the electronic structure of condensed matter systems. In the context of this report, Density Functional Theory is used to study the specific interactions of Silicon and of Zirconium at the oxide surface in order to judge the binding strength of both covalent and also of hydrogen bonding to the interface as well as hydrolytic stability. The band structure of alumina which is influenced by the incorporation of hetero-atoms is investigated using plane-wave Density Functional approaches.

In order to interpret the effect of Zirconium on the properties of the amorphous aluminium-oxide and on the final bonding characteristics of the Sol-Gel layer, the simulation studies first focus on the incorporation of Zirconium into the amorphous alumina. The simulation addresses the question whether Zirconium can be incorporated into the bulk oxide phase, or whether the effect will be limited to the surface exposed to the Sol-Gel layer.

Results for the effect of bridge protonation on bond stabilities are presented in BILD 5. In the case of Silica to alumina bonding, the bond strength is lowered, while in the case of Zirconium to alumina bonding, the formation of double bridges leads to an increased bond strength.

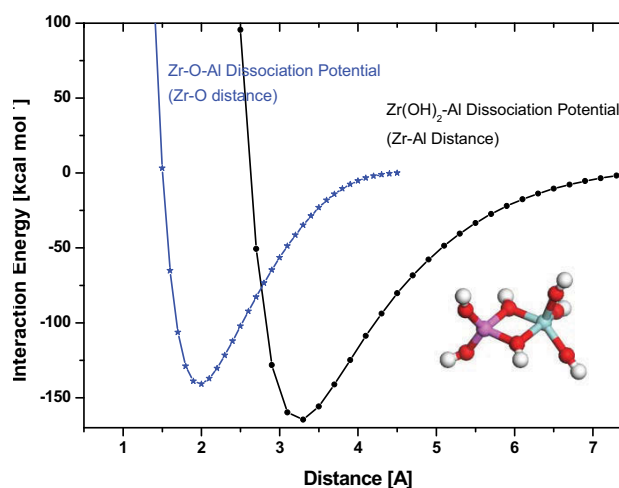
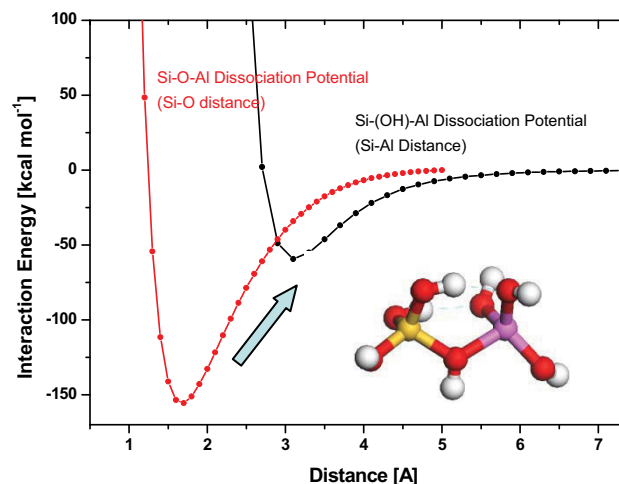


BILD 5. Changes to the potential energy for dissociation of an Ei-O-Al bond upon protonation of the bond. Note that in the figure, the distance corresponds either to the Ei-O distance (bridge) or to the Ei-Al distance (protonated bridge).

For both Silicon and Zirconium, the strength of bonding to the alumina surface depends on the pH-value. It is observed that with increasing proton concentration (decreasing pH), Zirconium can form bridged complexes which are not realised for the analogous Silica compounds. In the Zirconium complex, an increase in bond strength with decreasing pH is observed: Protonation of Si-O-Al bonds weakens the interaction while the protonation of Zr-O-Al bonds strengthens the interaction.

In comparison to experimental test results (peel and bondline corrosion) this positive effect of the Zirconium on the interphase stabilisation could not be confirmed. The Zirconium n-propoxide can not be organic cross linked, so that Sol-Gel film stability is decreased with increased Zr content. In relation to test results the conclusion can be drawn, that the theoretical positive effect of the interphase

stabilisation is probably super composed by increasing instability of the sol-gel film.

3. GALVANIC CORROSION

Corrosion protection plays a very important role in the design and maintenance of the aircraft. The alloys currently used are the compromise of high specific strength and corrosion resistance. The extreme long aircraft design life requires extremely durable protection systems to ensure acceptable operational cost during in-service.

In the aircraft industry more lightweight materials such as aluminium, magnesium, titanium and CFRP (Carbon Fibre Reinforced Plastics) are utilized in conjunction with conventional metals such as steel. Galvanic corrosion (GC) is one type of corrosion and can occur when two different materials with different electrochemical properties are coupled in the presence of a corrosive electrolyte. Therefore, galvanic corrosion is the undesirable result of this "mixed materials" usage. New aircraft designs contain a high degree of CFRP materials which are in contact with Aluminium in specific areas and can cause galvanic corrosion, since the carbon fibres behave electrochemically like a noble metal where cathodic corrosion reaction will take place. One of the general objectives of modelling GC is to tailor the corrosion protection measure in order to avoid GC for hybrid structures without performing a huge amount of laboratory testing [1].

This chapter gives an overview about development and experimental validation of a computational model for simulating galvanic corrosion in typical case scenarios appearing in an aircraft environment. The numerical approach is based on the three dimensional Boundary Element Method. The necessary input data are: Geometrical description and physical properties of the electrolyte, as well as macroscopic polarisation curves of the active electrodes. The main outcomes of the model are corrosion rates, electric current density and potential distribution [3].

The case study used for the validation consists of a co-planar pair of Aluminium AA 2024 and carbon fibre reinforced polymer (CFRP) immersed in saline solution with variable coating conditions. In particular, the case of a circular damage ("pinhole defect") of a coating of very high insulating properties on the anodic side of the sample is considered.

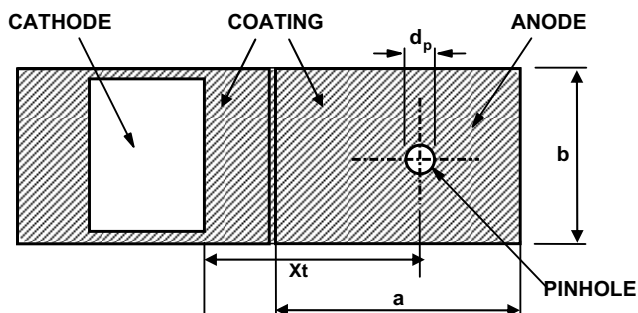


BILD 6. Sketch of a top view of the co-planar galvanic corrosion model indicating the main parametric notions

A comparison between experimental measurements and numerical results of total current flowing between anode and cathode and the corresponding potential for different electrolyte conductivities and various cathode anode ratios are shown in BILD 7 and BILD 8. Very good agreement has been obtained between experimental and simulated results for systematic variations of different case study which consider different locations of the damage in the sample, different surface area ratios between anodic and cathodic regions, and different electrolyte conductivities. The successful validation of the modelling approach has enabled its use for simulating galvanic corrosion in more complex structural components of an aircraft.

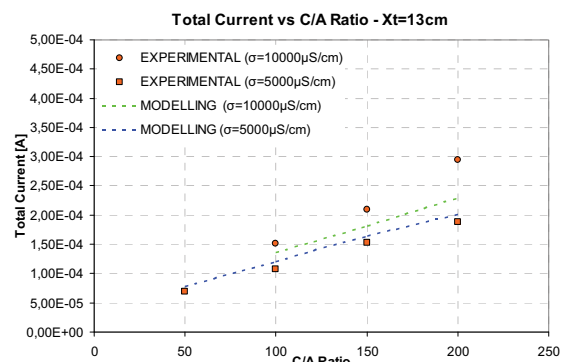


BILD 7. Comparison of modelling results against experiment for the variation of total current in function of the C/A ratio

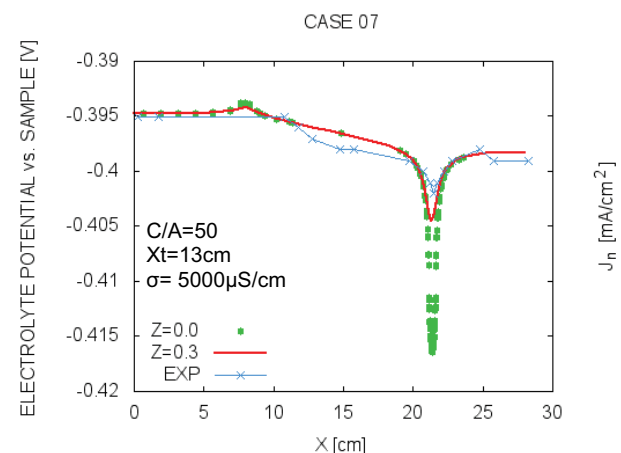


BILD 8. Potential measurement against distance in x-direction

Very good agreement has been obtained between observed and simulated results for systematic variations of the case study which consider different locations of the damage in the sample, different surface area ratios between anodic and cathodic regions, and different

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4. MODELLING OF FRETTING BEHAVIOUR

Fretting is a damaging process taking place in assemblies which can result in premature damage such as wear or cracking. Fretting is characterized by small oscillatory motion between components. In case of large oscillatory motion the main damaging process is wear whereas in case of small oscillatory motion it is cracking. In BILD 9 a typical fretting scar and a resulting crack is shown.

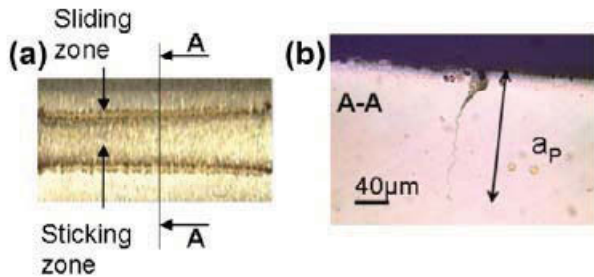


BILD 9. (a) Fretting scar and (b) illustration of crack observed in the cross section after polishing

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To predict the behaviour of anti-fretting coatings and to support numerical component/assembly design a non-local approach to account for stress gradient effect in fretting is proposed in [5] and [6]. A comparison between experimental results obtained in a setup with an Inconel 718 cylinders of different radii R and numerical results are shown in BILD 10.

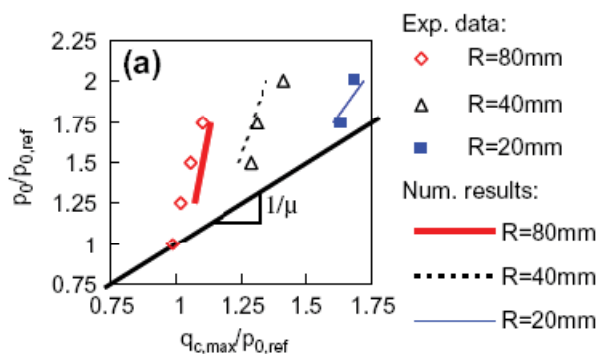


BILD 10. Experimental and numerical initiation boundaries in a p_0 - $q_{c,max}$ diagram.

The maximum pressure p_0 and the maximal value of the surface shear traction $q_{c,max}$ are normalized using the reference pressure $p_{0,ref}$. The numerical results show good correlation with experimental results. Compared to other models based on constant volume approach [7] or variable volume approach [8] the error between experimental and numerical results could be reduced down from 10% lower to 6%.

5. CONCLUSION

Modelling and simulation is identified as key for reduction of development time and cost for new materials and processes. Different modelling techniques like FEM, BEM or molecular modelling have been used to describe and understand aircraft relevant technical questions. A good understanding of physical and chemical models as well as numerical methods is mandatory for a sensible use. The highest benefit will be achieved by sensible combination of modelling and simulation methods, in service evaluation and experimental investigation. Airbus will continue modelling and simulation work in cooperation with scientific partners and material suppliers.

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