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From Molecular Aspects of Delamination to New Polymeric Coatings

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Summary: The delamination of organic coatings from reactive metal surfaces has been examined by different kinds of techniques. The electrochemical behavior of the delaminating system has been proven by the Scanning Kelvin Probe technique to be a combination of localized electrodes between the defect, delamination front and intact interface. A first idea of the extent of the delamination front could be gained. To achieve an even deeper insight in the characteristics of the delamination, Scanning Kelvin Probe Force Microscopy (SKPFM) has been used for in situ delamination experiments for the first time. This technique permits a high lateral resolution of the potential distribution and, at the same time, detection of the topographic changes of the substrate. An overview of the development of delamination research from macroscopic to submicroscopic resolution is given here.

Keywords: Kelvin probe; delamination; corrosion; coatings; cathodic debonding

Introduction

The delamination of polymers from reactive materials such as steel or galvanized steel has been investigated in the past by many techniques (1-4). Among others, the Scanning Kelvin Probe (SKP) has been used to analyze potential profiles along the delaminating interface. With this technique surface areas which are intact (anodic electrode potential) and those which are already delaminated (cathodic electrode potential) can be readily distinguished. Using these data, the kinetics of the delamination process is elucidated as a function of relevant parameters, e.g. ionic concentration of the electrolyte or the pre-treatment of the metal surface. Furthermore, principle reactions leading to delamination have been described using the SKP in combination with spectroscopic and gas exchange experiments (5-7).

However, little is known about the lateral extension of the reaction zone, which is defined as the

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transient area between the intact metal/polymer interface and the delaminated interface. Also kinetic details of the electrochemical and chemical reactions within this reaction zone are little understood. Therefore the lateral resolution of the electrochemical techniques being able to detect the local reaction zone is increased while the chemical und structural complexity of the interface is decreased, leading to improved applicability of sophisticated spectroscopic techniques. In this paper, first results which have been obtained in this research field are summarized.

EXPERIMENTAL

Only a short overview of the special experimental parameters of the new SKPFM technique is given here (8-9), since the number of different sample set-ups is high. For more detailed information on the other sample set-ups, see publications (5-6).

The SKPFM measurements have been carried out with a Dimension 3100 extended (Digital Instruments, Veeco) atomic force microscope. For the experiments n-doped silicon tapping mode tips were used. The measurements were carried out in a custom-made glass cell purged with humid air to control the relative humidity of the environment.

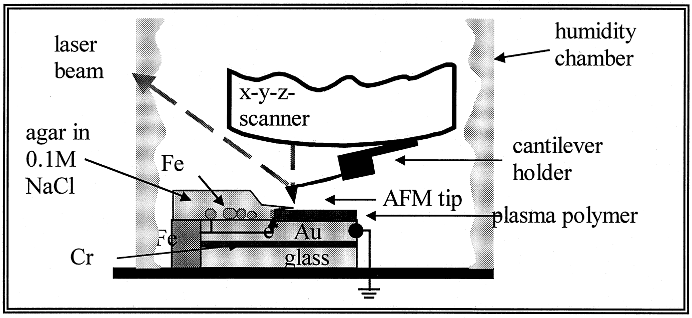

Figure 1: Schematic sample set-up for model cathodic delamination experiments.

To achieve a reasonable local resolution in this study, a specific optimized flat sample set-up was preferred (Fig.1). Flame annealed gold was covered by an ultrathin plasma polymer film made from hexamethyldisilane and electrochemically coupled to iron to set the electrode potential of the polymer coated gold to $-0.4V_{SHE}$. 0.1M NaCl in agar was used as the electrolyte and applied onto the surface. The gold surface, which allows electron transfer but no ion transfer reactions, behaved similar to a passive iron electrode below the organic coating and served as the local cathode during delamination while the iron acted as the local anode.

RESULTS AND DISCUSSION

Scanning Kelvin Probe

Some information on the lateral extension of the delamination zone was obtained by comparing potential profiles as measured by the SKP with local de-adhesion measurements (Fig.2). These data have been obtained for galvanized steel (5). The local de-adhesion was measured by detecting the force necessary to locally remove the polymer film from the substrate. The SKP showed a continuous transition from a detached interface represented by negative potentials to an intact interface represented by anodic electrode potentials. The corresponding plot showing the mechanical adhesion clearly reveals 3 regions: intact interface (tensile force 0.3N/mm), delaminated interface (tensile force approx. 0) and an area in between (tensile force 0.15N/mm) which could be attributed to the reaction zone, since the interface was already weakened but adhesion was not yet lost.

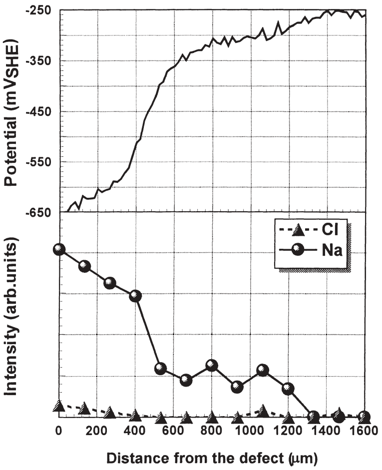

Figure 2: Galvanized steel. Top: Potential drop from delaminated (left) to intact interface (right). Bottom: Correlated tensile force. (5)

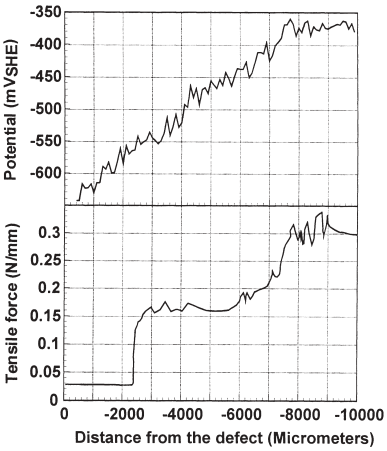

Figure 3: Top: Potential drop over delamination front. Bottom: Correlated ESCA line scans.

The information concerning the reaction zone of interest is even more precisely described, if the SKP potential profile is compared to the interfacial chemical analysis measured by ESCA (Fig.3) (5). Again the potential profile shows a continuous transition between negative and positive electrode potentials whereas the concentration profile, in particular of sodium ions, is quite interesting. The fact that the sodium concentration grossly exceeds the chloride concentration proves the existence of an electrochemical galvanic cell with the oxygen reduction taking place below the organic coating.

Between 0 and 400μm the coating was already delaminated, as seen by the low electrode potentials and the high sodium concentration. This points to a high rate of oxygen reduction. Between 600 and 1200μm the coating is still adherent (high potentials) but small amounts of sodium are already found at the interface. Obviously within this region oxygen is already reduced and the front of de-adhesion lags behind a front of oxygen reduction as marked by the incorporation of sodium. Therefore the zone between 600 and 1200μm could be identified as the crucial reaction zone. As the time necessary to shift the point of de-adhesion from 600 to 1200μm is in the order of 60min and the rate of oxygen reduction at the buried interface is in the range of 1μA/cm^2, the charge necessary to electrochemically destroy the interface amounts to approximately 4mC/cm^2. This corresponds to a consumption of 10 monolayers of oxygen.

Obviously, the SKP has a precision to detect unambiguously the size of the reaction zone for weak coatings. However, for better adherent coatings, the lateral extension of this zone is smaller and not easily detectable with the SKP. Moreover the delamination frontier appears to be even and any potential differences based on inhomogeneities on a mesoscopic scale is missing due to a lack of lateral resolution. This limit is overcome by the Scanning Kelvin Probe Force Microscopy (SKPFM).

Scanning Kelvin Probe Force Microscopy (SKPFM)

Set-up and principles of the SKPFM have been described elsewhere in detail (10-13). In particular, Frankel et al. have used the SKPFM technique extensively in order to analyze the corrosion of Al-based alloys (14-16). However, the delamination of organic coatings has not yet been analyzed with SKPFM. The special sample set-up already described in the experimental section successfully initiated cathodic delamination which proceeds similar to the cathodic delamination on iron. Fig.4 compares the AFM-topography a) with an SKPFM potential image b).

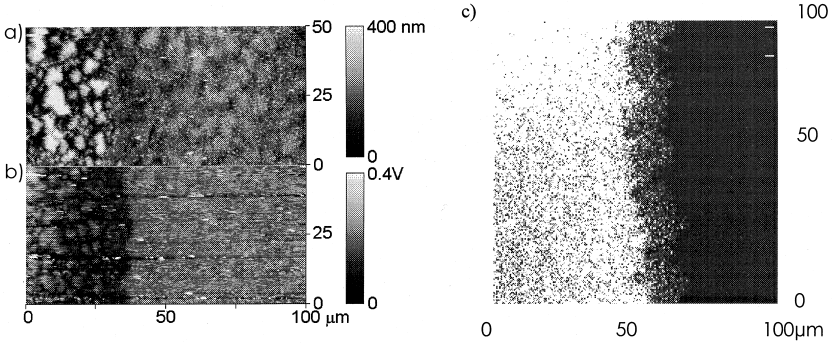

Figure 4: a) Topography of a plasma polymer coated gold surface during delamination. b) Correlated potential map. c) TOF-SIMS: Correlated sodium distribution.

Only the delamination front was visible which is situated at a distance approximately 5000µm from the defect. Delamination is seen in the AFM map as an elevated section and is therefore easily visible. The delamination front as deduced from the height profile is marked by the white dashed line. On the Voltapotential map the delamination is also clearly visible as a region of low potential similar to the conventional SKP results. However, the front of the negative electrode potential exceeds the delamination front by a constant distance of approximately 10µm.

The magnified cross-section of the potential map for a similar sample is shown in Fig.5. A potential transient is clearly visible over a distance of 7µm, which is rather comparable to the difference between the de-adhesion front and the sharp potential decline. Obviously this potential transient marks the reaction zone which leads to de-adhesion. The size of this reaction zone is well within the lateral resolution of the SKPFM technique and therefore lies easily within the detection limits. It is rather astonishing however, that the potential drop detected by SKPFM is quite small in comparison to the potential drop as measured by the SKP on the same surface (600mV). The reason for this difference is a subject of present investigations.

The dimension of the reaction zone was further confirmed by TOF-SIMS measurements as shown in Fig.4c. SIMS results prove that only sodium was incorporated into the interface and a sharp transition is seen between the delaminated area (bright region) the intact area (dark region) and the reaction zone (medium brightness) the width of the latter being again approximately 10µm. In contrast to the continuous potential profile, the chemistry between the reaction zone and the delaminated zone changes abruptly for reasons not yet understood.

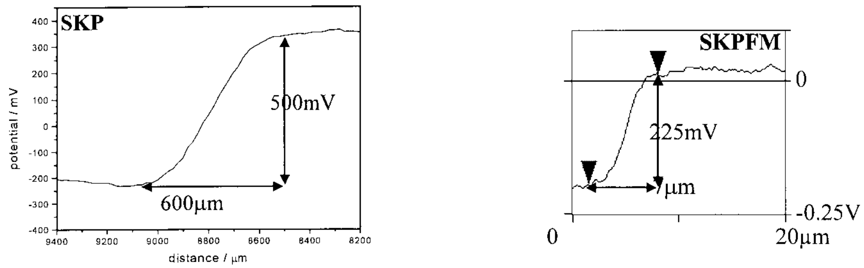

Figure 5: Potential scan at the delamination front a plasma polymer coated Au surface a) Scanning Kelvin Probe b) Scanning Kelvin Probe Force Microscopy.

However, it is quite obvious that a well defined reaction zone exists with dimensions well beyond molecular dimensions. The chemistry and electrochemistry going on within this reaction zone is the subject of ongoing studies.

Delamination of molecularly well defined interfaces

First studies have been undertaken on model interfaces whose chemical and structural composition is well defined (Fig.6a). Cathodic delamination was also initiated on these samples and the TOF-SIMS analysis of the reaction zone now shows a fine structure which was not seen on the disordered plasma polymer/metal interfaces (Fig.6b).

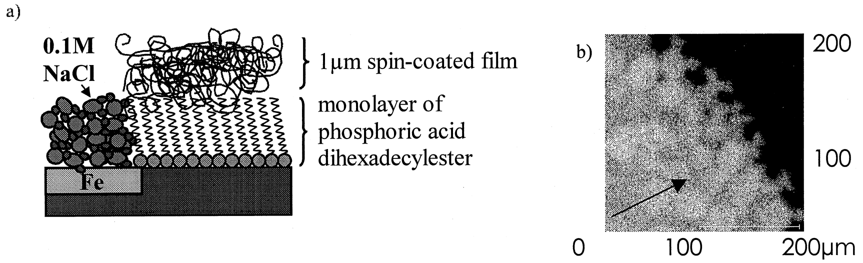

Figure 6: a) Schematic sketch of the sample set-up. b) TOF-SIMS: Sodium distribution at the delamination front (delamination direction indicated by arrow).

Once again, only sodium was incorporated into the interface not by a homogeneous front but by local patches which grow together and form domain-like structures. The size of the structures which incorporated sodium is quite comparable to the domain size of the underlying Langmuir-Blodgett film. This could point to the fact that the local diffusion path and the local electroreduction of oxygen is determined by the local disorder of the metal/polymer interface.

Conclusion

In this study, Volta potential profiles have been measured for the first time on a delaminating interface with a local resolution in the sub-µm range. A well defined reaction zone of approximately 10µm has been observed, which marks the transition from an adherent to a delaminated interface. Within the reaction zone a preferential incorporation of sodium is observed which demonstrates, that within this zone oxygen reduction is the predominant electrochemical reaction leading to delamination. The oxygen reduction and the corresponding incorporation of ions may be determined by the order and supermolecular chemistry of the interface.

Acknowledgements

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