Delamination of Poylmer Coatings from Metal Substrates: Submicroscopic and Molecular Aspects

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INTRODUCTION

Delamination of organic coatings from metal surfaces can occur in a number of different ways, e.g. as pure cathodic delamination, as Filiform corrosion or a mixture of these. In fact, in most technical systems the pure cases are the exception and, of course, delamination is usually very slow. It has been shown that in fast delaminating systems the length scales may range between several 100 μm and several millimetres, while in systems which show slow delamination the reaction zones can be confined to submicroscopic distances [1]. This underlines the importance of investigation methods with submicroscopic resolution. As a very promising new technique Scanning Kelvin Probe Force Microscopy (SKPFM) was applied for the investigation of cathodic delamination and filiform corrosion on a submicroscopic scale [1 , 2]. Indeed, these first investigations have shown that SKPFM gives basically the same information as the standard Scanning Kelvin Probe (SKP), but with a much improved resolution. It could be shown, for instance, that the extension of the reaction zone seems to be much narrower than would have to be assumed from the SKP measurements. Based on the knowledge about the different delamination types that was obtained from investigations with the standard SKP [3-12] the SKPFM should be the ideal tool to get information on the submicroscopic scale. However, SKPFM alone is not sufficient for revealing the underlying fundamental mechanisms; of even higher importance is the knowledge of the molecular and mesoscopic structure at the buried interface. In this paper a design for suitable model samples is proposed and first results are presented.

EXPERIMENTAL DETAILS

The in situ use of the SKPFM set-up for delamination experiments requires the use of a humidity cell to keep the delamination active. Therefore a custom-made glass cell for the Dimension 3100 (Veeco, Digital Instruments) was built. This cell can be purged with humid air. Depending on flow rate and washing flask parameters, relative humidities of up to 100% can be reached. Since the KPM works with low scan frequencies around 0.5Hz, only slow delamination systems can be investigated.

In order to achieve a high topographic and potential resolution, ultrathin coatings on model substrates have been chosen. For the cathodic delamination experiments discussed in this paper, gold evaporated on glass substrates served as a model surface. The defect was prepared on a part of the gold surface not covered by the polymer coating. The potential at the defect site was adjusted potentiostatically. The electrolyte was 0.1M NaCl in agar applied onto the surface. The gold surface, which allows electron transfer but no ion transfer reactions, behaves 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, thus effectively simulating cathodic

delamination [2, 9]. Indeed, special sample setup successfully initiated cathodic delamination which proceeds similar to the cathodic delamination on iron.

Self-assembled decane-thiol monolayers were chosen as a well characterized molecular monolayers at the interface. The self-assembled monolayer on gold was further coated by about 100 nm of model polymer.

DISCUSSION

As stated above, SKPFM should be the ideal tool for investigating submicroscopic aspects of delamination. However, a number of problems arise when SKPFM is tried to be applied for delamination studies with submicroscopic resolution. Firstly, a controlled environment of well defined humidity needs to be provided [2]. Secondly, special model samples with ultra-thin organic coatings have to be prepared in order to obtain a high resolution.

The concept for the preparation of model samples designed for the investigation of cathodic delamination is as follows: the interface layer is represented by a well characterized highly-ordered SA or LB monolayer. In the first case alkane-thiols are used, in the latter octadecyl amines (ODA). These molecular monolayers are transferred to the sample under control of the electrode potential. The electrode potential can be used to control the domain size and defect morphology of the SA monolayer in a very defined way [9;13]; in the case of the LB layer domain size and defect morphology remain unaffected because they are controlled already by the compression on the aqueous sub-phase. Here the electrode potential determines the incorporation of ions into the interface (to be published elsewhere). Thus, either the morphology of the layer of the alkane chains or the structure of the very headgroup/substrate interface is changed in a very defined way. The molecular monolayers are then covered by an ultra-thin spin-coating. While the thickness of the coating should directly influence the delamination rate in so far as its barrier properties depend on it, the nature of the reactions at the interface should be basically unaffected by this parameter. Hence ultra-thin coatings can be used to study the processes at the buried interface with a high resolution and transfer of the results from these studies to an analysis of the processes beneath thick coatings should be feasible. In the following first results for thiol monolayers at the buried interface will be reported.

Application of SKPFM for studying delamination of ultra-thin polymer coatings

The first investigations of the delamination of ultra-thin coatings showed that SKPFM has to cope with problems that are not observed for SKP experiments on thicker coatings. Fig.1 shows a series of successive AFM/SKPFM images of the delamination frontier of an ultra-thin (ca. 100 nm Ms Top-Lack ®) spin-coated film.

As can be seen especially from the optical images the ultra-thin polymer coatings have no sufficient stability to keep the electrolyte from the defect from seeping under the coating once the interface is delaminated.
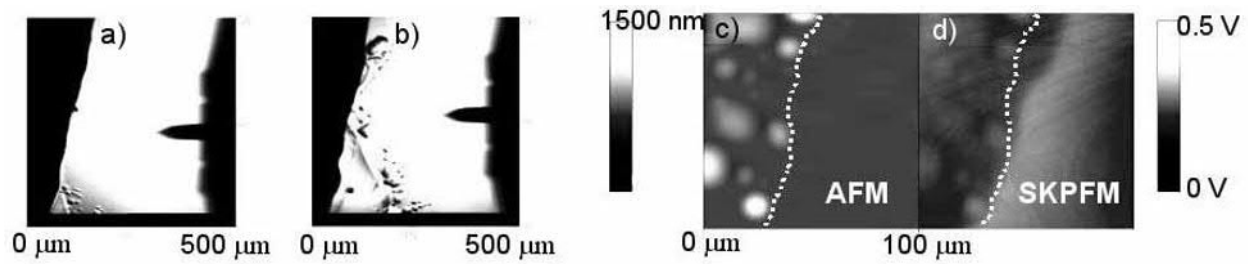
Fig.1: *the optical images a) and b) show the macroscopic delamination behaviour near the defect (black feature on the left). The images were taken after a) 2 and b) 3 hours of initialising the delamination process. It can be seen how electrolyte seeps under the coating and forms pockets. Images c) and d) show corresponding AFM and SKPFM images taken at the delamination frontier. Here nearly complete delamination has resulted in clearly discernible micro-blistering (left in the AFM imag ec)). This are is in the following referred to as "tpographically delaminated". The SKPFM image d) shows that an electrochemical delamination precedes at least partially*

Since these film posses only a low cohesive strength blisters or pockets of electrolyte form under the film which results in considerable bulging of the coating´s surface. These protuberances are an eminent danger for the experiment because even in tapping mode the ultra-thin coating covering the electrolyte underneath might tear open. This results in pulling down of the tip (caused by the high capillary forces) and subsequent contamination of the tip, rendering it unsuitable for further imaging in the Kelvin mode.

It is also obvious from the images that the delamination frontier proceeds very inhomogeneously. This is most likely due to the very low adhesion of the polymer coating to the metal surface. This amplifies the effect of even the slightest differences in the quality of the interface on the delamination. Indeed, for much better adhering ultra-thin plasma polymer coatings on gold a more homogeneous behaviour was found [1, 2]. This inhomogeneous behaviour is also obvious from a comparison of the topographical AFM images and the potential image of the Kelvin mode also depicted in fig.2. While in the faster delaminating upper part of the delamination frontier the electrochemical delamination (discernible from the Kelvin mode image by its lower potential) precedes the topographical delamination (as characterized by the blistering) by up to 15 μm, in the slower lower part no preceding electrochemical delamination is discernible.

Hence, a preceding electrochemical delamination plays an important role on the velocity and general behaviour of the delamination.

In the case of the more homogeneously and slower delaminating plasma polymer films a homogeneous separation of about 7 μm between electrochemical and topographical delamination was observed [1, 2].
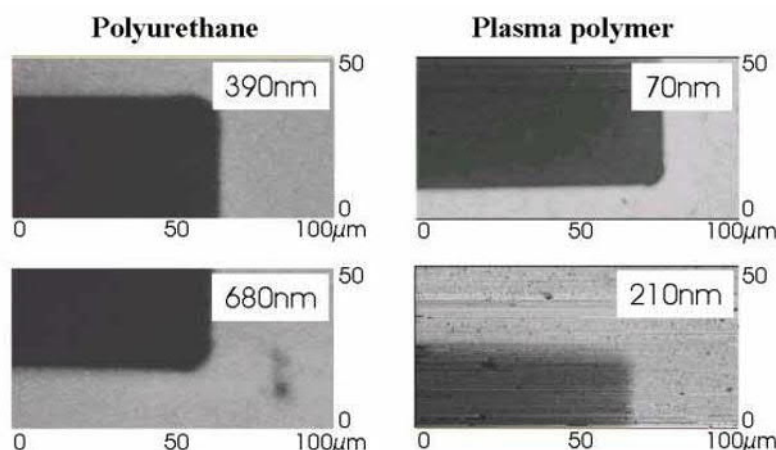
Polyurethane **Plasma polymer**

390nm 70nm

680nm 210nm

Fig.2 *Kelvin mode SKPFM images of evaporated nickel (low Volta potential) on gold, coated with polyurethane resp. a plasma polymer film of different thickness. Especially for the case of a 210 nm plasma polymer the nickel corner is significantly blurred, while for the 680 nm polyurethane coating it is still sharp.*

This emphasises the importance of a better understanding of the fundamental processes at the delamination frontier. Still not understood is why the measured potential in preceding electrochemical delaminating area shows the same value irrespective of the distance from the topographical frontier. While in the topographically visible delaminated area the coating is completely de-adhered from the substrate, in the preceding electrochemically delaminating area the interface is gradually being destroyed and one should assume that this destruction should be more advanced near the completely de-adhered area than further away from it. This is obviously not the case. Similar observations have also been made on a more macroscopic scale also on fast delaminating thicker coatings [1].

Because of the inhomogeneous quality of the interface in the case of polymer films directly spin-coated polymer on the Au substrate, for further studies only model systems with a molecularly well defined monolayer at the interface should be used. Even though this makes the nature of the polymer coating itself less important, the requirement for a resolution as high as possible directly affects the choice for the most suitable polymer. A drastic example for this is shown for in figure 2. As can be seen, the possible resolution depends strongly on the nature of the polymer. The reasons for this are object of ongoing research. It seems at least partly to be due to the fundamental mechanism of imaging with the Kelvin probe (SKP and SKPFM) in general, but may also have partly to do with special features of SKPFM such as the remaining high electrical ac fields at the surface (to be published elsewhere).

Delamination of model samples with a self-assemled thiol film as molecular interface

In figure 3 first results of the delamination studies on model samples with monolayer-modified interfaces are shown, in this case for a decanethiol monolayer at the interface. Usually, a defect potential of –400 mV (the corrosion potential of iron) is more than sufficient to initialise and maintain the cathodic delamination of polymer coatings from metal substrates [1], as is also the case in figure 1. For a thiol modified interface, however, no delamination can be observed at this potential, i.e. the interface is extremely resistant against cathodic delamination. Since the driving

force behind cathodic delamination is the potential difference of the galvanic element formed between defect (anodic reaction) and intact interface (oxygen reduction) [9], lowering of the potential in the defect should increase the attack on the interface.
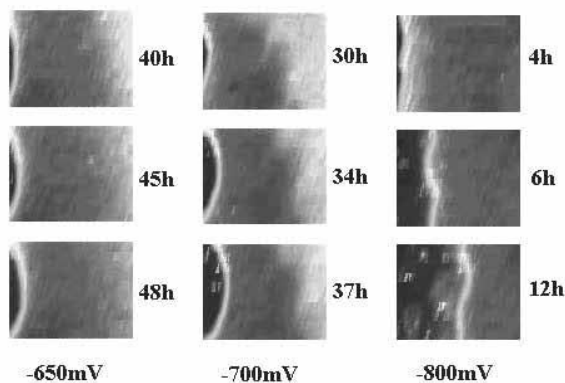

Fig3 *Successive SKP images (2000×4000 μm²) of the delamination behaviour of decane-thiol modified model samples for different defect potentials.*

It takes a defect potential as low as –650 mV to slowly initialize the delamination process. Only below this potential the delamination process is increasingly accelerated with increasingly negative potentials (see figure 4).
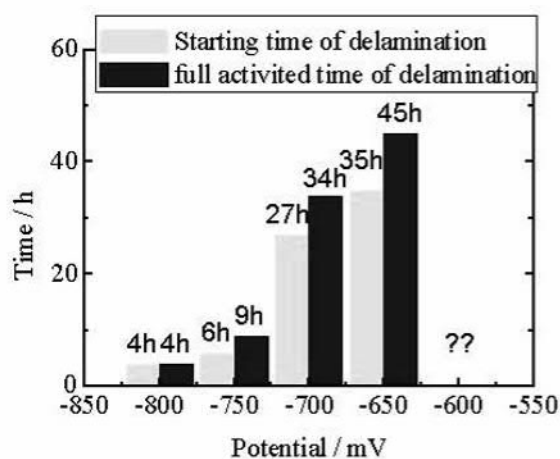

Fig4 *Starting time and full activation time of the delamination in dependence on the electrode potential at the defect site.*
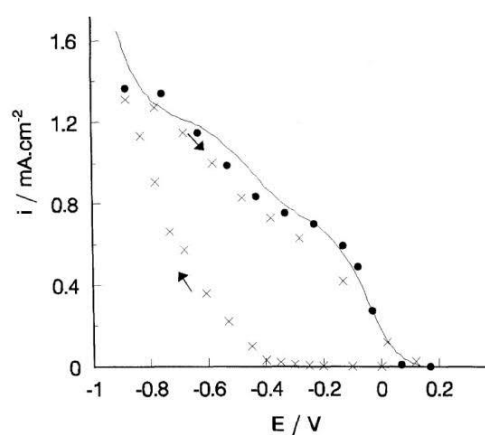
Fig5 *Oxygen reduction curves on thiol modified gold in oxygen purged borate buffer [14]. The thiol monolayer is completely inhibiting below -400 mV. Even at -600 mV the rates are very low. (×: thiol modified gold, first scan indicated by arrow; solid circles: bare gold)*

A similar behavior has been observed for the kinetics of oxygen reduction on pure self-assembled alkane-thiol monolayers [14] (see fig.5). It is proposed that the delamination behaviour of the model samples is controlled by the electrochemical properties of the thiol monolayer.

OUTLOOK

First SKPFM investigation on the model samples are subject of the current research. As a next step the degradation mechanism of the thiol monolayer at the buried interface will be analyzed and compared to that of a bare thiol monolayer on gold during oxygen reduction. This way it might be possible to learn about the fundamental steps of delamination. Later, these investigations will be extended to LB films at the buried interface.

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