ADSORPTION OF ORGANOPHOSPHONIC ACID MONOLAYERS ON ZnAl ALLOY COATINGS

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ABSTRACT
Formation and stability of octadecylphosphonic acid (ODPA) have been studied on ZnAl alloy coatings with contents of aluminum between 0% and 100%. The alloys and the native grown oxide films were characterized by X-ray photoelectron spectroscopy (XPS), polarization modulated infrared reflection absorption spectroscopy (PM-IRRAS) and scanning auger microscopy (SAM). XPS sputter profiles have shown that coatings with more than 5% aluminum in the bulk were able to build up a complete closed aluminum oxide covered surface. The ODPA films on the oxide surfaces were prepared by solution self-assembly under ambient conditions. PM-IRRAS was used to image the layer adsorption with a macro-scale, while the SAM was used to prove results with much higher local resolution. These methods indicate a strong dependency of formation and stability of ODPA from the surface chemistry. PM-IRRAS and SAM detected that self-assembled monolayers of ODPA are only built on complete aluminum oxide covered facilities of the surface. The stability of the coatings was tested in water. Together, the measurements show that ODPA is not stable in water on ZnAl alloy coatings but provides much more resistance on the aluminum oxide covered surfaces.

KEYWORDS
Organophosphonic acid; ZnAl alloy; aluminum oxide; adhesion promoter; PM-IRRAS; XPS; SAM;

INTRODUCTION
The corrosion resistance and the adhesion of organic coatings on oxide covered surfaces is of high importance and is mainly determined by the alloy composition, the surface chemistry of the alloy and the composition of the organic coating. To substitute anodizing processes or chromate layers, in recent years adhesion promoting, ultra-thin films or even monomolecular layers like self-assembled monolayers of organophosphonic acids have been investigated as new advanced interfacial layers for polymer coated aluminum alloys. γ-Aminophosphonic acid (APPA) for example is mixed to epoxy-amine coatings, enriches at the polymer/oxide interface during hardening and increases the adhesion force between organic layer and substrate. For a defined interface structure and in terms of economical use it is tried to reduce the amount of adhesion promoter to a single monolayer, which should also specifically bond to the coating [1]. Recent studies proved the applicability of phosphonate monolayers as adhesion promoters on aluminium [2, 3]. Pahnke et al.
presented a technique to specifically connect a benzophenone derivative to a hydrocarbon chain on the one hand and adhering it by a phosphonic acid anchor to an aluminium surface on the other hand \(^{(4)}\).

**RESULTS AND DISCUSSION**

For industrial applications a promising corrosion protective system involves the choice of a suitable substrate material, a compatible adhesion promoter and tailored coating. Besides the stability of the monolayer/oxide interface a highly stable monolayer/top coat interface is important, but was not specifically investigated so far.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Aluminum [%]</th>
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</thead>
<tbody>
<tr>
<td>Zinc</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>HDG</td>
<td>0.5</td>
</tr>
<tr>
<td>Galfan</td>
<td>5</td>
</tr>
<tr>
<td>Galvalume</td>
<td>55</td>
</tr>
<tr>
<td>Aluminum</td>
<td>&gt; 99.9</td>
</tr>
</tbody>
</table>

Galvalume (AZ; 55% Al; 1.6% Si), made by hot dip galvanization of steel, is a commercial product with improved corrosion resistance compared to those purely zinc coated. This property is attributed to the high aluminium content of the coats which allow the formation of comparatively close layers with a high passive barrier effect. The surface oxide structure of Galvalume is essential for the binding of organic adhesion mediators over condensation reactions and therefore was investigated by means of XPS. Within the first 2-3 nm the surface mainly comprises of an aluminium oxide at a ratio of 2:3 which points at Al\(_2\)O\(_3\) composition. The zinc content is nearly negligible and increases at the expense of the oxygen signal after 5 nm. The aluminum amount stays stable. In agreement with literature data it can be expected that ZnAl alloy interphases are formed. For estimation of the hydroxyl function density on the surface the O1s-peak was investigated concerning the contribution of oxides and hydroxides. Compared to native aluminium oxide surfaces the hydroxide amount appeared to be in the same range. For adhesion promoting molecules with hydrophilic anchor group this improves the formation of a dense self-assembling monolayer.

![Figure 1: Side cut of Galvalume steel coating](image-url)
The Galvalume surface does not consist of homogeneous Si-Al-Zn alloy layer. Figure 1 shows a characteristic surface structure. The elemental surface distribution was received by EDX spectroscopy. It comprises characteristic spangles with aluminium dendrites, Zn-rich interdendritic regions and a fine dispersion of Si particles. These characteristics develop during cooling after the dipping process. The resulting composition depends on the cooling rates and arises from the Fe-Al-Zn intermetallic alloy layer between steel substrate and molten Zn layer. Si exclusions grow up from this alloy layer with Al-dendrites developing at the Si channels. This process results in a dense mesh of ledges (Si and Zn interdendritics) pervading the entire Zn layer up to the surface.

One idea of the present study is to investigate the influence of a heterogeneously distributed oxide covered surface on the formation and stability of organic coatings.

![Graph](image1.png)

![Graph](image2.png)

Figure 2: PM-IRRAS of ODPA adsorbed on zinc, HDG, Galfan, Galvalume and aluminum. Spectra of the pure substrates were used as background.
The upper spectra in figure 2 show the range of 2800–3000 cm\(^{-1}\) with the symmetric and asymmetric stretching vibrations of the CH\(_2\) chains with a CH\(_3\) head group. In the lower part in figure 2 the range of 800–1600 cm\(^{-1}\) with a broad line with a centre at 1080 cm\(^{-1}\) is shown, which can be assigned to a convolution of symmetric and asymmetric stretching bands of the phosphonate groups. For long chain aliphatic phosphonates, salts of the alkylphosphonic acids give characteristic stretching vibrations at 1125–970 cm\(^{-1}\) and at 1000–960 cm\(^{-1}\). Based on this argument the broad absorption at 1080 cm\(^{-1}\) indicates that bonding to the oxide covered surface occurs via a tridentate bonding. In the range of 1470 cm\(^{-1}\) only two adsorbed layers give a peak which can be adapted to the CH\(_2\) chain deformation. Together with the higher intensities in all other ranges, this indicates the ODPA not to adsorb as monolayer on the zinc and HDG.

The stability of the coatings was tested in water. All coatings were covered with ODPA monolayer and stored in water for 24 h. The water penetration was characterized by means of PM-IRRAS and SAM. Together, the measurements show that ODPA is not stable in water on ZnAl alloy coatings but provides much more resistance on the aluminum oxide covered surfaces.

**ACKNOWLEDGEMENTS**

The financial support of Bundesministerium für Bildung und Forschung (BMBF) is gratefully acknowledged.

**LITERATURE**


