Corrosion Performance of heavy metal free inorganic-organic Nanocomposite Coating Systems on Aluminium synthesized by sol-gel Processing

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1 Introduction

Aluminium and its alloys are in widespread use as lightweight construction materials especially in manufacture of cars and planes. To date corrosion protection of aluminium alloys relies strongly on heavy metal-containing coatings. Therefore environmental protection agencies and lawmakers seek to exclude the use of heavy metals, especially chromium, in corrosion protection systems. Sol-gel based inorganic-organic nanocomposite coating systems offer the possibility for such heavy metal free corrosion protection. H. Schmidt, S. Langenfeld and R. Naß have already shown that a nanocomposite coating can be employed to effectively protect and seal pressure-cast aluminium parts made of AlMgSi1 and wrought aluminium sheets made of Al99,5 and AlMg3 [1,2]. Based on these successful systems the aim of the present study is to determine the influence of the organic crosslinker on the corrosion protection properties to achieve further improvements in the heavy metal free corrosion protection on AlMg3.

2 Experimental

2.1 Cleaning of the AlMg3-alloy and synthesis of the coating systems

Before coating the aluminium sheets are cleaned with Unibond T5400®.The basic system consists of 3-Glycidyloxypropyltrimethoxysilane (GPTS), Bisphenol A (BPA) and Methylimidazole (MI) as catalyst. GPTS is mixed with 0,1 molar phosphoric acid and stirred for 2 hours. A solution of BPA in Ethanol and Isopropylethylether is added. After 1,5 h of further mixing 0,005 mol MI are added. After 20-30 min the final lacquer mixture is applied to AlMg3 sheets by spin coating and thermally cured (130°C, 2 h). The additional lacquer systems are synthesised by exchanging BPA against 2,2'-bis-(4-hydroxyphenyl)-sulfon (BPS), 4,4'-dihydroxybenzophenone (DBP4) and 2,2'-bis-(4-hydroxyphenyl)-perfluorpropane (BPAF).

2.2 Characterisation of the coatings

The corrosion protection properties of the coatings are determined by corrosion tests (Salt-Spray and CASS-test according to DIN 50021) and by electrochemical impedance spectroscopy (EIS). The evaluation of corrosion damage takes place according to ISO 4628/1-6, whereas the infiltration is determined according to DIN 53167. The electrochemical impedance is measured at an amplitude of 20 mV at frequencies between 10^{-3} and 10^{5} Hz on a coated area of 10 cm^2. Five measurements are conducted per decade at the equilibrium potential of the system in 5 wt.-% NaCl-solution which serves as electrolyte and corrosive agent. Adhesion of the coatings was tested by crosshatch and tape test (DIN 58196), their contact angle against water was determined by goniometry.

3 Results

Aluminium sheets coated with the base system (BPA) show very good adhesion before and after the corrosion tests in crosshatch and tape test. No blisters no corrosion damage and no infiltration after 1000 h in the salt-spray test can be detected. In the CASS-test first blisters already appear after 48 h. After 168 h some of them have bursted, creating holes in the coating followed by corrosion (degree of rust: 2-3). The infiltration of the coating at this point amounts to 0,65 mm. In EIS the GPTS/BPA coating system applied on AlMg3 was examined for 672 h (4 weeks). Figure 1 shows the corresponding impedance curves. All curves show a plateau in the high and the low frequency range. This behaviour is caused by pores permitting access of the electrolyte to the metal surface. With increasing immersion time the layer resistance of the coating, decreases, while its capacitance increases due to water uptake. After 4 weeks the coating is completely penetrated. These results of the corrosion test and EIS show that the GPTS/BPA system provides adequate corrosion protection to AlMg3, but lacks of long term stability and finally permits access of the electrolyte to the metal surface.

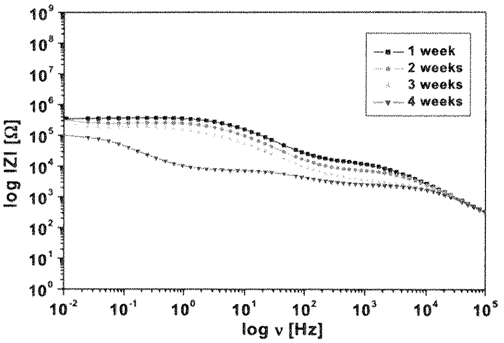

Figure 1 Bode-plot of the logarithm of the modulus of impedance |Z| versus the logarithm of frequency ν of the basic system GPTS/BPA on AlMg3 after 1 to 4 weeks immersion in 5 wt.-% NaCl-solution.

To study the influence of the organic crosslinker with regard to the permeability of the coating, BPA is substituted by BPS, DBP4 and BPAF. The alternative systems show the same excellent adhesion like the base system in crosshatch and tape test. In neutral salt spray test all systems perform very well, even after 1000 h salt-spray treatment no corrosion damage can be detected. To determine the differences, more stringent conditions have to be applied. Therefore CASS-tests are conducted. In figure 2 the results of CASS-test over a time period of 160 h are shown. According to these results the corrosion protection performance of the coatings can be accurately ranked as follows: BPAF>BPA>BPS>DBP4.

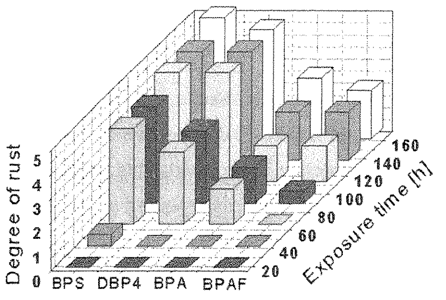

Figure 2 Degree of rust after up to 160 h CASS-test with hybrid coatings containing different bisphenols as organic crosslinkers

The anti-corrosive properties of the coatings were also investigated by EIS after one and four weeks immersion in 5 wt.-% NaCl solution. The corresponding spectra are presented in figure 3.

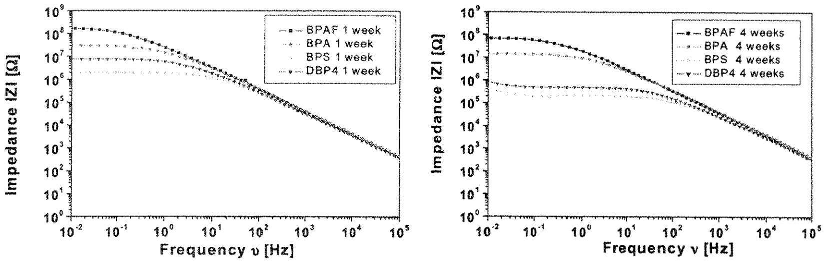

Figure 3 Bode-plot of impedance IZI versus frequency ν of hybrid coatings on AlMg3 with BPAF, BPA, BPS and DBP4 as bisphenolic crosslinkers after immersion in 5 wt.-% NaCl-solution for one week.

After one week, according to its layer resistance, the BPAF system ($1{,}6\cdot10^{8}\,\Omega$) provides the best isolation from corrosive media if compared to BPA ($2{,}9\cdot10^{7}\,\Omega$), DBP4 ($7{,}4\cdot10^{6}\,\Omega$) and BPS ($2{,}1\cdot10^{6}\,\Omega$). The linear decrease of impedance in the high frequency region points towards purely capacitive behaviour of all coatings. After four weeks immersion the coatings with BPA and BPAF do not show any principal change, only their layer resistance is slightly decreased (BPAF: $6{,}8 \cdot 10^7\ \Omega$, BPA: $1{,}5 \cdot 10^7\ \Omega$). In case of the BPS and DBP4 coatings the layer resistance decreases much faster and the impedance curve already shows the beginning of corrosion in the low frequency range. This result proves the long term stability of the BPAF and BPA coatings in corrosive media, which is confirmed by long term corrosion tests with the BPAF system (no corrosion damage after 8000 h neutral salt spray treatment).

These EIS results are in exact agreement with the CASS test results. Therefore it can be concluded that the BPAF coating possesses the best anti-corrosion performance, while by replacing BPA with BPS and DBP4 the corrosion protection is impaired. This behaviour can be attributed to the different hydrophobicity of the coating systems reflected in their contact angle against water (BPAF: 83°, BPA: 81°, DBP4: 74° and BPS: 70°).

4 Summary

To determine the influence of the organic crosslinker on the corrosion protection properties of organic-inorganic nanocomposite coating systems on AlMg3, four different bisphenolic crosslinkers were employed (BPAF, BPA, BPS and DBP4). The coating mixtures were synthesised by sol-gel processing, applied to AlMg3 sheets by spin coating and thermally cured. The resulting samples were submitted to conventional corrosion tests (neutral salt-spray and CASS-test) and to EIS. The results consistently show that the coating system containing BPAF confers the best corrosion protection to AlMg3. Because of its comparatively high hydrophobicity (contact angle against water: 83°) it possesses the highest layer resistance (approximately $10^8\ \Omega$) in EIS and the best long term stability in corrosive environments (no corrosion damage after 8000 h neutral salt spray treatment).

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[1] H. Schmidt, S. Langenfeld, R. Naß, Materials & Design, **18** 309-313 (1997).

[2] S. Langenfeld, G. Jonschker, H. Schmidt, Mat.-Wiss. u. Werkstofftech., **28** 1-15 (1997).