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Adhesion pretreatment of aluminum by sol–gel processing

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ABSTRACT

A waterborne coating system for aluminum sheets is described with advantageous properties for adhesion pretreatment. The system is based on ethylene glycol-modified silanes and acetic acid-modified titanium or zirconium alkoxides as precursors for sol–gel processing. The precursor mixture was optimized with regard to the influence of the titanium/zirconium, epoxy-substituted silane and water proportion on the shear strength of lap joints. The coatings have sufficient long-term stability of the bonding under corrosive conditions, where the lap shear strength slightly increased during the neutral salt spray test. The latter phenomenon was investigated by infrared reflection absorption spectroscopy and electron energy loss spectroscopy.

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1. Introduction

Lightweight construction is gaining more and more importance in the automotive and aircraft industry, and therefore adhesive bonding is getting more interesting as well. As steel is progressively replaced by aluminum, in some cases also by magnesium and carbon fiber-reinforced plastics, it is often the only method to join these materials.

Key requirements are a high adhesive strength and good long-term stability. To this end, aluminum sheets must be pretreated prior to adhesive bonding. FPL etch (dichromate–sulfuric acid pickling) and anodizing methods, such as chromic acid or phosphoric acid anodizing, are the best pretreatment methods [1], but all of them have serious disadvantages. The use of Cr(VI)-containing pretreatments has been banned in Europe and the US because of toxicity and carcinogenicity, and anodizing is an expensive and energy-consuming process. Conversion coatings based on zirconium, titanium/zirconium or lanthanides [2] can potentially substitute chromium-containing pretreatments, but they do not ensure sufficient corrosion protection especially for copper-containing aluminum alloys [3].

Sol–gel coatings are a good alternative. Their production is environmentally friendly, they are non-toxic and their properties can be tuned easily by modifying the precursor mixture. Sol–gel coatings for aluminum or magnesium were intensively investigated

for corrosion protection, but hardly for adhesion pretreatment. The goal of the work described in this article was the development of a waterborne adhesion pretreatment for aluminum sheets with a good long-term stability.

Ferreira et al. [4] developed corrosion protection coatings based on 3-glycidoxypropyltrimethoxysilane (GLYMO) doped with zirconia, titania or different inhibitors. When used for large scale applications, they would require special explosion protection because they are alcohol-based. The so-called self-assembled nanophase particle (SNAP) coatings are waterborne and consist of functionalized silica nanoparticles cross-linked by organic amines [5] or amino-substituted silanes [6]. Their pot life is not sufficiently long, however, because the amines increase the pH.

A patent of Boeing [7] describes a waterborne, zirconia-doped coating based on GLYMO. As the used silicon alkoxides are not water-soluble, the precursor mixture requires 4–6 h to form a homogeneous solution and to ensure sufficient hydrolysis of the precursors. This “induction time” is an important factor to obtain good adhesion of the coating on the metal surface.

Taking the corrosion-protection coatings described in the Boeing work as a starting point, we chose ethylene glycol-modified precursors [8] instead of the commonly used silicon methoxides or ethoxides. The glycolate derivatives are water-soluble and have higher reaction rates. Ethylene glycol is liberated during hydrolysis instead of volatile methanol or ethanol and thus reduces efforts for explosion protection of large-scale applications. Additionally it is compatible with standard adhesives, ensures a sufficient long-term stability of the bonding and shows a long pot life. The performance of the new coatings was tested by lap shear

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strength measurements in the as-prepared and aged state with two different alloys, viz. AA6016 T4 EDT (named 6016 in the remainder of the article) which is used in the automotive industry as well as AA 7075 T6 (named 7075), well-known in the aircraft industry with first applications also in car body engineering. To this end, single lap joints were prepared of coated aluminum sheets and an epoxy reactive hotmelt used in automotive industry. The maximum strength at break compared with the evaluation of the fracture pattern provided information on the suitability of the coating for adhesion pretreatment and the weakest interface.

2. Experimental

2.1. Materials

Rolled aluminum sheets (1 mm thick) of AA6016 (EN AW-AlSi1.2Mg0.4) in temper T4 with an EDT (electro discharge texturing) surface texture and AA7075 (EN AW-AlZn5.5MgCu) in temper T6 were used. 100 × 25 mm² specimens were used for the lap shear tests.

2.2. Preparation of the ethylene glycol-modified precursors

The ethylene glycolate-substituted silane (EGMS) was prepared by alcohol exchange of the ethoxy groups of Si(OEt)₄ (TEOS) by ethylene glycol. To this end, 1 eq. of TEOS was reacted with 4 M eq. of dry ethylene glycol as described by Brandhuber et al. [8]. For the preparation of ethylene glycol modified GLYMO (EGM-GLYMO), 1 eq. of GLYMO was reacted with 3 eq. of ethylene glycol in the same manner.

2.3. Pretreatment and coating of the aluminum sheets

Before coating, the samples were degreased in an aqueous solution of 30 g/l GARDOCLEAN S 5160 for 1 min at 60 °C followed by pickling in an aqueous solution of 12.5 g/l GARDOCLEAN S 5240/2 and 5 g/l GARDOBOND-ADDITIVE H 7269 for 1 min at 50 °C (all from Chemetall GmbH). Each step was followed by rinsing with deionized water. The samples were finally dried at 200 °C for 2 min.

Sol 1 was prepared by mixing EGMS, EGM-GLYMO and water in a 4:1:990 ratio. Sol 2 was independently prepared by mixing Zr(OBu)₄ or Ti(OiPr)₄ with acetic acid (AA) in a 1:6 ratio. 10 M eq. of water were added dropwise (total 1000 eq.) under vigorous stirring after 5 min. Sol 2 was added to sol 1 after additional 10 min. The final solution (Table 1) was stirred for 1.5 h. For varying the film thickness, different water proportions (from 600 to 1400 eq. in 200 eq. fractions) were used for the coating with 20 mol% Zr in sol 1. The ratio of EGMS and EGM-GLYMO was also varied to test a potential influence on the adhesive strength (Table 2).

The aluminum sheets were coated by dip-coating at a constant withdrawal rate of 24 cm/min and the coating was then dried at

Table 1

Variation of the transition metal proportion (EGMS 4 eq., EGM-GLYMO 1 eq., H₂O 1000 eq.; M=Ti or Zr). The composition is given in molar equivalents.

M proportion (%)	M (OR) ₄	Acetic acid
0		1.2
5	0.3	2
10	0.6	3
15	0.9	5
20	1.3	8
25	1.7	10

Table 2

Variation of the EGMS:EGM-GLYMO ratio (M(OR)₄ [M=Ti or Zr] 0.6 eq., acetic acid 3 eq., H₂O 1000 eq.). The composition is given in molar equivalents.

EGMS	EGM-GLYMO
4	1
3	2
2	3
1	4

200 °C for 1 min. The drying conditions were predefined by the industrial process in which the coating shall be implemented.

2.4. Preparation of single lap joints

The coated sheets were assembled with an overlap of 10 mm. BETAMATE 1496 V (Dow Automotive Systems), a one-component epoxy resin, was used as adhesive. A glue line thickness of about 300 μm was adjusted by glass spheres as spacers. Curing was performed at 125 °C for 12 min and at 175 °C for 15 min (holding period starting when the specified temperature was reached).

2.5. Characterization

The lap shear strength was investigated with a tensile testing device (Zwick Z050) at ambient conditions with a constant speed of 10 mm/min. The lap shear joints were tested as-prepared and aged. Ageing was carried out by the neutral salt spray test (NSS) (50 ± 5 g/l NaCl, pH 6.5–7.2) for 500 h according to DIN EN ISO 9227.

For infrared reflection absorption spectroscopy (IRRAS) measurements the sheets were polished with polishing paper (SiC) up to 4000 mesh. Then they were coated and dried as usual, and cut to 25 × 30 mm² pieces. IRRAS measurements were performed using a Spectrum 2000 of Perkin Elmer, Germany, connected to the self-built in-situ IRRAS weathering unit [9], which allows one to obtain time-lapse IR data, while samples are weathered under controlled atmospheric conditions. The incident IR beam passes the zinc selenide window of the weathering unit and hits the surface of the gazing angle of incidence (78° off normal). It is then reflected from the sample surface to the MCT detector with an angle equal to the angle of incidence. An uncoated but polished sheet of the respective alloy, measured under atmospheric conditions, was used as reference (R_0) for all the spectra. The spectra show the relative reflectance/absorption (expressed in $R\%=R/R_0$) of the weathered samples in comparison to the non-weathered. This means that only the ratio spectra, showing the changes of the surface, are obtained. For the in-situ IRRAS measurements the samples were weathered in synthetic air containing 500 ppb SO₂ and 90% relative humidity (a salt spray treatment was not possible in this case). These conditions are similar to a standardized corrosion test (Kesternich test, DIN EN ISO 6988).

Microscopic investigation of the film morphology was carried out by a digital light microscope of Leica (MAG 50 ×). Transmission electron microscopy (TEM) images and electron energy loss spectra (EELS) were recorded on a FEI TECNAI G20 analytical transmission electron microscope with a GIF 2001 EELS/EFTEM. The sample preparation was carried out by a Dual Beam Focused Ion Beam Quanta 200 3D.

3. Results and discussion

The precursors used in this work were the ethylene glycol-modified alkoxy silanes EGMS and EGM-GLYMO, and acetic acid-modified

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