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Polyelectrolytes to promote adhesive bonds of laser-structured aluminium

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ABSTRACT

Aluminium is one of the most popular construction materials in machine and equipment manufacture as well as vehicle and aircraft construction. Particularly, in automotive and aircraft industries, the adhesive bonding of aluminium requires the pre-treatment of the adhesive surfaces. In this study laser pre-treatments were used to laterally control the surface roughness and clean the substrate surfaces by forming fresh aluminium oxide layers. In order to keep the adhesive properties stable over time, the laser pre-treated aluminium surfaces were subsequently coated with weak polyelectrolytes. The applied polyelectrolytes lower the driving forces for the adsorption of unwanted surface contaminations and provide reactive amino groups for the subsequent coupling of reactive adhesives. The surface topographies of the laser-treated aluminium surfaces were investigated in relation to the applied laser parameters (such as pulse frequency, and laser power) by means of scanning electron microscopy (SEM) and light-microscopic techniques (confocal microscopy). The adsorption of the polyelectrolytes was studied by X-ray photoelectron spectroscopy (XPS). Inverse water contact angle measurements using captive air bubbles were carried out to study the wettability (hydrophilicity/hydrophobicity) of the modified aluminium surfaces. Single lap joint tests carried out on joined AlMg3 sheets showed that the shear strengths can be significantly increased by pre-treatment with laser and coating of the alloy surfaces with weak polyelectrolytes. Furthermore, the application of polyelectrolytes improved the stability against corrosion. The article shows the increase of tensile shear strengths at adhesively bonded single lap shear samples after laser pre-treatment and also an increase in long-term stability due to of the combination of laser pre-treatment and coating with polyelectrolytes. Adhesive bonds of laser treated samples with and without polyelectrolyte coating have a higher stability against corrosion compared to untreated samples.

1. Introduction

The use of aluminium as a construction material is unimaginable without its spontaneously formed stable oxide layer. The dense oxide layer protects the metal against further oxidation because aluminium is an ignoble metal. The artificial enhancement of the oxide layer improves the protection against corrosion. For this purpose, anodic oxidation is commonly applied. After pickling the native oxide layer, a fresh oxide layer of defined thickness is grown on the metal surface in an electroplating process. Different subsequent treatments can be applied to remove incorporated water and heighten the density of the freshly prepared oxide layer. In this way, not only the chemical resistance but also the mechanical properties of the oxide layer, such as hardness, can be improved. The presence of the corrosion-protective oxide layer onto the surface of aluminium and aluminium alloys causes the interaction of an adhesive with the oxide but not with the metal surface.

Early studies into the adhesive bonding of aluminium in aircraft industries have shown that the quality of adhesive bonds depends on the properties of the oxide layer [1]. Hence, beside the formation of aluminium oxide layers with defined thicknesses, densities and mechanical properties, additional pre-treatments are deemed necessary to produce stable adhesive bonds [2]. The surface pre-treatment has the essential task of obtaining a surface state that will produce stable adhesive bonds. It is auspicious to develop surface pre-treatments that lead to adhesive bonds of the same quality but without additional pre-treatment of the joining parts' surfaces.

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However, according to Zisman's classification [3] the aluminium oxide surfaces have to be considered as high-energy surfaces, which are characterized by their spontaneous coverage with films of water and organic contaminations. The driving force for these non-specific adsorptions is the thermodynamically controlled minimization of the surface free energy. The formation of specific interactions between reactive groups of the adhesive and suitable surface sites of the oxide layer partly displays contaminations. However, the majority of the organic contaminations remain on the oxide surface. Compared to the weakly bonded organic contaminations, water molecules are fixed more strongly on the oxide surface by their ability to form hydrogen bonds. Common pre-treatments such as vapour-degreasing with acetone are applied to degrease the oxide surfaces whilst the surface roughness is increased via blasting with corundum. This process also changes the surface chemical composition through the introduction of silica or zirconia. The SACO technique, which was developed by the Delo Industrie Klebstoffe GmbH & Co. KGaA, Windach, Germany [4], is also well known. Surfaces of joining parts were blasted with silicate-coated corundum particles. The impact of the particles roughen the sample surface and removes weakly bonded components. Simultaneously, the treated surface is coated by the silicates because the particles' impact is sufficient to embed parts of the corundum's silicate shell irreversibly in the metal oxide layer of the joining parts. In addition, common silane-based adhesion promoters can be used to improve the adhesive strength of composites produced according to the SACO technique [5].

Other common pre-treatment processes are the treatment of jointing parts with concentrated nitric acid (HNO_3) to oxidize organic species and desorb surface contaminations [6,7]. Immersion pickling with dilute sodium hydroxide (NaOH) solution decomposes the contaminated oxide layer and the subsequent rinsing and pickling treatment with dilute nitric acid forms a fresh highly reactive oxide layer. Ciba laser pre-treatments (CLP) combine a laser surface pre-treatment with the application of an adhesion promoter [8]. Although the importance of the pre-treatments is undisputed and well known, problems can arise in the context of their implementation in service or repair works, which are provided by third parties.

The aim of our work was the development of a new route to produce aluminium oxide surfaces, which retain excellent wettability and reactivity properties to an adhesive over a long storage time. Surfaces treated in this way should be bonded without additional pre-treatment. The permanent preservation of the bond quality of aluminium was achieved by the introduction of a reactive polymer into a freshly prepared porous oxide layer. In order to produce fresh oxide layers with adjustable pore structures laser ablation was employed. Advances in the laser treatment provide an intensive surface treatment with a high lateral precision, the partial removal of coatings or varnish layers, and the freedom in choosing the shape of the area to be treated. By adjustment of the laser parameters, it is possible to control the roughness and porosity of the oxide surface [9–14]. Laser treatment has been applied to aluminium surfaces [11–14] and other lightweight metals and alloys (e.g. titanium and magnesium) [15–18] as well as fibre-reinforced composites [19]. Micro-porous oxide layers do not only increase the adhesive surface, they also serve as micro-containers for the adhesion-promoting polymer. In order to produce an irreversibly bonded and stably interlocked polymer/oxide composite layer, some of the functional groups of the incorporated polymer can be inter- and intra-molecularly cross-linked. The plastic and ductile polymer phase is able to contribute to the mechanical stability of the brittle aluminium oxide layer [20]. Particularly, the amino groups of polyamines can be easily reacted with oxirane groups provided by adhesives but also with carbonyl compounds. Polyamines can be considered as weak polyelectrolytes because their amino groups can be protonated. The resulting polycations can be dissolved in aqueous solutions allowing their sustainable and safe application.

2. Experimentals

2.1. Materials

Commercially available cold-rolled aluminium wrought alloy sheets (AlMg1, EN AW-5005 and AlMg3, EN AW-5754) were laser or water cut into pieces (100 mm × 25 mm × 3 mm). Pieces of 20 mm × 25 mm × 3 mm were produced for XPS analysis. All samples were washed with ethanol in an ultrasonic bath for 5 min prior to laser treatment. Four fields (each 9 mm × 10 mm) were laser-machined on each of the smaller samples using a variation of laser settings. The other samples having lengths of 100 mm were laser-treated in their full width on a length of 12.5 mm measured from the sample's end.

Corresponding to the reactive potential of the adhesives, which are commonly used to bond aluminium, several polyamines, such as poly(vinyl formamide-*co*-vinyl amine) (PVAm), poly(ethyleneimine) (PEI), poly(allylamine) (PAAm), and chitosan were used to modify the laser-treated aluminium surfaces (Table 1). In the case of PVAm, more than 90% of all vinyl formamide monomer units of the pre-polymer poly(vinyl formamide) were converted into vinyl amine sequences [21]. Poly(acrylic acid) (PAAc) was employed for the build-up of polyelectrolyte bi-layers (Table 1). In order to compare the effect of the polyelectrolyte adhesion promoters with common coupling agents, laser-treated aluminium sheets were also modified with 3-(triethoxysilyl)propylamine (APS) provided by Merck Schuchard OHG, Hohenbrunn, Germany.

A two-component epoxy resin (Leuna-Harze GmbH, Leuna, Germany), was employed as the adhesive (Table 2). The low viscosity of the resin allowed access to the cavities of the substrates, which were produced during the laser pre-treatment.

2.2. Laser pre-treatment

Pieces of the aluminium alloys were treated with a pulsed ytterbium-doped fibre laser CL 50 (Clean-Lasersysteme GmbH, Herzogenrath, Germany). The laser process settings are given in Table 3. The excellent quality of the Gaussian-shaped laser beam profile allowed focusing the beam ($\lambda = 1060–1070$ nm) diameter between 16 μm and 50 μm. Due to the short pulse duration of a few nanoseconds, a maximum pulse power of 20 kW can be achieved, which is in contrast to the relatively low average laser power of a theoretical maximum of 50 W. The energy density that was introduced into the material was sufficient to sublimate near surface layers, form a fresh mountain-like aluminium oxide layer and purify the surface in one step. Dust-like side-products of the laser treatment were vacuumed or mechanically removed from the surface.

Table 1
Reactive polyelectrolytes used to coat laser-treated aluminium surfaces.

Polyelectrolyte	Manufacturer	Molecular weight (M_w) (g mol^{-1})
PVAm	BASF SE	340,000
PEI	SIGMA-ALDRICH	750,000
PAAm	SIGMA-ALDRICH	70,000
Chitosan	BioLog Biotechnologie und Logistik GmbH Halle-Queis	2,500,000
PAAc	Sigma-Aldrich	100,000