Conversion layers by plasma-electrolytic oxidation of aluminum in acrylate and benzoate electrolytes

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Abstract. Within this work, aluminum is oxidized via plasma-electrolytic oxidation (PEO) in the presence of organic substances, including reactive monomers. The aim of this approach is to generate polymers and simultaneously bind them to the surface of the freshly generated oxide layers. For this purpose, sheets of aluminum were immersed into electrolytes that comprised either 4 \% of sodium acrylate or 10 \% of sodium benzoate. The aluminum sheets were oxidized by anodic pulse current at 0.25 A/cm\textsuperscript{2} for 30–90 s. By this process, predominantly oxidic conversion layers were produced. The presence of the monomers in the electrolyte influenced the passivation and discharge behavior and finally the microstructure of the layers. It further gave rise to organic material in the layer. In particular, infrared attenuated total reflection spectroscopy (ATR-IR) and X-ray photoemission spectroscopy (XPS) show that layers which were generated in the presence of acrylate or benzoate comprised -C-C-, -C=O, and C=O bonds.

1. Introduction

In general, adhesion-promoting surface structures or interlayers have to be used in order to provide a strong adhesion between the metallic and polymer counterparts of hybrid material compounds [1]. In the case that the polymer surface is newly formed during the compound production (e.g. by injection molding) or at least reshaped (e.g. by hot pressing), the adhesion-promoting structure or layer can only be applied to the metallic partner. A wide variety of mechanical or chemical surface treatments and coatings has been discussed in the literature, whereby the highest adhesion strength of thermally joined aluminum-polyamide hybrid laminates was found for surface structures with pronounced undercuts in general [1] and for plasma-electrolytic oxidation (PEO) in particular [2]. This process enables the generation of highly adherent oxide-ceramic conversion layers due to the reaction of the locally molten substrate material and the anodically generated oxygen in the direct vicinity of microarc discharges [3]. PEO layers exhibit an open-pored surface, which is suitable for the mechanical interlocking of polymers and therefore provides an excellent adhesion of polymer counterparts on PEO-treated aluminum and magnesium alloys [4–6]. Moreover, the PEO layers are generally characterized by a compact electrically insulating barrier layer at the substrate-oxide interface, which is suitable for the protection of susceptible
substrates in corrosive environments [7]. Due to the electrical insulation, oxidic conversion layers also prevent contact corrosion of base metals in the presence of more noble carbon fibers [8].

To the best of our knowledge, there was no attempt so far to create thin polymer films on structured or coated metals in order to promote the chemical adhesion of the polymer counterpart and to further increase the adhesion strength. The innovative approach of this investigation comprises the production of an adhesion promoting porous oxide surface, which is covered with a thin polymer film. Besides the formation of an oxide-ceramic conversion layer at high local temperature, light emission and radicals are associated to the microarc discharges. Similar to conventional plasma polymerization, the radicals shall be used to initiate the polymerization of monomers, which are dissolved in the electrolyte. The polymerization of the reactive species might be initiated at the PEO surface (grafting from) or in the electrolyte (grafting to). The aim of this research work is to illustrate the PEO-layer topography and to prove the existence of adherent organic compounds.

2. Materials and experimental methods

Pure aluminum (Al99.9) sheets with a sample area of 4 cm² were used as substrates. As a pretreatment, the samples were pickled into a solution of 10 % by weight of NaOH in water for 2 minutes, rinsed 2 times with distilled water for 30 seconds, one time with isopropyl alcohol, and dried in air. The PEO electrolytes were aqueous solutions of 4 % by weight of sodium acrylate (H₂CCHCOONa) or 10 % by weight of sodium benzoate (C₆H₅COONa). An aqueous solution of 5 % NaOH was used to produce reference PEO layers. The PEO experiments were conducted in a beaker (electrolyte volume: 250 ml) using rectangular pulsed current with a peak current density of 0.25 A/cm² and a pulse frequency of 50 Hz at room temperature. The process duration was limited to 60 s as the early low-energy micro-arcs tend to be more suitable for the plasma-induced polymerization of monomers. The sample acted as the anode; a platinum electrode was used as the cathode. The bath was agitated by a magnetic stirrer. After the PEO treatment, the samples were rinsed by distilled water for 100 s.

Prior to the scanning electron microscopy (SEM) investigations, the samples were rinsed in pure water, a mixture of water and isopropyl alcohol (50:50), and pure isopropyl alcohol in order to dissolve soluble compounds off the surface and to ensure that only insoluble and adherent compounds remained at the sample surface. Subsequently, the samples were dried at 55 °C in air for at least 4 h and again dried at 55 °C in rough vacuum (> 1 mbar). Overview images were captured and energy-dispersive X-ray spectroscopy (EDX) was performed at a working distance of 14.5 mm and an amplification voltage of 25 kV using the SEM LEO1455VP (Zeiss). More detailed views of selected PEO surfaces were taken at a working distance of 3 mm and an amplification voltage of 1 kV using a field emission (FE) SEM NEON40EsB (Zeiss).

Infrared attenuated total reflection spectroscopy (ATR-IR) was conducted using a Nicolet 6700 FT-IR (Thermo Scientific). The sample chamber is additionally equipped with an ATR unit (type MIRacle-ATR, PIKE Technologies), which is permanently flushed with dry, CO₂-free air and enables the recording of spectra in ATR mode. A single reflection using a diamond ATR crystal was used. The ATR-IR spectra were recorded using 20 scans at a resolution of 4 cm⁻¹. The ATR-IR data were analyzed by means of the software Omnic7.4.

X-ray photoemission spectroscopy (XPS) measurements were performed with an ESCALAB 250Xi (Thermo Scientific) photoelectron spectrometer equipped with a monochromated Al Kα X-ray source (photon energy 1486.7 eV). The system was operated at a base pressure of 5·10⁻¹⁰ mbar. The spectra were collected in a constant analyzer pass energy mode, at pass energies of 200 and 20 eV for survey and high-resolution spectra (with a spectral resolution of 0.5 eV), respectively. A stripe of a half PEO-treated a half pristine Al sample was mounted on a metallic sample holder to achieve an electrical contact with the unprotected Al part. To minimize charging effects, a built-in charge compensation setup was used. Fitting of the spectra was performed with Voigt profiles using the Avantage software.
3. Results and discussion

3.1. Scanning electron microscopy investigations

In the early stage of a PEO process, a passive layer is formed under anodic polarization in a suitable substrate-electrolyte system and an oxygen-rich gas layer is formed around the substrate. After exceeding a critical potential gradient, microarc discharges are initiated that are ranging from the outer surface of the ionized gas layer (quasi-cathode) to the substrate. Regarding short-time PEO processes, the oxide surface typically exhibits an irregular porosity which represents the discharge channels of the fine dispersed early microarcs. Furthermore, the early PEO layers are typically characterized by a low thickness and a high content of amorphous phases. A topography characteristic for this stage is visible in the secondary electron (SE) image of aluminum treated with plasma-electrolytic oxidation in presence of sodium acrylate (figure 1). If oxidation progresses further, the oxide thickness increases and the surface topography becomes more complex, including an increasing number of undercuts. These surface characteristics can already be observed for samples, which were PEO-treated with benzoate addition to the electrolyte (figure 2), although the process time was the same. This indicates that different monomers influence the initial stage of the PEO process and the corresponding oxide microstructure in different ways. This can be explained by adsorbed benzoate molecules, which act as an electrical insulator, resulting in a faster increase of the potential gradient over the dielectric layer and an earlier ignition of the microarc discharges. Therefore, the plasma-induced layer formation took place for a longer time and an advanced oxide formation state was reached.

Figure 1. SE image of the sample surface after PEO on the presence of 4 % sodium acrylate showing the discharge channels of the initial microarcs

Figure 2. SE image of the sample surface after PEO in presence of 10 % sodium benzoate showing a more complex topography, being characteristic for an advanced PEO stage

Despite using a low amplification voltage of 1 kV, the existence of organic compounds or a thin polymer film could not be verified by SEM imaging. However, the presence of carbon-rich compounds was evidently shown by EDX spectroscopy. In the case of the PEO in aqueous NaOH solution, only the usual environmental trace contamination of carbon (approximately one percent of C) was detected at the oxide surface. After PEO in a solution of 4 % sodium acrylate (topography shown in figure 1), a molar fraction of 7 % C was measured, which could be explained by the presence of a thin adherent organic layer. An exceptionally high C-content of 66 % was detected after PEO in a solution of 10 % sodium benzoate (topography shown in figure 2). This could also indicate the thermal decomposition of organic molecules and the incorporation of carbon into the PEO layer. Clear evidence for the presence of organic compounds on the PEO surface can only be provided by the analysis of the atomic bonds using ATR-IR and XPS.
3.2. Attenuated total reflection infrared spectroscopy

The generation of organic species on the sample surface during the PEO process is demonstrated for the addition of sodium benzoate to the electrolyte in figure 3. To check for organic compounds, infrared light was guided within the diamond crystal by total reflection at its surfaces. The light excites vibrations of organic functional groups on the surface of the samples and in turn is attenuated via absorption at wavelengths that are characteristic for these groups. Thus, the resulting spectra show characteristic extinction peaks that allow for the identification of organic groups on the sample surface. The black graph shows the ATR-IR spectrum of a reference sample after PEO in pure NaOH solution without any additive (referred to as “NaOH”). In this case, no characteristic bindings of organic compounds can be recognized. Another reference sample was dipped in a PEO solution containing 10 % sodium benzoate after PEO in the pure NaOH solution (referred to as “dip benzoate”). As can be seen from the blue-colored graph in figure 3, this sample contains additional bands of the adherent, unaffected benzoate structures. Finally, the red-colored graph is related to a sample after PEO in an electrolyte containing 10 % sodium benzoate (referred to as “benzoate”), hence, reaction products of the sodium benzoate as well as unaffected but bound or strongly adsorbed benzoate are present at the sample surface. By comparing the spectra of “benzoate” and “dip benzoate”, significant deviations of the molecular structure can be observed. In the case of the “benzoate” spectrum, a new carbonyl band (C=O) can be observed in the range of 1700 cm\(^{-1}\) (marked by “1” in figure 3), which also exhibits a small shoulder at higher wavenumbers (about 1740 cm\(^{-1}\)). The strong signals between 1600 and 1300 cm\(^{-1}\) can be attributed to different C-H, C=C, C-C, and C-O bonds. It is noteworthy that these bonds were shifted towards higher wavenumbers after the PEO process, which can be explained by currently unknown structural changes or polarization effects. A sharp new signal appears at about 1500 cm\(^{-1}\) (marked by “2” in figure 3) in the “benzoate” spectrum, which means that new bonds formed during the PEO process, which were not present in the original benzoate molecule. Additionally, new signals can be observed at 1300–1100 cm\(^{-1}\) (marked by “3” in figure 3) and further spectral changes are present at 1100–800 cm\(^{-1}\).

**Figure 3.** ATR-IR spectra corresponding to: PEO in NaOH solution without any additions (“NaOH”), dipping in 10 % sodium benzoate solution after PEO in NaOH solution (“dip benzoate”), and PEO in 10 % sodium benzoate solution (“benzoate”) showing characteristic changes due to the PEO process
It is evident from the ATR-IR measurements of the “benzoate” and “dip benzoate” samples that organic compounds are present at the sample surface, which can be clearly differentiated from the original compounds in the PEO electrolyte according to their characteristic ATR-IR fingerprint.

Apart from the C=O bond, a clear allocation of the C-H, C=C, C-C, COH, and C-O bonds to distinct organic compounds is subject of further research. The interpretation of the ATR-IR spectra is further complicated as the possible bonds might be present in unaffected, adherent monomers as well as in newly developed polymers.

The ATR-IR spectra after PEO in NaOH solution (“NaOH”), dipping in 10 % sodium acrylate solution after PEO in NaOH solution (“dip acrylate”), and PEO in 4 % sodium acrylate solution (“acrylate”) are shown in figure 4. In comparison to “dip acrylate”, no additional ATR-IR bands can be observed in the “acrylate” spectrum, indicating that no new chemical bonds were formed during the PEO process. However, the two peaks around 1500 cm\(^{-1}\) are wider and less specific for the “acrylate” sample. This can be explained by the formation of polymers from the activated monomers. The “acrylate” sample was further investigated by XPS measurements in order to gain more detailed information on the molecular bonds.

3.3. X-ray photoemission spectroscopy
Composition and chemical states of the elements on the surface were additionally investigated by X-ray photoemission spectroscopy (XPS). Since the inelastic mean free path (IMFP) of electrons which are excited by Al K\(_{\alpha}\) radiation is in the range of several nanometers, the information provided corresponds to a surface layer thinner than approximately 10 nm [9]. The survey spectrum of the “acrylate” sample (figure 5(a)) reveals carbon, oxygen, and aluminum with molar contents of 32.4, 44.0, and 22.0 %, respectively. This fact indicates the presence of an organic layer in addition to an aluminum compound. The surface additionally contains 0.7 % of nitrogen, 0.7 % of sodium, and 0.2 % of calcium, which are residues adsorbed on the surface during the electrochemical reaction.

In order to clarify the chemical states, the high-resolution XPS spectra were analyzed. The Al2p spectrum (figure 5(d)) consists of two spin-orbit doublets with Al2p\(_{3/2}\) peaks at (74.3 ± 0.2) eV and (75.8 ± 0.2) eV, respectively. A reference spectrum taken on a clean metallic Al surface reveals an Al2p\(_{3/2}\) peak at (71.5 ± 0.2) eV. Therefore, the chemical states at the PEO-treated Al surface (4 % sodium acrylate solution) are unambiguously attributed to cationic aluminum compounds. According to the chemical shifts, the higher binding-energy peak can be attributed to bulk-like Al\(_2\)O\(_3\), while the stronger peak at lower binding energy corresponds to surface non-stoichiometric oxides. Complementary, in the O1s spectra (figure 5(e)), the peak at (530.8 ± 0.2) eV stems from aluminum oxides [9]. The O1s peak at (532.1 ± 0.2) eV corresponds to binding-energy values typical for C-O and O-C=O groups [10]. However, according to the literature, it may be attributed to surface Al hydroxides or carbonates formed due to exposure to the atmosphere as well [9]. In the C1s spectrum (figure 5(c)), three major peaks are revealed by fitting. The peak at (288.5 ± 0.2) eV stems from organic O-C=O functional groups or inorganic Al(CO\(_3\))\(_n\) compound. The peak at (285.5 ± 0.2) eV is typical for C-O or C-N groups. The peak at (284.6 ± 0.2) eV corresponds to aliphatic hydrocarbons. The high-resolution N1s spectrum (figure 5(b)) is fitted with two components at (399.4 ± 0.2) eV and (400.7 ± 0.2) eV, which usually correspond to free and protonated amine or amide groups, respectively [10]. Thus, the XPS study shows that the surface is composed of Al-containing cationic compounds, e.g. oxides, while metallic Al is not detected.

As the detected O-C=O and C-O bonds are present both in the sodium acrylate monomer and possible polyacrylates, there is no clear evidence that polymerization took place during the PEO in 4 % sodium acrylate solution.
Figure 5. (a) Survey XPS spectrum of the “acrylate” sample showing the composition and the chemical states of the elements and (b–e) high resolution N1s, C1s, Al2p, and O1s spectra proving the existence of Al2O3 and organic compounds, respectively.

4. Conclusions
Within this research work, orienting investigations were conducted, regarding the PEO in electrolytes that contain sodium acrylate or sodium benzoate. After a short process time of 60 s, the PEO layers exhibited a typical surface topography. There is some evidence that the presence of the organic compound in the PEO electrolyte influences the process initiation. More detailed studies of the passivation behavior in presence of absorbed monomers are planned. A significant increase of the carbon concentration on the top of the oxide was detected by EDX measurements. This might also be explained by the absorption of unchanged organic molecules and the existence of carbon-rich decomposition products or reaction products. However, by comparing the ATR-IR spectra of samples after PEO in the benzoate electrolyte and suitable reference samples, it was clearly shown that new organic bonds were formed during the PEO process. Thus, the feasibility of the plasma-induced activation of monomers and the generation of adherent, new organic compounds during the PEO process was successfully proved.

The presence of organic compounds at the sample surface was also verified by XPS measurements after PEO in an acrylate-containing electrolyte, although they might not have formed during the PEO process. Additional research work will be performed in the future in order to identify the newly formed organic compounds and to evaluate their suitability for the adhesion promotion of polymers.

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References

[1] Saborowski E, Steinert P, Dittes A, Lindner T, Schubert A and Lampke T 2020 Introducing fractal dimension for interlaminar shear and tensile strength assessment of mechanically interlocked polymer-metal interfaces Materials 13 2171

[2] Nestler D, Arnold S, Jung H, Wielage B and Kroll L 2014 Untersuchung geeigneter Oberflächenbehandlungsverfahren der Metallkomponente thermoplastbasierter hybrider Laminate Wissenschaftliche Schriftenreihe Werkstoffe und Werkstofftechnische Anwendungen 53 208–216

[3] Simchen F, Sieber M, Kopp A and Lampke T Introduction to Plasma Electrolytic Oxidation—An Overview of the Process and Applications Coatings 10 628

[4] Tang Y, Zhao X, Jiang K, Chen J and Zuo Y 2010 The influences of duty cycle on the bonding strength of AZ31B magnesium alloy by microarc oxidation treatment Surf. Coat. Tech. 205 1789–1792

[5] Pan Y, Wu X, Huang G, Wu S, Sun S, Ye H and Zhang Z 2018 A new approach to enhancing interlaminar strength and galvanic corrosion resistance of CFRP/Mg laminates Compos. Part A-App. 105 78–86

[6] Aliasghari S, Ghorbani M, Skeldon P, Karami H and Movahedi M 2017 Effect of plasma electrolytic oxidation on joining of AA 5052 aluminium alloy to polypropylene using friction stir spot welding Surf. Coat. Tech. 313 274–281

[7] Sieber M, Simchen F, Scharf I, and Lampke T 2016 Formation of a Spinel Coating on AZ31 Magnesium Alloy by Plasma Electrolytic Oxidation J. Mater. Eng. Perform. 25 1157–1162

[8] Shan M, Guo K, Gou G, Fu Z, Yang B and Lu W 2019 Effect of anodizing on galvanic corrosion behavior of T300 CFRP/5083P-O Al bolted joints Mater. Corros. 71 409–418

[9] Strohmeier B R 1990 An ESCA Method for Determining the Oxide Thickness on Aluminum Alloys Surf. Interface Anal. 15 51–56

[10] Naumkin A V, Kraut-Vass A, Gaarenstroom S W and Powell C J 2012 NIST X-ray Photoelectron Spectroscopy Database (NIST)