Superhydrophobic Aluminum Surfaces: Preparation routes, properties and artificial weathering impact

M. Thieme¹, C. Blank¹, A. Pereira de Oliveira², H. Woroch¹, R. Frenzel³, S. Höhne³, F. Simon³, H. G. Pryce Lewis⁴, A. J. White⁴

¹ Technische Universität Dresden (TUD), Institute of Materials Science, Dresden, Germany
² TUD, now at: Unicamp, Campinas, Brazil
³ Leibniz Institute of Polymer Research Dresden, Dresden, Germany
⁴ GVD Corporation, Cambridge, MA, USA

Abstract

Among the materials that can show superhydrophobic properties are hydrophilic metals which must undergo a sequential treatment, including roughening and hydrophobic coating. This contribution presents various preparation routes along with characterization work employing dynamic contact angle measurements (CA), scanning electron microscopy (SEM) and spectrometric techniques (FT-IRRAS, XPS, EIS).

Micro-rough surfaces of pure and alloyed aluminum were generated most easily by using a special sulfuric acid anodization (SAAi), which produces a micro-mountain-like oxide morphology with peak-to-valley distances of 2 µm and sub-µm roughness components. Additionally, micro-embossed and micro-blasted surfaces were involved. These initial states were combined with a number of dissolved compounds both of low-molecular and of polymer nature, such as the reactive fluoroalkyl silane PFATES, the reactive alkyl group containing polymer POMA, and Teflon® AF. The chemical modification was alternatively done by the Hot Filament Chemical Vapor Deposition of a PTFE layer. The latter can form a fundamentally higher thickness than the wet-born coatings, without any leveling of the subjacent microprofile. The inherent and controllable morphology of the PTFE layers represents an important feature. Further, the impacts of a standardized artificial weathering onto the wetting behavior and the surface-chemical properties were studied and discussed in terms of possible damage mechanisms. A very high stability of superhydrophobicity was observed with the fluorinated wet-born coatings PFATES and AS/TAF as well as with the PTFE variant AC, each on SAAi-pretreated substrates. Very good results were also gained for specimens produced by appropriate mechanical roughening and PTFE coating.

Key words

aluminum, superhydrophobicity, anodic oxidation, micro-embossing, wet-born coatings, PTFE layers, artificial weathering
Introduction

The physicochemical phenomenon superhydrophobicity (SH, earlier designated as ultrahydrophobicity) has been paid attention for more than one decade by numerous research groups, with the exciting investigations of Barthlott and Neinhuis [1] as a crucial point. SH defined by water contact angles (CA) of more than 150°, a negligible hysteresis (as the difference of the advancing and receding CAs, $\theta_a$ and $\theta_r$, respectively) and minute droplet rolling-off angles is based on the interplay of morphological and surface-chemical properties lowering the surface free energy down to dramatically low values. Surveying the vast literature, the micro-roughness has mostly more than one lateral/transversal component covering micro- and sub-microscalic dimensions [2-4]. Some researchers even postulated a fractal character [5]. Regarding the structural and chemical nature of superhydrophobic surfaces, the spectrum covers layered structures with self-assembling monolayers (SAM) of the water-repelling compounds up to polymer layers of considerable thickness as well as compact polymers with suitable morphology. It was stated that the surface free energies of molecular groups rank according to $\text{CH}_2>\text{CH}_3>\text{CF}_2>\text{CF}_3$ [6]. Fluorine-substituted organic compounds are therefore generally preferred for equipping a surface with SH. Moreover, they are characterized by an exceptionally high strength as well as by a high chemical and biological inertness [7]. There are literature surveys that reflect the experimental variety in a greater detail [8-10]. A special survey over superhydrophobic aluminum is given elsewhere [11]. Because Al, as an oxide film covered metal, has a hydrophilic character, it must undergo sequential roughening and coating treatment steps to be furnished with superhydrophobic properties.

The far-reaching prospects in terms of a commercial application of the so-called Lotus effect®, however, are being only hesitantly fulfilled in the factual development of superhydrophobic products. Apart from concurrent principles (as with photocatalytically acting superhydrophilic glass [12]), the major reason for this must be seen in that SH is intimately associated with the utmost surface of a part. Thus, SH is generally extremely sensitive to impacts, among others, from the mechanical as from the (photo-)chemical sides, i.e. from handling operations and weathering.

This contribution addresses the behavior of superhydrophobic Al material under artificial weathering on the background of different preparation routes regarding both micro-roughening and chemical modification. In addition to our anodization approach [13, 14], we present the novel variant of enhanced-temperature micro-embossing and micro-blasting as purely mechanical ways for achieving a suitably roughened surface [cf. 11]. Anodization based on phosphoric acid as well as laser ablation [13, 15-17] is not considered here. As for the coating step, the application of perfluorooalkylethyltriethoxy silane (PFATES) and [3-(2-aminoethyl) aminopropyl] trimethoxysilane plus Teflon® AF (AS/TAF) [13, 15] was amended by another wet-chemical route, the utilization of the reactive polymer poly(octadecen-alt-maleic anhydride), POMA, which can be grafted to previously deposited chitosan, Chs, as an anchor [18, 22]. It will be further shown that a PTFE layer deposited by HFCVD [19, 20] is able to confer SH on differently roughened Al substrates.
Mechanical properties of the produced systems as received from micro- and nanohardness measurements as well as from a gentle abrasion test are reported in ref. [11].

**Experimental**

**Substrate materials:** Sheets (26x38x1 mm³) of analytical grade Al 99.95 (Merck), pure Al 99.5 (AA 1050) and Al Mg1 (AA 5005); rod specimens (Ø5x40 mm²) of Al MgSi0.5 (AA 6060).

**Sulfuric Acid Anodization under intensified conditions SAAi:** sulfate concn. 2.3 mol/L, (40±1) °C, 30 mA/cm², 1200 s [13, 14]; cf. usual anodization SAAu at <20 °C, 15 mA/cm².

**Intermediate Treatment:** i) Deposition of chitosan (N-Amino-2-desoxy-β-D-glycopyranose) by cathodic precipitation (Chs-e; 1 % Chs soln. in 1 % acetic acid, pH = 3.8, -5 mA/cm², 40 s) or immersion (Chs-i; 1800 s) [18].

**Micro-embossing under tempered conditions ME:** Forming at 350 °C, 120 MPa using a laser-structured SiC tool (stamp diameter 18 mm, hexagonally arranged holes of about 25 µm depth and of 23 µm distance).

**Micro-blasting MB:** Corundum powders (grit 600, 800, 1000, 1200) applied as a fine beam at 6 bar pressure under manual control.

**Wet-chemical dip coating treatments:** i) Poly(octadecen-alt-maleic anhydride) (POMA) in acetone (0.1 %), 30 min; ii) perfluoroalkylethyltriethoxysilane (PFATES) in tert-butyl methyl ether, 180 min; iii) N-(2-aminoethyl)-3-aminopropytrimethoxysilane in Ethanol (96 %), 180 min, followed by spincoating (5000 min⁻¹, 30 s) with a solution of the copolymer Teflon® AF (1 % in FC 75) (AS/TAF); all steps were followed by mild tempering at 120 °C.

**HFCVD:** Thermal decomposition (>150 °C) of the precursor hexafluoropropylene oxide associated with radical formation producing PTFE layers of 50-1000 nm thickness, where besides standard coating conditions (SC) other variants were employed (A1, A2 - post-processing anneals, AC - alternative conditions with deposition at a different substrate temperature, LP - lower pressure conditions than with SC).

**Artificial weathering:** i) Normal exposure (WTH; 360 h = 15 d) comprising continuous xenon-arc irradiation filtered corresponding to day-light spectral distribution at a black-standard temperature of 55 °C and a sequence of shower wetting (18 min) and drying at relative air humidity of 60-80 % (102 min); ii) special exposure excluding moisture (WTH-L) (Xenotest Alpha; Atlas, Chicago, IL).

**Characterization:** i) Dynamic contact angle measurement (DCA; DSA 10, Krüss/ Germany); ii) Scanning electron microscopy (SEM; acc. voltage 2 keV; DSM 982 Gemini, Zeiss/ Germany); iii) Fourier-transform reflection-absorption infrared spectrometry (FT-IRRAS; 550-4,000 cm⁻¹, spot ca. Ø100 μm; FTS 2000, Perkin-Elmer/ Germany); iv) X-ray photoelectron spectroscopy (XPS; monochromatic Al Kα irradiation, charge compensation, step width 0.3 eV for survey spectra and 0.02 eV for high-resolution spectra, scale calibration based on C 1s binding energy of saturated hydrocarbons equal to 285 eV, maximum information depth for the C 1s peak about 10 nm [23-25]; Axis Ultra, Kratos/ UK); v) Electrochemical impedance spectrometry (EIS; 100 kHz - 0.5 mHz; IM 6, Zahner/ Germany; using sheet specimens
in an O-ring cell setup or rod specimens (cf. [21]); 0.133 mol L\(^{-1}\) phosphate buffer test solution pH = 6.0).

**Results**

**Substrate surfaces**

Independently of the materials employed the SAAi pretreatment leads to a specific morphology of the produced oxidic layer characterized by an irregularly ordered mountain-like structure showing typical top-to-valley and lateral distance dimensions of about 2 µm each (Fig. 1a). This structure is produced more uniform on pure Al as compared with the technical Al sorts. Higher magnification reveals that the morphology is overlaid with a sub-µm, fibre-like roughness (Fig. 1b).

(Figure 1)

In contrast, surfaces treated by the usual SAAu method have a more or less flat, shell-like shaped morphology (Fig. 1c). For details of layer formation, their structures and compositions see refs. [13, 14, 21].

(Figure 2)

As an alternative to the anodic route of micro-roughening, Figs. 2a, b show the SiC embossing die with its regular array of laser-abraded cavities and the embossed Al Mg1 metal surface, respectively. The protrusions of the latter have a shape which is very similar to the lotus-leaf. Dismantling of the embossing die did not cause damages neither to the metal nor to the tool. It should be noted that the hardness of Al Mg1 amounts to about 52 HBW 2.5/62.5. Therefore, it was necessary to employ an enhanced-temperature technique. As it was stated earlier for first attempts of ambient temperature forming, the bumps were developed to a very low degree only. However, ambient-temperature embossing was found to be suitable for Al 99.5, which has about one half of the hardness of Al Mg1.

The additional blasting treatment furnished the surface with a uniform roughness, however, connected with considerable abrasion and deformation of the protruding bumps. The latter was more pronounced with the rather coarse 600 grit powder than with 1200 grit (Figs. 2c, d). Chitosan was involved into the experiments to test for possible strengthening effects onto the anodic oxide and to utilize its chemical reactivity for grafting the hydrophobizing compound POMA [18, 22]. Chitosan may be dissolved in weakly acid medium due to protonation of the amino side group attached to the polymer backbone. It is possible to deposit the polycationic chitosan by means of a cathodic process, which is joint by interfacial alkalization and, hence, deprotonation of the polycations. For optimized conditions of this process, the organic material is homogeneously precipitated and practically not visible by SEM (Fig. 3a). With too high pH, current density and duration, inhomogeneous precipitation occurs (Fig. 3b). Cone-like microscopic defects form additionally, probably due to concurrent hydrogen formation and bubble expansion at the metal-oxide interface.

(Figures 3, 4)
EIS indicated that defects are present indeed (Fig. 4). As the diagram shows, the curve of the impedance modulus $\log|Z|$ vs. $\log f$ is markedly shifted to lower values for $f < 1$ kHz in comparison with the original anodized state $SAAi$. This observation conforms to the formation of a more porous oxide structure connected with a lower protective character [21]. However, structural alterations take place even in the course of the elaborated Chs-e treatment. Contrarily, specimens that were merely immersed in chitosan solution ($SAAi + Chs-i$) gave practically the same impedance spectrum as $SAAi$. An analogous situation was found for $SAAu$-based specimens.

### 3.2 Coated surfaces

The application of $POMA$ as a hydrophobizing grafted-to polymer is associated with very thin films, comparable to the wet-born coatings $PFATES$ and $AS/TAF$. Thus, the pre-formed micro-mountain-like morphology is preserved (Fig. 3a).

(Figure 5)

With HFCVD-generated $PTFE$ layers, the microscopic shape is noticeably different, because of the inherent morphological properties in the sub-μm range. The specific shape arises with increasing thickness (50-1000 nm) and may be adjusted through the employed formation conditions. While the SC conditions produce a budded shape with very small protrusions of about 0.1 μm dimension (Fig. 5a, d), other regimes ($A1, A2, AC, LP$) give interpenetrating filmy flakes of 0.2-0.4 μm in diameter (Fig. 5b). In the case of the micro-profiled $SAAi$ substrates cryo-fracturing or cross-sectioning confirm a projected thickness of 1 μm (Fig. 5a). This image documents also that the layer is nestled to the substrate, where the micro-profile is a little bit rounded without being leveled out. Fig. 5c shows the situation with an $SC$-coated, $ME/MB$-pretreated substrate.

Nearly all the addressed combinations of roughening and coating treatments led to superhydrophobic properties with CAs around 150° and a generally negligible hysteresis. For the states displayed in Figs. 5a-d the inserted DCA data were determined. The entire wetting results may be taken from Table 1.

Interestingly, restrictions of the roughening treatments caused different impacts on the SH:

i) replacing $SAAi$ by less intensive electrochemical roughening:
   \[ \theta_a = (153\pm2)^\circ \parallel \theta_r = (144\pm3)^\circ \] (for $SAAu + SC$-1000 nm);

ii) replacing 600 grid blasting by 1200 grid:
   \[ (155\pm1)^\circ / (153\pm1)^\circ \rightarrow (151\pm2)^\circ / (146\pm2)^\circ \] (for $ME + MB$-xxx + SC-1000) and
   \[ (157\pm1)^\circ / (155\pm1)^\circ \rightarrow (151\pm1)^\circ / (146\pm2)^\circ \] (for $MB$-xxx + SC-1000);

iii) omitting the micro-blasting step:
   \[ (155\pm1)^\circ / (153\pm1)^\circ \rightarrow (151\pm3)^\circ / (147\pm5)^\circ \] (for $ME$ [+ $MB$-600] + SC-1000);

iv) omitting $ME$ and $MB$:
   \[ (144\pm3)^\circ / (94\pm6)^\circ \] (for microscopically flat surface, cf. Fig. 5a).

The results indicates that the considerably less roughness of an $SAAu$ surface vs. $SAAi$ can be compensated for only in a limited degree by the $SC$'s inherent budded roughness and that micro-blasting is an important step in combination with micro-embossing to achieve SH.
The chemistries of the substrate-coating systems were investigated by means of FT-IRRAS and XPS. The infrared spectra for four examined positions each were highly reproducible so that one spectrum was arbitrarily selected for the display. The POMA-modified surface showed C-H stretch bands at 2851 and 2923 cm\(^{-1}\) (Fig. 6a) indicating the presence of long alkyl chains, which are responsible for diminishing the surface free energy. The presence of C-O bindings is reflected by small bands at 1700-1770 cm\(^{-1}\). For the F-containing coating compounds the typical C-F stretch vibrations were recorded in the clearest form with PTFE coatings on 'naked' ME/MB substrates (Fig. 6g). The two bands at 1150 and 1205 cm\(^{-1}\) (shoulder at 1260 cm\(^{-1}\)) agree with literature data [19, 20]. With SAAi-pretreated specimens the position of these bands deviates somewhat. Changing the SC thickness, the band at about 1175 cm\(^{-1}\) remains constant in contrast to the band beyond 1200 cm\(^{-1}\), which undergoes some shifting. Obviously, this results from a superposition with a band owing to the oxidic substrate. With the different SAAi + PTFE sorts the absorbance pattern varies a little bit (Fig. 6, curves d-f), where SC is alike to A2 and AC.

(Figure 6)

For the employment of XPS to specimens with a rough surface it should be noted that the real take-off-angles and, hence the information depth, are characterized by a local variation. This is especially true for SAAi-based objects with their microscopically steep flanks. According to the findings, the C 1s HR spectra reveal a more or less complexity due to the respective structure and binding situations of the coatings analyzed. With the thin wet-born coatings Chs + POMA the C 1s spectrum of the composite layer (Fig. 7b) shows a dominant component peak (A) mainly arising from the saturated hydrocarbons of POMA’s octadecyl rests. The two component peaks C and D, which are typical for the C–O–(H, C) and O–C–O (acetal) groups of chitosan (Fig. 7a), are strongly diminished. This indicates that the chitosan layer is completely covered by POMA. Amide and imide groups formed during the reaction between chitosan and POMA were identified as component peaks E and G [22]. The situation is similarly complex in the case of PFATES (-CF\(_3\), >CF\(_2\), >CH\(_2\)) or AS/TAF (Fig. 7c) with contributions of both the aminosilane and the copolymer above. Here, additional peaks occur corresponding to -CF\(_3\), >CF\(_2\), >COF, and other structure elements of the polymer molecule. The C-F bindings are characterized by high binding energies of \(E_0 \geq 292\) eV. It should be noted that in these cases of coatings the high oxygen contents of about 30 at% do not represent the coatings alone, but also subjacent Al oxide regions. This is confirmed by the detection of Al (ca. 9 at %).

(Figure 7)

For specimens with different 500 nm thick PTFE-coatings the F/C ratios were higher than in the cases of the F-containing wet-born coatings (Table 1). The determined values were in the range 1.8-2.2, i.e. near to the theoretical value. In the case of bulk PTFE a ratio of 2.1 was determined. Most of the C 1s spectra are dominated by the peak at 292 eV attributable to the >CF\(_2\) units in the polymer chains (Fig. 7d). The coating variant LP is characterized by a different situation (Fig. 7e), where the component peak at 293 eV is due to a higher portion of –CF\(_3\) bindings. Further, there is a noticeable contribution of carbon with lower binding energy. This is consistent with the considerable oxygen content of about 13 at % (generally not ex-
ceeding 2 at %). These findings indicate that the corresponding formation conditions of \( LP \) result in marked deviations from the regular \( PTFE \) composition. Obviously, the compound trifluoroacetyl fluoride \( CF_3CFO \), which represents one of the products formed by the thermal decomposition of hexafluoropropylene oxide [20], plays a certain role for this polymer coating type.

(Table 1)

Comparative EIS measurements yielded quite similar results for \( SAAu + SC \) specimens in comparison with different wet-born coatings [21]. An increasing \( SC \) thickness leads to higher impedance levels of the intermediate plateaus in the \( \log|Z| - \log|f| \) curves (Fig. 8). However, the resistance of the anodic barrier layer is the highest in the entire system, as is expressed by the impedance in the sub-mHz region. Measurements with \( SAAi \)-based sheet specimens failed because of an inconsistent effective area during the immersion due to capillary effects.

(Figure 8)

3.3 Coated surfaces following artificial weathering

The influence \( WTH \) exposure on the specimens properties were characterized in the same manner as for the as-coated states. Visually no alterations were observed. Moreover, the SEM examination suggested practically unchanged morphological properties.

The wetting behavior in the post-\( WTH \) state as the crucial property presents a different picture. As the CA data clearly document (Table 1, third column), degradation phenomena were observed, the degree of which being influenced by the respective treatment. Practically no changes in the CA were observed for \( PFATES, AS/TAF, A1-500, AC-500, ME + SC-1000 \), and \( ME + MB-1200/ 600 + SC-1000 \), whereas other states suffered a moderate or even a dramatical drop (\( SAAi + Chs/POMA, SAAu + SC, Pickled + SC-1000, Flat + SC-1000, MB-1200 + SC-1000 \)).

It was attempted to relate the actual wetting properties and their changes to the corresponding surface-chemistry findings. FT-IRRAS revealed that the content of water in the layered surface region of all specimen types was a little bit higher than before the exposure. The C-F-related region at 1150-1200 cm\(^{-1}\) was not influenced by \( WTH \) as seen from the spectra cutouts of Fig. 9 for different layer systems, although these showed different impacts on their wetting behaviors.

(Figure 9)

The XPS results are of higher importance, because this method is much more sensitive to changes in the utmost surface, which governs in turn the wetting behavior. For \( SAAi \)-based specimens furnished with \( PFATES \) or \( AS/TAF \), where are no significant changes in the wetting properties following \( WTH \), interesting features were detected by XPS. The important F/C concentration ratio decreased a little bit in the case of \( PFATES \) with practically unchanged C 1s HR spectra (Figs. 10a, b). These findings reveal a very high stability of this compound under the conditions of the exposure. With \( AS/TAF \), however, the F/C ratio increased along
with a decreasing portion of the low-energy bound carbon in the C 1s spectrum. The F-bound carbon remains on a high level. Obviously, the primary coating component aminosilane undergoes degradation in the course of the exposure.

With SC-type PTFE coatings the weathering impact was found to be generally higher. At least part of the SAAi-based specimens underwent noticeable drops in the receding angles (Table 1) so that SH was not fully maintained in these cases. Fig. 10c indicates that the portion of electropositively bound carbon has increased as a result of the WTH exposure (cf. Fig. 7d). This finding is associated with increased oxygen contents, which represent some newly generated side groups or disruptions of the polymer backbone (Table 1).

The intermediate deposition of Chs proved to have a negative influence on the wetting behavior. The underlying reason is not yet clear.

With SAAu + SC specimens the unfavorable contact angle changes were rather dramatical in spite of the initially same surface chemistry (Table 1). On the other hand, a markedly better stability was demonstrated in most cases of mechanical pretreatments (ME, MB, ME + MB), where the receding angles showed a generally moderate decrease below the 150° threshold (Table 1). It appears that specimens with incomplete or limited roughness prerequisites underwent a more pronounced worsening of their wetting behavior during WTH.

As for alternative PTFE coatings on SAAi substrates, a fairly good weathering behavior was stated for the types A1, A2, and LP. The presumably best behavior may be stated for SAAi + AC-500. XPS confirms that the portion of electropositively bound carbon remained lower than with SC-type PTFE (Fig. 10d).

(Figure 10)

An additional weathering experiment excluded moisture so that a permanent dry irradiation took place over 360 h (WTH-L). The advancing contact angles remained on the same level as after the regular WTH procedure, but the receding CAs diminished drastically, generally connected with a higher scattering. At best, \((150\pm3)^\circ/(119\pm10)^\circ\) were measured for SAAi + AC-500 + WTH-L. In spite of these findings, the C 1s HR spectra for the PTFE-coated specimens were generally very similar to those for regular WTH (Figs. 10c, d). With the generally very stable PFATES coating type \([(146\pm2)^\circ/(86\pm2)^\circ]\) some minor impact was observed also in the C 1s spectrum (insert in Fig. 10b).

These findings suggest on the one hand that the various coating compounds may have been affected by the dry exposure in a different way. On the other hand, the damaging mechanism without moisture may deviate from that under regular WTH conditions, where the water is expected to influence the actual degradation. In the light of the XPS findings, the worsened wetting properties for WTH-L may be explained in that the irradiation causes small local coating defects, which are responsible for local pinning towards the receding movement of the wetting triple line in the course of the dynamic CA measurement.
Conclusions

In order to investigate preparative effects onto superhydrophobicity (SH) and to judge its weathering stability, quite different variants of the roughening pretreatment (electrochemically, mechanically) and the water-repelling coatings (wet-born thin-filming, hot-filament chemical vapor deposition of PTFE films) were taken into consideration. The chemical stability was preliminarily judged by the application of a standardized artificial weathering test. Within the employed experimental conditions, noticeable influences onto the wetting properties of the total systems were found to be exerted from the manner of roughening. Superhydrophobicity was achieved in those cases, where the pretreatment provided for a suitable degree of sub-micro-roughness and micro-roughness components, e.g. with the anodization route SAAi or with micro-embossed plus micro-blasted surface types. The usual anodization SAAu and mere pickling worsened the repelling properties, although the latter were supported by the inherent micro-roughness of the HFCVD-produced PTFE films.

As for the impact of the artificial weathering exposure, it can be stated that a very high stability of superhydrophobicity was observed with the fluorinated wet-born coatings PFATES and AS/TAF as well as with the PTFE variant AC, each on SAAi-pretreated substrates. Very good results were also gained for specimens produced by appropriate mechanical roughening and PTFE coating. As a rule, the more noticeable the worsening of the water-repelling properties was, the more the XPS-derived element concentration criteria c(F) and c(F)/c(C) decreased, whereas c(O) increased. AS/TAF underwent noticeable changes in its composition due to weathering. The stability of the 'standard' PTFE coating SC was found to be higher with SAAi as the subjacent state as compared to SAAu or pickling.

Acknowledgments

Partly, this work was supported by a grant of the Saxon State Ministry of Science and the Fine Art (Saechsisches Staatsministerium fuer Wissenschaft und Kunst, SMWK). One of us (A.P.) appreciates the support of the German Academic Exchange Service (DAAD). The micro-embossing and micro-blasting steps were elaborated of Mr. T. Burkhardt and J. Engelmann (FhG-IWU Chemnitz). Likewise, the preparation work of Mrs. K. Galle (TUD) and Mrs. B. Schneider (IPF) are acknowledged.

References

Fig. 1. SEM images of anodized surfaces referring to different substrates; (a) SAAi (Al 99.95); (b) SAAi (Al Mg1); (c) SAAu (Al Mg1).

Fig. 2. SEM images of the laser-structured tool (a, up left; top view) and of mechanically structured Al Mg1 surfaces; (b) ME; (c) ME + MB-1200; (d) ME + MB-600 (2b-d specs. tilted).
Fig. 3. SEM images of specimen surfaces following the cathodic chitosan deposition on SAAi-treated surfaces; (a) Al Mg1, SAAi + Chs-e; (b) Al99.5, but with higher pH, current density and time of Chs deposition.

Fig. 4. EIS spectra for SAAi, SAAi + Chs-e and SAAi + Chs-i in phosphate buffer; rod specimens.
Fig. 5. SEM images and DCA data ($\theta_a/\theta_r$, inserted) of different treatment states; (a) SAAi + SC-1000 nm, fractured specimen showing its outer surface (upper part) and the fractured area (lower part), PTFE layer marked by arrows; (b) SAAi + A1-500 nm; (c) ME + MB-600 + SC-1000 nm; (d) Flat substrate + SC-1000 nm (5a-c specs. tilted by 35°, 5d top view, 5b 10 kV).

Fig. 6. FT-IRRAS absorbance curves for different states; (a) SAAi + Chs-e + POMA; (b) SAAi + PFATES; (c) SAAi + AS/TAF; (d) SAAi + SC-500 nm; (e) SAAi + A1-500 nm; (f) SAAi + LP-500; (g) MB + SC-1000 nm (from top to bottom).
Fig. 7. C 1s HR spectra of SAAi-based specimens provided with different coatings; (a) SAAi + Chs; (b) SAAi + Chs + POMA; (c) SAAi + AS/TAF; (d) SAAi + SC-500; (e) SAAi + LP-500.

Fig. 8. EIS spectra for SAAu, SAAu + SC-50, and SAAu + SC-1000 in phosphate buffer; sheet specs.
Fig. 9. FT-IRRAS absorbance curves for different states before and after WTH; (a) SAAi + AS/TAF; (b) SAAi + AS/TAF + WTH; (c) SAAi + SC-500; (d) SAAi + SC-500 + WTH; (e) SAAi + AC-500; (g) SAAi + AC-500 + WTH (from top to bottom).

Fig. 10. C 1s HR spectra for artificially weathered, SAAi-based specimens provided with different coatings; (a) SAAi + PFATES; (b) SAAi + PFATES + WTH (insert: SAAi + PFATES + WTH-L); (c) SAAi + SC-500 + WTH (insert: SAAi + SC-500 + WTH-L); (d) SAAi + AC-500 + WTH (insert: SAAi + AC-500 + WTH-L).
Table 1. Data compilation for the as-coated states and after the artificial weathering exposure; columns 2 and 3: wetting properties according to DCA measurements (std. deviations are given for single specimens, whereas spans are stated, if several specimens of the same type were measured); column 4: carbon to fluorine ratios acc. to XPS (single specimens).

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Contact angles (θ_a / ° // θ_r / °) (as coated)</th>
<th>Contact angles (θ_a / ° // θ_r / °) (after WTH)</th>
<th>c(F) / c(C) (before WTH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAAi + Chs/POMA (3 pcs.)</td>
<td>153 // 152 superhydrophilic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SAAi + PFATES (2 pcs.)</td>
<td>153 // 152</td>
<td>152-154 // 148-150</td>
<td>1.8 → 1.6</td>
</tr>
<tr>
<td>SAAi + AS/TAF (2 pcs.)</td>
<td>152 // 151-152</td>
<td>154 // 151-152</td>
<td>1.4 → 1.7</td>
</tr>
<tr>
<td>SAAi + SC (250-1000 nm, 6 pcs.)</td>
<td>151-152 // 148-151</td>
<td>142-153 // 130-147</td>
<td>2.1 → 1.9</td>
</tr>
<tr>
<td>SAAi + Chs + SC (250-1000 nm, 4 pcs.)</td>
<td>151-152 // 149-151</td>
<td>133-150 // 99-130</td>
<td></td>
</tr>
<tr>
<td>SAAi + AI-500</td>
<td>151±1 // 151±1</td>
<td>152±1 // 147±1</td>
<td>2.0 → 2.0</td>
</tr>
<tr>
<td>SAAi + A2-500</td>
<td>153±1 // 151±1</td>
<td>152±2 // 142±2</td>
<td>2.1 → 2.1</td>
</tr>
<tr>
<td>SAAi + AC-500</td>
<td>151±1 // 150±1</td>
<td>152±1 // 150±1</td>
<td>2.2 → 2.1</td>
</tr>
<tr>
<td>SAAi + LP-500</td>
<td>152±1 // 151±1</td>
<td>154±1 // 141±1</td>
<td>1.8 → 2.0</td>
</tr>
<tr>
<td>SAAu + SC (50-1000 nm, 3 pcs.)</td>
<td>151-153 // 140-144</td>
<td>127-134 // 47-70</td>
<td>2.1 → 1.6</td>
</tr>
<tr>
<td>Pickled + SC-500</td>
<td>153±1 // 149±1</td>
<td>137±4 // 79±2</td>
<td></td>
</tr>
<tr>
<td>SC-1000</td>
<td>144 ± 3 // 94 ± 6</td>
<td>112 ± 4 // 73 ± 11</td>
<td></td>
</tr>
<tr>
<td>ME + SC-1000</td>
<td>151 ± 3 // 147 ± 5</td>
<td>154 ± 1 // 149 ± 1</td>
<td></td>
</tr>
<tr>
<td>MB-1200 + SC-1000</td>
<td>151 ± 1 // 146 ± 2</td>
<td>127 ± 11 // 84 ± 27</td>
<td></td>
</tr>
<tr>
<td>ME + MB-1200 + SC-1000</td>
<td>151 ± 2 // 146 ± 2</td>
<td>150 ± 1 // 146 ± 3</td>
<td></td>
</tr>
<tr>
<td>MB-600 + SC-1000</td>
<td>157 ± 1 // 155 ± 1</td>
<td>151 ± 2 // 141 ± 7</td>
<td></td>
</tr>
<tr>
<td>ME + MB-600 + SC-1000</td>
<td>155 ± 1 // 153 ± 1</td>
<td>152 ± 1 // 146 ± 1</td>
<td></td>
</tr>
</tbody>
</table>