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Wetting behavior and remarkable durability of amphiphobic aluminum alloys surfaces in a wide range of environmental conditions

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HIGHLIGHTS

- Aluminum alloys surfaces with strong repellence against water and low-surface tension liquids were obtained.
- Favorable wetting/dewetting behavior is preserved after chemical attack and ageing tests.
- A wide range of exposure and wearing conditions were evaluated.
- Materials with coated surfaces can be thought as “smart” component in many industrial fields.

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ABSTRACT

In this work the amphiphobic behavior and durability of engineered aluminum alloy surfaces are highlighted. Functional, hybrid organic–inorganic coatings were obtained by a classic sol–gel route, followed by a controlled dipping on the substrate in order to achieve surface nanostructuring. The characterization of surfaces revealed outstanding results in terms of static contact angle (higher than 170°) and hysteresis (lower than 5°) with water, as well of contact angle (about 145°) with low-surface tension liquids. In relationship with the latest scientific improvements on this topic, the development of materials coupling favorable static and dynamic repellence against low-surface tension liquids can find applications as corrosion protective components, stain-resistant and self-cleaning materials, de-icing or anti-biofouling paints, and so on. In each area, one of the most important issue to be concerned is the materials’ ability to withstand adverse conditions (i.e. attacks by chemical agents and wearing phenomena), avoiding the quick loss of superhydrophobicity/oleophobicity. In this context, functional coatings developed on aluminum alloy stand out for the excellent capability of keeping unchanged their performances over the time and after simulation of rather severe working environments, matching by this way some of the basic requirements connected with their employment as innovative industrial structural materials and components.

1. Introduction

The repellence to liquids is a key aspect of materials engineering. The ability to control the wetting behavior of bulk or surfaces is an important challenge in many different fields where corrosion-resistant components, low-friction elements, drag-reduction systems, de-icing materials, etc. are needed.

The current state of the art suggests that superhydrophobic materials with an increased repellence against water can be generated by different methodologies [1–5]. Among them, the surface functionalization by inorganic or hybrid organic/inorganic nanoscaled and rough featured thin layers, obtained by sol–gel method, is widely described as one of the simplest [6–9]. Over this, the present work propose the innovation stemming from the water-based synthesis of the functional oxide layer, with great advantages in terms of eco-compatibility, versatility and future up-scaling with respect to the current literature which usually presents solvent-based preparation [10,11].

Up today, one of the major hindrance for any practical application of strongly water repellent surfaces is their mechanical fragility and poor durability [12–16]. Moderate forces (i.e. surface touching or rubbing) or particular chemical environments can be enough to destroy the surface nanostructures, leading to the loss of the outstanding superhydrophobic properties. To create more robust materials and surfaces, new strategies have been recently

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proposed as, for example, the modification of the working *solid* interface by realizing materials with a *liquid* surface, replacing or covering the structured, solid one [17–19]. By this strategy, the repellence against fluids of different nature and with different chemico-physical properties – termed as amphiphobicity (hydrophobicity plus oleophobicity) or, more generally, as omniphobicity (repellence against everything) – have been conceived, paying also attention to the design of self healing and high pressure resistant synthetic surfaces [20–23]. However, the realization of durable amphiphobic products, applicable in a wide range of environmental conditions, still represents a great challenge to be overcome, which is addressing extraordinary efforts in the research community. In this context, the authors of the present work have pursued the goal of achieving amphiphobicity on surfaces with different working interfaces (respectively, *solid* and *liquid* ones), bestowing on them outstanding repellence, durability and chemical stability over the time. The obtained results also strengthen the assumption that, when properly designed, nanostructured *solid* interfaces, working in the Cassie-Baxter state [24,25], are themself effective in facing up severe operating conditions showing performances comparable to that of the so-called *SLIP* ones, so frequently investigated in the most recent literature [26–29].

All functional materials presented in this work have been deeply characterized in terms of wetting behavior (water and oils contact angles, contact angle hysteresis by tensiometry), surface energy (OWK method) and microstructure by FESEM observations. Any variations against functionalities and microstructure were detected after simulation of a wide spectrum of exposure environments and ageing steps, comparing the experimental response of nanostructured *solid* surfaces with those obtained by the additional treatment with a high density, low-surface tension lubricant [28].

Results suggest that the nanostructured hybrid coating deposited on aluminum are able to brightly withstand a large number of severe environments and mechanical stress (at least up to 4 N) without any noticeable loss in their amphiphobic behavior. These circumstance allow to consider them as potential anti-sticking products suitable to be applied as self cleaning, icephobic, antifouling, low friction components, and so on.

2. Materials and methods

2.1. Preparation of amphiphobic aluminum alloy surfaces

Alumina nanoparticles in form of aqueous sol were prepared as following: ethyl acetoacetate (>99%, Sigma–Aldrich), as chelating agent, was added to distilled water and mixed for few minutes. Once temperature reached 70 °C, aluminum-tri-sec-butoxide (97%, Sigma–Aldrich) and then nitric acid (0.5 M) were added, this latter to promote peptization. The reaction mixture was left under stirring at 70 °C for 24 h. The molar ratios of chelating agent, nitric acid and total water with respect to the metal alkoxide were set to 1, 0.3 and 90, respectively. The pH of the as-prepared sol was 3.5.

Particle size distribution of the alumina suspension, in terms of hydrodynamic diameter, was evaluated by dynamic light scattering (DLS) analyzer (DLS Zetasizer Nano S, Malvern Instrument) working in backscattering modus (2ϑ equal to 173°) at 25 °C. Average values corresponding to four different measurements have been provided. Hydrodynamic diameter includes the coordination sphere and the species adsorbed on the particle surface such as stabilizers, surfactants, and so forth. DLS analysis also provides a polydispersion index (PDI, adim.), ranging from 0 to 1, whose value is related to the dispersion degree of colloidal suspension. The samples prepared in the present work showed a Gaussian-type particle size distribution with a PDI of 0.4: the observed curve was monomodal, the medium particle size being 44 nm (Fig. 1).

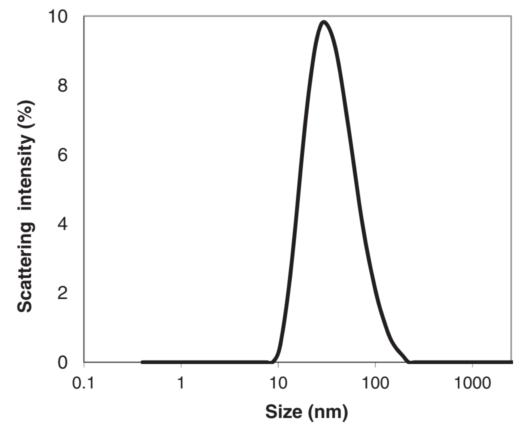

Fig. 1. DLS spectrum of as-prepared alumina sol showing a monomodal size distribution. Medium particle size of 44 nm and PDI of 0.4.

Sandblasted aluminum alloy (Al1050 99% H24) foils, with dimensions of 100 × 50 × 1.5 mm and surface roughness R_a (measured by 3-D profylometer Talysurf CCI 3000) in the 4–5 μm range, have been considered as reference samples (R). After ultrasonication in ethanol for 5 min to remove impurities, Al foils were coated with the aqueous Al_2O_3 sol by dip-coating under the following conditions: dipping-withdrawing speed of 2 mm/s and residence time of 5 s. After drying at room temperature, coated samples were treated at 400 °C for 60 min, then boiled in distilled water for 30 min to form flaky bohemite, and thermally treated again at 400 °C for 10 min getting the final transformation to γ-alumina [30–32]. Finally, a fluoroalkylsilane (FAS) solution (Dynasylan® SIVO CLEAR EC, Evonik) was dip-coated on samples surfaces (dipping-withdrawing speed: 2 mm/s, residence time: 120 s), followed by consolidation at 150 °C for 30 min [31]. By this way, aluminum foils with a hybrid organic/inorganic surface layer, characterized by an air-filled nanostructure, have been produced (S samples). With the aim of changing the chemistry of the working interface, some of them were additionally processed by immersion in a high-density, low-surface tension lubricant (FC-43 provided by 3 M, γ = 19 mN/m at 20 °C), spreading by capillarity into the substrate thus replacing the air present in the nano porous structure and forming an over-coated *liquid* layer. After 5 min, samples were withdrawn with care, allowing the lubricant excess to slip off the surface, then dried at room temperature (SI samples).

2.2. Static, dynamic contact angles and surface energy

Contact angle measurements were performed by an optical tensiometer equipped with a CCD camera (OCA 15 Plus, DataPhysic Instruments). Measurements of static contact angle with water (WCA) and six different liquids, having surface tension at 20 °C between 50.8 mN/m of diiodomethane ($C_2H_2I_2$) and 21.6 mN/m of *n*-octane (C_8H_{18}), were carried out with the sessile drop method (drop volume of 1 μl). An image of the droplets formed by water, $C_2H_2I_2$ and hexadecane on coated aluminum alloy surface is displayed in Fig. 2.

The dynamic wetting against water was assessed by the needle-in/needle-out technique [33] measuring the advancing (ϑ_A) and receding (ϑ_R) contact angle of a sessile drop (volume of 2 μl) and calculating the contact angle hysteresis (CAH) as the difference $\vartheta_A - \vartheta_R$. The whole survey of wetting data, calculated as the average of five to ten measurements on different points of S, SI and uncoated R surfaces, is disclosed in Tables 1 and 2.

Surface energy (SE) is the thermodynamic parameter describing the equilibrium state of surface atoms. The Young equation [34] constitutes the basis for the determination of SE of solids.