Effects of aluminium surface morphology and chemical modification on wettability

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ABSTRACT

Aluminium alloys are some of the predominant metals in industrial applications such as production of heat exchangers, heat pumps. They have high heat conductivity coupled with a low specific weight. In cold working conditions, there is a risk of frost formation on the surface of aluminium in the presence of water vapour, which can lead to the deterioration of equipment performance. This work addresses the methods of surface modification of aluminium and their effect of the underlying surface morphology and wettability, which are the important parameters for frost formation. Three groups of real-life aluminium surfaces of different morphology: unpolished aluminium, polished aluminium, and aluminium foil, were subjected to surface modification procedures which involved the formation of a layer of hydrophilic hyperbranched polyethyleneglycol via *in situ* polymerization, molecular vapour deposition of a mono-layer of fluorinated silane, and a combination of those. The effect of these surface modification techniques on roughness and wettability of the aluminium surfaces was elucidated by ellipsometry, contact angle measurements and atomic force microscopy. We demonstrated that by employing different types of surface modifications the contact angle of water droplets on aluminium samples can be varied from 12° to more than 120°. A crossover from Cassie–Baxter to Wenzel regime upon changing the surface roughness was also observed.

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1. Introduction

Aluminium alloys play an important role in modern industry, for instance in the production of aircrafts, vehicles, different types of heat exchangers and heat pumps [1,2]. This is due to their particular characteristics such as its high heat conductivity, low specific weight, and high specific strength. Moreover aluminium has self-passivation properties due to the formation of a stable native oxide layer, hence protecting the bulk material from further oxidation and corrosion [3–5]. In cold working conditions in the presence of water vapour, condensation of water vapour or frost formation can occur when the temperature of aluminium surface drops below the dew point. The condensation of water vapour or accretion of frost is mostly undesirable, for example frost accretion on aircraft wings can pose a serious problem. In addition, this can lead to the deterioration of equipment performance. For example, frost formation can clog or narrow the air passages of heat exchangers hence increasing the pressure difference. Moreover, it increases thermal and flow resistance and consequently lowers heat performance of heat exchangers and overall reduces the system performance [6,7].

Alongside with the importance of psychrometric parameters such as air temperature, velocity, humidity and surface temperature on the frost formation process, surface conditions such as surface temperature, roughness, drop adhesion to the surface and consequently contact angle are also important parameters for frost formation [8–10]. Therefore surface characteristics and surface modifications of aluminium strongly affect the performance characteristics of a whole range of different machinery involving aluminium and its alloys.

Different strategies and methods need to be applied in order to delay or prevent the frost formation on the surface of aluminium. One of the key factors of frost formation on solid surfaces is adhesion of a droplet to the surface and its wettability. The drop adhesion can be measured by dedicated experimental techniques such as centrifugal adhesion balance (CAB). This technique allows the study of the relation between lateral adhesion forces at a solid–liquid interface and the resting time of a droplet prior to sliding off the surface [10]. The wettability can be controlled by varying the surface chemistry, e.g., by chemical modification of the surface, or by changing the surface morphology, e.g., by forming micro/nanostructures on the surface [11]. The relation between the surface morphology and contact angle is generally described by two models, which address the wettability of rough surfaces: the Wenzel and the Cassie–Baxter model [12–14]. Both models

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denote the wettability in terms of the angle that a liquid droplet forms on a solid surface (contact angle) [15–17]. Although these models are commonly used for the interpretation of data related to the wettability of surfaces, it should be mentioned that there is some ongoing discussion about the validity of these models in recent scientific literature. We can refer the reader to a recent comprehensive review by Gao and McCarthy summarizing this issue [18]. They claim that the contact angle is not only related to the contact area and the interfacial free energies, which the Wenzel and the Cassie–Baxter models are based upon, but also to other parameters such as the activation energies that the contact line has to overcome to move from one metastable state to another one and demonstrated that the Wenzel and the Cassie–Baxter model are unsuitable for interpreting certain experimental results [19]. On the other hand, as has been pointed out by Marmur and Bittoun, the contact angle predicted by the Wenzel and Cassie–Baxter models matches the experimental results in the case where the droplet is sufficiently large compared to the wavelength of the surface roughness or chemical inhomogeneity, i.e. within the limits of applicability of the models [20].

The Wenzel model is based on the assumption that the liquid has the ability to penetrate into the surface roughness and is always in contact with the substrate surface. According to this model the contact angle of liquid droplets on solid substrate is described by Wenzel's equation [13]:

$$\cos\theta_r = R\cos\theta_s \tag{1}$$

where θ_s and θ_r are the contact angles on perfectly smooth and rough surfaces of the same composition, respectively. R is the roughness factor defined as the ratio of actual (wetted) surface area to that of flat material (geometrical area). By increasing roughness of a hydrophilic surface, it should become more hydrophilic and a hydrophobic surface should become more hydrophobic according to the Wenzel model [21].

The Cassie–Baxter model treats the solid surface as microscopically mosaic composed of several components, each of which possesses their specific wetting properties. If, for instance, a surface is composed of two materials, where material 1 and 2 occupy the surface area fractions f_1 and f_2 and exhibit the contact angles θ_1 and θ_2, respectively, the contact angle of a liquid on such a surface is [14]:

$$\cos\theta = f_1\cos\theta_1 + f_2\cos\theta_2 \tag{2}$$

In the case when component 2 is air and, as the contact angle of air θ_2 is 180°, the contact angle of liquid on such a substrate is:

$$\cos\theta = f_1\cos\theta_1 - f_2 \tag{3}$$

The aforementioned phenomenon commonly occurs on rough surfaces, in particular hydrophobic ones, where air remains entrapped in the surface depressions. The entrapped air below the liquid reduces the interfacial contact area between the solid surface and the liquid and, therefore, causes an increase in contact angle [22].

Another phenomenon that should be taken into account when dealing with contact angle measurements is the contact angle hysteresis. On a real surface, which contains imperfections, the actual contact angle is not equal to the equilibrium contact angle (θ_{eq}) as defined by the Young equation [23]. The observed contact angle is different for a liquid droplet advancing on a dry surface (advancing contact angle, θ_{adv}) or receding on a previously wetted surface (receding contact angle, θ_{rec}) [24–26]. The difference between the advancing and receding contact angles is the contact angle hysteresis. Any deviation from the ideal surface condition can cause the contact angle hysteresis, for instance, chemical heterogeneities of the surface or surface roughness or local defects [27]. Therefore, measurement of both advancing and receding angles is necessary

to characterize a surface [23]. In many cases, due to small size of droplets commonly used in experiments, evaporation of a sessile droplet on the surface provides a convenient receding rate to perform the measurements (see, for instance [28]) and was also employed in the present paper. During the initial stages of evaporation of a sessile drop, the wetting diameter stays constant, and the contact angle and height of the droplet decrease constantly. It means that the three-phase contact line is pinned to the surface. At a certain point, the three-phase contact line is de-pinned and the wetting diameter and drop height start to decrease with a more-or-less constant contact angle. This constant contact angle is commonly taken as the receding contact angle (θ_{rec}). Finally, in the last stage, the contact angle, drop height and the wetting diameter are decreased until the droplet disappears [29–31].

Shanahan and Bourgès-Monnier observed that on rough surfaces the three-phase contact line remains pinned after the initial stage [30]. This means that the subsequent stage, where the contact angle of a sessile droplet is constant, does not exist on rough surfaces. They have also found that it is not possible to introduce a specific value of a receding contact angle due to the constant decrease of the contact angle and height of droplet till the moment of total evaporation of the droplet. This phenomenon has been also observed on aluminium and steel surfaces by Bormashenko et al. [28]. Besides the surface roughness and its effect on the contact angle and wettability, the other effective parameter of wettability is surface chemistry. Solid surface properties can be tailored by coating the surfaces with a material with a different surface energy. For instance, to make a surface hydrophobic, it can be covered by low surface-energy materials in order to decrease water attraction toward the surface [4,32,33]. Even coating with a monolayer of molecules can be sufficient to obtain the required hydrophobic or hydrophilic characteristics [34]. A relatively recent approach, so called molecular vapour deposition, relies on gas-phase deposition of a self-assembled monolayer of surface-modifying molecules. Using this method, extremely thin and uniform layers of, e.g., silane molecules can be created on glass, aluminium oxide as well as many other oxide surfaces. The process is commonly carried out in vacuum to prevent contamination of the surface and minimise unwanted reactions between the surface-modifying molecules [35]. There are also other methods reported in literature to obtain superhydrophobic surfaces on aluminium using silane chemistry. For example, Saleema et al. have introduced a one-step process to make a superhyrdrophobic aluminium alloy surface by immersing aluminium alloy substrates in a solution containing fluoroalkyl-silane (FAS-17) molecules as well as NaOH as an etchant to induce micro roughness of the surface [36].

Another approach to modifying solid surface properties involves grafting of a dense polymer brush layer covalently attached to the surface. For example, a surface can be made more hydrophilic by forming a layer of hyperbranched polyethylene glycol (PEG) on the surface. This can be done by *in situ* polymerization (synthesis of the polymer directly on the surface—"grafting from") of glycidol on the surface of aluminium with a native aluminium oxide layer. One method of *in situ* polymerization is a surface initiated, anionic, ring-opening polymerization proposed by Khan and Huck, 2003 for modification of glass surfaces [37,38]. In this method the polymerization is initiated on the surface and then continues forming a polymer brush on the surface until the monomer is used up [35]. In the present paper we adapted this method to form a dense hyperbranched PEG layer on aluminium surfaces. Moreover, we demonstrated that the surface of hyperbranched PEG can be further modified (e.g., rendered hydrophobic) using molecular vapour deposition of silanes, which, to our knowledge, has not been demonstrated elsewhere.

In the present work, we applied the aforementioned techniques of surface modification to three different real-life aluminium