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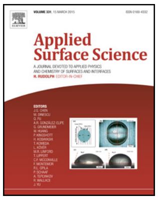

Anisotropic wetting characteristics versus roughness on machined surfaces of hydrophilic and hydrophobic materials

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ABSTRACT

Anisotropic wetting of machined surfaces is widely applied in industries which can be greatly affected by roughness and solid's chemical properties. However, there has not been much work on it. A free-energy thermodynamic model is presented by analyzing geometry morphology of machined surfaces (2-D model surfaces), which demonstrates the influence of roughness on anisotropic wetting. It can be concluded that the energy barrier is one of the main reasons for the anisotropic wetting existing in the direction perpendicular to the lay. In addition, experiments in investigating anisotropic wetting, which was characterized by the static contact angle and droplet's distortion, were performed on machined surfaces with different roughness on hydrophilic and hydrophobic materials. The droplet's anisotropy found on machined surfaces increased with mean slope of roughness profile *Kr*. It indicates that roughness on anisotropic wetting on hydrophilic materials has a stronger effect than that on hydrophobic materials. Furthermore, the contact angles predicted by the model are basically consistent with the experimentally ones.

1. Introduction

Wetting phenomenon occurs when a solid–gas interface turns into a solid–liquid interface on a solid surface [1]. It is a critical issue in controlling the wettability of solid materials in surface engineering, including oil recovery, lubrication, coating, sealing, printing and liquid adhesion [2–7]. For example, the flange surfaces is usually designed and processed to the expected spiral lay so as to obtain strong anisotropic wettability, which performs a better sealing effect. For ideal solid surfaces which are perfectly smooth and chemically homogeneous, the wetting characteristics are defined as a function of surfaces tension (interfacial free energy), which was studied by Young in 1805 [8]. The three-phase contact line (TPCL) of a droplet on ideal solid surfaces is circular. However, most of the surfaces are anisotropic [9]. A droplet can be distorted by geometrically anisotropic structure of the surface. Therefore, the static contact angle differs along the TPCL. Some researchers addressed the wetting characteristic as "anisotropic wetting", as opposed to the isotropic wetting [10–14]. Due to the capacity of restricting liquids to flow toward desired direction, the anisotropic wetting has attracted remarkable attentions on microfluidic devices [15–18]. Wang et al. [19] developed a one-way valve for microfluidic systems based on the array of Janus Si pillars with anisotropic surface wetting behavior. It has been proved that anisotropic wetting can be achieved by spatial gradients (surface chemistry, morphology) or asymmetric asperities through experiments and numerical analysis [20,21]. Zhao et al. [22] reported the effect of roughness on anisotropic wetting on submicrometer-scale periodic structures consisting of parallel grooves by laser interference. Li et al. [23] built a 3-D thermodynamic methodology to investigate anisotropic wetting on surfaces with micrometer-scale parallel grooves. Morita et al. [24] studied the anisotropic wetting on the line-patterned surface of fluoroalkylsilane monolayers with liquidphilic/liquidphobic area. Nevertheless, the former work mainly focused on micropatterned surfaces, and there have not been many studies on machined surfaces which have been widely applied. Machined surfaces present physical surface roughness, non-uniformity, and chemical heterogeneity, which differ from

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micropatterned surfaces. Kubiak et al. [25,26] accomplished a series of researches on wetting characteristics of machined surfaces. They presented the relationships between roughness parameters and the contact angle of a droplet on machined surfaces on hydrophilic materials by experiments in 2009. Then they proposed experiments and numerical analysis to investigate the dynamics of contact line motion during the wetting of rough surfaces and its correlation with topographical surface parameters in 2011 [27]. Although they studied the influence of roughness on wetting on machined surfaces, they did not analyze the effect on hydrophobic materials and the phenomenon of anisotropic wetting on such surfaces.

In this paper, we built a thermodynamic model to demonstrate the influence of roughness on anisotropic wetting by analyzing geometry morphology of machined surfaces (2-D model surfaces). We also designed experiments on machined surfaces with a wide range of roughness of hydrophilic and hydrophobic materials to investigate anisotropic wetting characterized by the static contact angle and droplet's distortion. Furthermore, we discuss the effect of roughness on anisotropic wetting characteristics on machined surfaces with two materials and the mechanism through the comparison between theoretical analysis and experimental investigation.

2. Modeling of roughness effect on anisotropic wetting

It is necessary to analyze the surface morphology and the wetting process on machined surfaces for a better understanding of roughness effect on the anisotropic wetting. 2-D surface morphology in the simplified model can be separated into sine wave, square wave and triangular wave on machined surfaces. The most common morphology simplified model of machined surfaces is triangular according to relative researches in actual morphology by different manufacturing methods, materials and surface treatment processes [28–30]. Hence, the surface profile with triangular wave is considered in this paper.

The TPCL of a droplet on machined surfaces starts from a point, and then it moves forward gradually to keep the minimum of the overall free energy. When the TPCL moves in the direction perpendicular to the lay, the droplet needs to overcome the energy barrier due to the existence of groove. Not until the free energy of the system is smaller than the energy barrier does the position of TPCL stabilize. The related contact angle $\theta_{\|}$ can be observed from the direction parallel to the lay, which is similar to advancing contact angle θ_A in contact angle hysteresis. When moving in the direction parallel to the lay, the TPCL spreads forward owing to the existence of capillary force instead of the energy barrier. The related contact angle $\theta_{\perp}$ can be observed from the direction perpendicular to the lay, which is between receding contact angle θ_R and intrinsic contact angle θ_s.

A thermodynamic model is developed on the 2-D surface with triangular wave based on above analysis. It demonstrates the change of the free energy is a function of the instantaneous contact angle during the movement of TPCL along with the direction perpendicular to the lay. Schematic of a droplet on machined surfaces with isosceles triangular wave shape on cross section is shown in Fig. 1(a). It is known that a droplet on rough surfaces may exhibit either of two wetting states: noncomposite state (Wenzel state [31]) or composite state (Cassie-Baxter state [32]), which depends on whether the droplet completely penetrates into the grooves, as shown in Fig. 1(b). It needs to be settled that how deep the liquid penetrates into grooves if a composite state is formed. If the effect of gravity can be ignored, capillary force will be the main driving factor in whether the liquid can penetrate inside grooves. If the capillary force (*Fc*) concave menisci are formed in grooves, *Fc* will drive the liquid to fill the grooves until it is completely filled. If the convex menisci are formed in grooves, *Fc* will drive the liquid to move out of the grooves [33]. Ideally, the droplet in the noncomposite state completely penetrates into grooves and the droplet in the composite state do not penetrates into grooves. For the composite state, the droplet basically exhibits an isotropic wetting behavior through the numerical analysis [23]. Hence, only the noncomposite state could be studied in this paper.

The droplet volume is 5 ± 0.1 μl which is so small that the effects of gravity can be ignored. We assume the droplet's profile is circle and the drop size is much larger than the feature size of surface lay. In such a system, we set that the instantaneous contact angle is 90° as the reference state, where $y = 0$ (point B), as shown in Fig. 1(c). Combined with the analysis by Long et al. [34], total free energy change (ΔG) of the three-phase contact point from B to C can be represented as

$$\Delta G_{B\to C} = -L\gamma_{\mathrm{lg}}\left(\cos\theta_s \frac{y}{\cos\alpha} + \sqrt{(H_0 - z(y))^2 + y^2} - H_0\right) \tag{1}$$

where L is the length of TPCL in the x direction; y is the horizontal projection of the distance that the TPCL has moved across; H_0 is the initial length of the liquid front; γ_{lg} is interfacial tension of liquid–gas; θ_s is intrinsic contact angle defined by Yong's equation [8]; $z(y)$ is the height of the three-phase contact point; and α is the geometric angle of micropatterned surfaces.

According to ISO 4287, the mean height of profile elements of the assessed profile R_c on machined surfaces represents column height on micropatterned surfaces [35]. Similarly, the mean width of profile elements of the assessed profile R_{sm} on machined surface stands for column width on micropatterned surfaces. In this paper, $z(y)$ in a single cycle can be expressed as

$$z(y) = \begin{cases} \dfrac{2R_c}{R_{sm}} y & 0 \le y \le \dfrac{R_{sm}}{2} \\ \dfrac{2R_c}{R_{sm}}(R_{sm} - y) & \dfrac{R_{sm}}{2} \le y \le R_{sm} \end{cases} \tag{2}$$

On the basis of Eq. (2), α can be calculated by

$$\alpha = \arctan\frac{2R_c}{R_{sm}} \tag{3}$$

Through the geometrical analysis, the relationship between the motion of TPCL and the instantaneous contact angle is expressed as

$$\tan\,\theta = \frac{H_0 - z(y)}{y} \tag{4}$$

Based on the analysis of Eq. (1), we can find out that L and γ_{lg} have no effect on the analysis of $\Delta G_{B\to C}$. By normalizing of Eq. (1), the following equation can thus be obtained

$$\Delta F = \sqrt{(H_0 - z(y))^2 + y^2} - H_0 - \cos\,\theta_s \frac{y}{\cos\alpha} \tag{5}$$

3. Experiments of roughness and contact angle measurement

3.1. Sample preparation

Materials can be categorized into hydrophilic materials and hydrophobic materials, which are distinguished by the size of its θ_s. The hydrophilic materials' θ_s is less than 90°, while the hydrophobic materials' θ_s is bigger than 90°.

Aluminum alloy AA6061-T651 (hydrophilic material) and nylon GF30 (hydrophobic material) were selected to evaluate the influences of intrinsic wettability on anisotropic wetting. Ten samples in each material were cut into a uniform size of 20 mm × 10 mm × 4 mm, with one surface polished by different grit sandpaper (16, 60, 100, 200, 400, 800, 2000, 3000, 5000 and 8000) in a consistent direction. A wide range of roughness R_c = 0.1–25 μm on surfaces with parallel lay can be obtained. According to ISO 1302,