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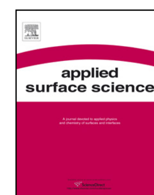

Fabrication of high wettability gradient on copper substrate

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ABSTRACT

Copper is one of the most widely used materials in condensation heat transfer. Recently there has been great interest in improving the condensation heat transfer efficiency through copper surface modification. In this study, we describe the fabrication processes of how copper surfaces were modified to be superhydrophilic (CA ≤ 10°) and superhydrophobic (CA > 150°) by means of H_2O_2 immersion and fluorination with Teflon. The wettability gradient of copper surfaces with contact angles (CA) changing from superhydrophilic to superhydrophobic are also demonstrated. Unlike previous studies on gradient surfaces in which the wettability gradient is controlled either non-precisely or entirely uncontrolled, in this study, the contact angles along wettability gradient copper surfaces vary with a precisely designed gradient. It is demonstrated that a high wettability gradient copper surface can be successfully fabricated using photolithography to define the area ratios between superhydrophilic and superhydrophobic patterns within a short distance. The fabricated wettability gradient of copper surfaces is expected to be able to enhance the condensation heat transfer efficiency.

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1. Introduction

In recent decades, surface engineering researchers have been highly interested in surface wettability. Varieties of surface modification methods have been developed for making the surface either hydrophobic (CA ≥ 90°) or hydrophilic (CA < 90°). Recently, superhydrophobic (CA ≥ 150°) and superhydrophilic surface (CA ≤ 10°) modifications have been demonstrated [1–9]. Many surface modification methods have been proposed to modify materials such as silicon [10–12], glass [13–15], aluminum [1,16–21], copper [1–9,22–35], gold [36], magnesium [37] and alloy substrates [18,38]. The relevant applications of surface modification include self-cleaning [39,40], anti-icing [17–21], drag reduction [5], chemical corrosion resistance enhancement [24,37] and others. Usually, a hydrophobic surface has properties that keep the surface clean, which allows some exterior-induced surface failure to be minimized [24]. For example, Kulinich and Farzaneh [20] showed that silane or TiO_2-copolymer compound can be used to coat an aluminum surface to form a hydrophobic surface. The results proved that glazed ice deposited on a fabricated hydrophobic aluminum alloy surface can be more easily removed than ice deposited on a polished aluminum surface. Wang et al. [37] fabricated a flower-like superhydrophobic film on a pure magnesium surface. Their experiment revealed that the electron transfer resistance of the superhydrophobic surface was increased about 4 times more than a bare magnesium surface in a 0.1 M NaCl solution. Shirtcliffe et al. [2] have produced rough and patterned copper surfaces using etching, coating with a fluorocarbon agent and electro-deposition. The surface roughness can be varied in a well-controlled manner, and its contact angle can be increased up to 160°. Qian and Shen [1] used “Livingstone’s dislocation-selective etchant” to etch the dislocation sites in the grains of polycrystalline copper substrate, and then proceeded fluorination on the etched copper substrate with the water contact angle reaching as high as 153°. Guo et al. [24] fabricated tri-basic copper sulfate film ($CuSO_4{\cdot}3Cu(OH)H_2O$) or Cu_2O film on a copper surface using copper sulfate solutions. They modified copper sulfate and Cu_2O film surfaces by spin-coating poly(dimethysiloxane) vinyl terminated (PDMSVT) on the films to form a superhydrophobic surface. Not only was a contact angle of 170° obtained along with a sliding angle (SA) lower than 5° on modified film surfaces, but also the modified surfaces possessed better chemical resistance within wider pH ranges of corrosive chemical solutions. Pan et al. [26] produced cupric hydroxide nanowires on copper substrate via solution-immersion. They further modified the nanowires on copper substrate with dodecanoic acid to form a self-assembled monolayer of copper carboxylate. A high contact angle of about 160° was obtained and the sliding angle was lower than 4°. After that development, Pan et al. [27,28] built boat-like and water-strider-like floating devices using fabricated copper plates,

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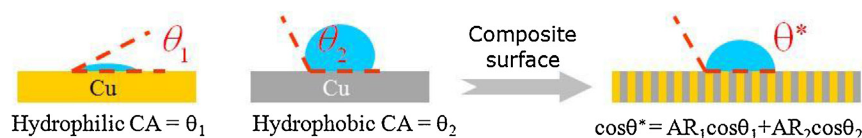

Fig. 1. Cassie–Baxter theory for the design of new composite surface with contact angle θ^* on a copper substrate [45].

and the results showed better loading capacity on water due to the superhydrophobic copper surface. Yao et al. [29] have produced the bio-inspired $Cu(OH)_2$ ribbed nano-needle arrays (RNNA) with hydrophobicized treatment on a copper substrate. The copper substrate was changed to a superhydrophobic surface, and the water contact angle was very stable in periodic compression/relaxation experiments.These results prove that water hardly penetrated and adhered to the RNNA.

While much research has been conducted on superhydrophobic copper surfaces, not so many studies have investigated the role of hydrophilic copper surfaces. Wang et al. [3] used the self-assembly monolayer of n-alkanoic acids with different chain-lengths to modify copper substrates, and they found that the surface become superhydrophilic if propanoic acid with carbon number 3 was used. Wu and Shi [4] employed phosphoric acid and oxygen to form copper phosphate dehydrate ($Cu_3(PO_4)_2{\cdot}2H_2O$) film on a copper substrate, which resulted in the CA of the film-coated copper substrate being approximately 2°. Chaudhary and Barshilia [7] utilized oxygen plasma treatment to transform a superhydrophobic $CuO/Cu(OH)_2$ surface into a superhydrophilic one, however the effects of the superhydrophilic surface were not long-lasting.

Several scientists have brought the fabrication methods for tunable wettability [3,6,7,14,36,41] into focus. Both superhydrophobicity and superhydrophilicity can be achieved on the same material surface. Interestingly, materials have been made that have a substrate surface which is hydrophobic on one side and hydrophilic on the other using the same fabrication process [14]. Thus, the variation of CAs with different distance intervals on a surface has been fabricated. This is the so-called gradient surface. For a material surface, this effect can be used to propel sessile water droplets from the hydrophobic into the hydrophilic side, so that the droplets can be pulled and pushed spontaneously when they cross the borders of the regions with wettability differences. Chaudhury and Whitesides [41] developed a surface with different surface free energies on an Si wafer using diffusion of decyltrichlorosilane ($Cl_3Si(CH_2)_9CH_3$) vapor. The silane diffusion generated a concentration gradient on the wafer surface. They demonstrated that a sessile droplet can move uphill along the inclined wafer due to the imbalance of surface tension acting on the droplet. Daniel et al. [42,43] used silanization diffusion to fabricate a gradient surface similar to the one described above on a silicon wafer. They analyzed the force acting on droplets due to surface wettability variation. Zhang et al. [44] manufactured a morphology gradient by changing polystyrene (PS) microsphere topography in a gradual temperature field. The CAs of sessile water droplets changed from 88.7° to 148.1° when the distance on the film surface was extended from the heated side to the unheated side in sequence. Yu et al. [36] employed a self-assembly monolayer of thiol molecules on rough gold surfaces with controlled immersion time. The CAs along the gradient surface ranged from superhydrophilicity (CA < 10°) to superhydrophobicity (CA = 156.4°). Recently, our research team has used photolithography to define patterns on both silicon and copper substrates to fabricate gradient surfaces with thiol-coating [45] and chemical etching [46] methods. In this paper, the means by which a copper gradient surface can be fabricated is demonstrated since copper is a widely used material in heat transfer applications [25,31,32]. Superhydrophilic and superhydrophobic surface modification methods for a copper substrate will be described first. Cassie–Baxter theory is applied for the design of a copper gradient surface, as shown in Fig. 1. Fig. 1 illustrates that one can precisely control the contact angle of a surface by defining the area ratio between superhydrophobic and superhydrophilic regions. Using a photolithography fabrication process, the wettability gradient on copper substrates is verified at the end of the paper. During each fabrication process, copper surfaces are investigated using SEM, XPS and CA measurement instruments.

2. Experimental process

2.1. Copper substrate modification

Fig. 2 shows the experiment processes for surface modification of copper substrates. They include the following steps:

2.1.1. Copper substrate cleaning

Initially, 60 mm × 43 mm × 3 mm copper plates (purity 99.9%) were immersed in a 15 wt% nitric acid (HNO_3) solution with appropriate stirring for 15 min to remove the native oxide on the copper substrate and remove the impurities [1]. This cleaning method is also called “chemical polishing” since copper oxide and impurities can be removed efficiently using HNO_3. After cleaning, the cleaned copper substrates were washed with deionized water, blown dry with air, and heated at 60 °C on a hot plate for at least 10 min.

2.1.2. Superhydrophilic copper surface

After the chemical cleaning, the cleaned copper substrates were immersed in 30 wt% hydrogen peroxide (H_2O_2) aqueous solution with stirring [25]. During this immersion process (see Ref. [25]. for a full description of the chemical reaction), cupric oxide (CuO) film appeared on the copper surface. After H_2O_2-immersion, the copper substrates were rinsed with deionized water, blown dry with air, and heated on a hot plate at 60 °C for 10 min, after which the fabrication of superhydrophilic copper substrate was complete.

2.1.3. Superhydrophobic copper substrate

At the start of the procedure, a 1 wt% Teflon solution was prepared by dipping Teflon AF1600 (Dupont, U.S.A.) and FC-770 fluorinert (3 M, U.S.A.) liquid. Next, the superhydrophilic copper substrates were spin-coated with the prepared Teflon solution. The spin coating speed was 4000 rpm, and the spin time was 30 s after

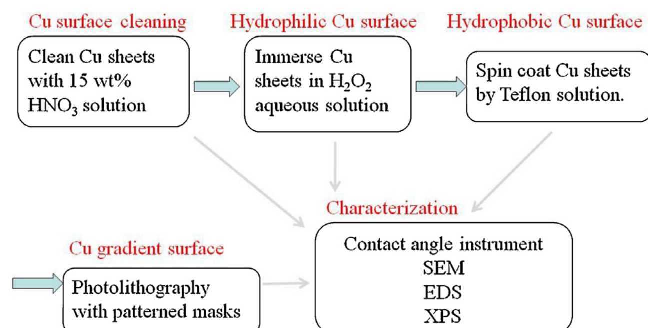

Fig. 2. Process flow chart for surface modification and fabrication of wettability gradient of copper substrate.

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