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Full Length Article

Nanosecond laser ablated copper superhydrophobic surface with tunable ultrahigh adhesion and its renewability with low temperature annealing

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ABSTRACT

Recently, metallic superhydrophobic surfaces with ultrahigh adhesion have got plentiful attention on account of their significance in scientific researches and industrial applications like droplet transport, drug delivery and novel microfluidic devices. However, the long lead time and transience hindered its in-depth development and industrial application. In this work, nanosecond laser ablation was carried out to construct grid of micro-grooves on copper surface, whereafter, by applying fast ethanol assisted low-temperature annealing, we obtained surface with superhydrophobicity and ultrahigh adhesion within hours. And the ultrahigh adhesion force was found tunable by varying the groove spacing. Using ultrasonic cleaning as the simulation of natural wear and tear in service, the renewability of superhydrophobicity was also investigated, and the result shows that the contact angle can rehabilitate promptly by the processing of ethanol assisted low-temperature annealing, which gives a promising fast and cheap circuitous strategy to realize the long wish durable metallic superhydrophobic surfaces in practical applications.

1. Introduction

In nature, the lotus leaf, with an ultrahigh contact angle (CA) but ultralow water adhesion, is demonstrated as the ideal water-repellent superhydrophobic surface [1,2]. Water droplets on such surfaces can easily roll off to remove loosely adherent dirt particles and debris from the surfaces while the substrate**s are** slightly tilted [1]. By contrast, another kind of sticky superhydrophobic surface with ultrahigh water adhesion like a rose petal has also been reported [3], which has the characteristic that water droplet is stuck and will not roll off even with the surface upside down. By mimicking nature in a general way rather than a specific one, a recent surge of research on manmade metallic superhydrophobic surfaces with ultrahigh adhesion has been conducted in order to benefit the biological, nautical, mechanical, and medical fields [4–8].

Although there have been many methods for fabrication of the metallic superhydrophobic surfaces, such as one-step solution-immersion [9], electroless galvanic deposition [10] and top-down fabrication method [11], laser ablation plays a vital role in preparation of the various surface micro/nanostructures on metallic substrate [12–15]. However, subsequent chemical coating treatments are needed in order to lower the surface energy of the fresh ablated metal surface and create the metallic superhydrophobic surface [16–19]. In recent years, many efforts are made on developing one-step fabrication of **the** metal**lic** superhydrophobic surface with only laser ablation **but** no additional coating step [20–24]. Copper alloys are reported to show their superhydrophilic nature at first after being laser beam machined and finally generate a superhydrophobic metal oxide coating after being exposed in air for several weeks to even several months [14,25,26]. Unfortunately, the metal oxide coating can be easily worn out in service. Some solutions including spontaneous wrinkling of Teflon AF, thermal evaporation and two-step anodization have been proposed, but the lack of massive productivity hindered their real extensive application in industry [27,28]. Fortunately, F.M. Chang has recently introduced an ethanol assisted low-temperature annealing method which could cut down the time to several hours for fresh textured brass surface to transfer from superhydrophilic to superhydrophobic [29].

In this work, superhydrophobic hierarchical micro/nano textures on copper surface were fabricated with nanosecond laser ablation and ethanol assisted low-temperature annealing. The tunable ultrahigh adhesion property **wa**s obtained by adjusting the spacing of grid micro-grooves. And a simple, precise method was designed for measuring the accurate value of the corresponding adhesion force. Moreover, we have found that the CA could reha-

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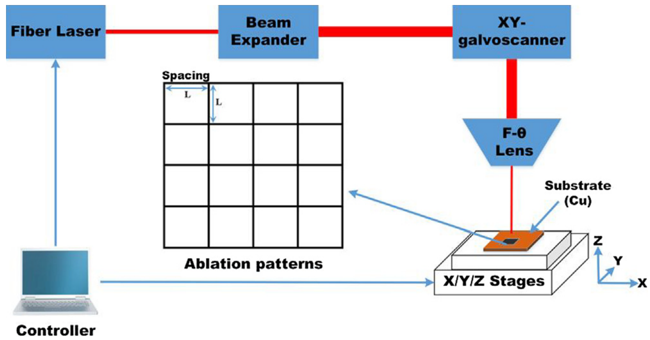

Fig. 1. Schematic images of laser micro-machining system and the ablation patterns.

bilitate promptly by adopting low-temperature annealing with ethanol when the superhydrophobicity was worn out in service. Herein, due to its superiority of simplicity and celerity, this rapid renewable method may be a circuitous strategy to figure out the weakness of instability and transience of superhydrophobic surfaces.

2. Materials and methods

Polished pure copper plates (99.99 wt.%) are used as the substrate with the size of $10 \times 10 \times 1\,mm^3$. A nanosecond laser micromachining system consists of the pulsed fiber laser, beam expander, X-Y galvo-scanner, and *F-theta* lens with the focal length of 250 mm is used for precision ablating grid groove patterns on copper surfaces, **as** shown in Fig. 1. The output characteristics of the nanosecond fiber laser have the average power of 5 W, wavelength of 1060 nm and pulse width of 25 ns. The diameter of the focused laser spot is 30 μm. Various laser scanning spacings L of 50, 100, 150, 200, 250 and 300 μm are set to study the influence of contact area between water drops and substrate on adhesion. All the experiments and tests are carried out in the laboratory room with well controlled temperature and humidity, where the temperature and relative humidity are 25 °C and 65%, respectively, and the dust level approximates to 10^5 (US FED STD 209E).

During the nanosecond laser ablation of copper in air, copper atoms in molten pool can easily combine with the oxygen in air to form CuO which is hydrophilic and unstable [29]. Then, the laser ablated groove patterns are post processed with ethanol assisted low-temperature annealing (110 °C) for 2.5 h in air for accelerating the transition from CuO to Cu_2O and the formation of hydrophobic organics matter on the patterns. The chemical reactions are represented by Eq. (1) [30].

$$12CuO + CH_3CH_2OH \rightarrow 6Cu_2O + 2CO_2 + 3H_2O \quad (1)$$

$$6Cu_2O + CH_3CH_2OH \rightarrow 12Cu + 2CO_2 + 3H_2O$$

The effects of low-temperature annealing with/without ethanol are studied. In order to study the renewability of superhydrophobicity, ultrasonic cleaning is used to simulate the natural wear and tear on superhydrophobic surfaces in service. The surface characteristics are evaluated by SEM (FEI, QUANTA 200F), Laser Scanning Confocal Microscopy (OLYMPUS, OSL 4100), and EDS (EDAX, Octane Pro). The CAs are measured five times at each tested area with 4 μL volume of water by video optic CA instrument (Dataphysics, OCA15EC).

There are only a few methods for estimating the value of water adhesion force on substrate surface, such as slide angle [31] (obviously not suitable for the situation of ultrahigh adhesion), high-sensitivity micro electromechanical balance system [4] (expensive calibrated apparatus required), and the theoretical modelling and calculation [32] (round-about way). Thus, a novel equivalent inertial force (EIF) method for straightforward measuring the specific magnitude of the ultrahigh adhesion is employed in this work. Firstly, the mass of the superhydrophobic Cu substrate m_{cu} and the water droplet m_{wd} are successively obtained by electronic balance. Then the specimen with water droplet is placed and fixed to a servo motor driven linear slide block that can precisely apply either a horizontal impulsive force *F* from the left side or a rightward acceleration *a* to the specimen. The water droplet will get a relative motion to the left due to the inertia correspondingly, which is recorded by the high speed camera. Therefore, the water adhesion force *f* is equivalent to the minimum inertial force of the droplet, namely the maximum static friction force, which just initiates the droplet motion. The water adhesion force *f* can be calculated by the Eq. (2).

$$F - f = m_{cu} \cdot a \text{ and } f = m_{wd} \cdot a \quad (2)$$

3. Results and discussion

The surface morphologies with micro-grooves after laser ablation and ethanol assisted low-temperature annealing are shown in Fig. 2. Micro-grooves are fabricated by the focused nanosecond laser beam scanning on the copper surface, where the induced melting pool expands and bursts out of the focal spot by which result the rough surface textures. Superhydrophobicity is achieved in short time using the ethanol assisted low-temperature annealing which not only transforms the initially hydrophilic CuO after laser ablation to hydrophobic Cu_2O, but also forms abundant hydrophobic organics adherent to the rough textures. The large burrs covered with micro/nano particles and organics act as hierarchical pillar structures that can suspend water droplets and minimize the contact area with the water droplets which enhance the super-

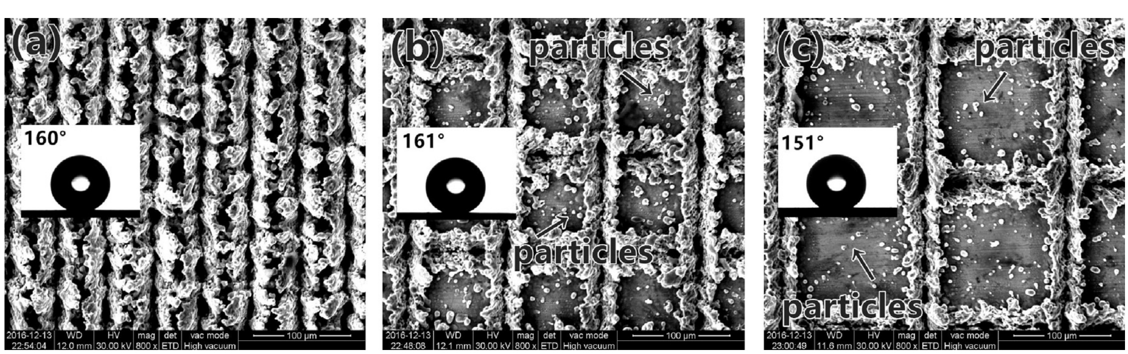

Fig. 2. Surface morphologies and CAs of the laser ablated copper plate after ethanol assisted low-temperature annealing, (a) spacing L is 50 μm; (b) spacing L is 100 μm; (**c**) spacing L is 150 μm.