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Selective laser melting of ink-printed (SLM-IP) copper (Cu) nanoparticles (NPs) for facile controllable fabrication of super-hydrophobic surface

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A method of selective laser melting of ink-printed (SLM-IP) Cu nanoparticles (NPs) for facile controllable fabrication of super-hydrophobic surface structure is reported in this paper. A hierarchical structure composed of micro/nano-scaling copper (Cu) meshing texture was obtained by SLM-IP NPs. The meshing sizes are varied from 0.05 mm to 0.23 mm. By applying the analysis of SEM, XRD, Confocal Laser Scanning Microscope (CLSM), apparent contact angle (CA) measurement and water droplet dynamic behavior analysis, the effects of both mesh size and nano-sized structures on the hydrophobicity were discussed. The results show that the mesh surface fabricated by SLM-IP Cu NPs expresses an excellent super-hydrophobicity with a CA as high as 160° and sliding angle as low as 3.9° with a mesh grid size of 0.05 mm. An apparent CA model for double roughness structure was used to predict the CAs. The calculated CAs show a good agreement with the measurements when the mesh grid size is far less than the radius of water drop. SLM-IP Cu NPs takes the advantages of additive manufacturing and provides a flexible way for the functional surface structure fabrication.

1. Introduction

Wettability that plays an important role in the industrial and daily life is a fundamental feature of solid surface [1–3]. Over the past few decades, achieving the super-hydrophobic surfaces with water contact angle (CA) greater than 150° and sliding angle (SA) less than 10° has aroused great interest because of its importance in potential practical applications, such as self-cleaning, lubricity, micro-fluidic devices and resisting water coalescence [4–6]. As can be known, to fabricate a hydrophobic/super-hydrophobic surface, two key factors of surface free energy and surface roughness have to be considered [7]. Up to now, numerous methods have been developed for the preparation of super-hydrophobic surface, such as sol-gel processing [8,9], electrochemical deposition [10,11], chemical etching [12,13], self-assembly technology [14–16], spraying method [17,18] as well as hybrid method [19] (i.e. combination mechanical roughening with chemical etching), Response to [1.2]: laser-induced periodic surface structures (LIPSS) [20,21] and so on. Response to [1.2]: Laser is a typical technique for hydrophobic surface fabrication like LIPSS [22] and laser ablation [23]. The methods are all based on the principle of subtraction, we would like to develop an additive method of hydrophobic surface fabrication by laser. In order to create a super-hydrophobic surface, a common two-step process has been commonly utilized, one usually fabricates a rough surface with interesting structures (i.e. fractal structure, lotus leaf structure) and then the surface is modified with materials of low surface free energy (such as organic modification agent, fluorinated or silicon compounds) [24].

However, Response to [1.2]: either special equipment, complex process control, expensive materials or extreme conditions are required in many above mentioned cases. Therefore, it could be desirable to develop a novel simple and facile way of fabricating super-hydrophobic surfaces on the various substrates.

As a vital element for the super-hydrophobic surface fabrication, the nano-sized structure is difficult to control and construct. So we would like to introduce the nano-sized particles to work as the original material to be sintered. Recently, researchers use inks with Cu oxide or Cu complex to fabricate electrode and conductive circuit on polymer films [25–28]. Cu oxide or Cu complex were synthesized and dissolved in an alcohol solvent with the dispersing agent [28–30]. Inspired by the formation of copper electrode, we have demonstrated a novel process of SLM-IP Cu NPs for the fabrication of friction-reducing surface texture on the metallic surface in ambient condition in our previous work [31]. The method of SLM-IP Cu NPs is based on the principle of additive manufacturing, which has high process flexibility, high material utilization for metal component manufacturing.

In this paper, we would like to apply the method of SLM-IP NPs to

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fabricate the super-hydrophobic surface structures. The structures of squared mesh were prepared with the size varied from 0.05 mm to 0.23 mm. Two processes of removing the unreacted ink were treated to indicate the function of hierarchical micro/nano structures to wettability. Contact angles (CAs), sliding angles (SAs) and dynamic behaviors of droplet on the surface were studied to evaluate the wettability of the prepared samples. Scribe-Grid Test and micro-hardness were carried out to evaluate the mechanical stability of surface materials based on the literatures methods [32–35]. The whole process was facile to execute, which makes it widely applicable, flexible and easy for large-area, complex component production.

2. Method and materials

2.1. Preparation of the materials

All materials were used as received. Cu NPs with the size of 70–100 nm were applied for SLM process in this work. Polyvinylpyrrolidone (PVP, MW 10000) was adopted to stabilize the NPs in the solvent mixture. ANSI 304 stainless steel plate with a thickness of 2 mm was utilized as the substrate. The surface modification was conducted with 1H,1H,2H,2H-perfluoro-decyl-triethoxysilane (PFDTS, Sigma-Aldrich Co. LLC). Firstly, the organic solvent of PVP (20.2 wt%) and ethylene glycol (36.5 wt%) were produced to prevent the agglomeration and oxidation of Cu NPs during SLM. Then, the Cu NPs (43.3 wt%) were dispersed in the organic solvent and stirred by an ultrasonic vibration for 25 min.

2.2. SLM-IP Cu NPs process and experimental setup

The process of SLM-IP Cu NPs was introduced to fabricate the hydrophobic surface based on the principle of selective laser melting. The schematic of sample preparation is illustrated in Fig. 1.

Firstly, the Cu NPs solvent was ink-printed on the substrate. Then, the Cu NPs ink was selectively heated by a fiber laser(wavelength: 1070 nm) controlled by a galvanometer (focal length: 255 mm). Response to [1.3]: A collimated Gaussian profile laser beam with a diameter of 4.88 mm was expanded by a beam expander (6 ×). Then, the expanded beam was made incident into a galvanometric scanner through an aperture of 30 mm. The galvanometric scanner combined with an f-theta lens (focal length 255 mm) was used to steer the laser beam and maintain a uniform spot size on the scanning surface. The calculated laser spot size was ~20 μm. The detailed description of the experimental setup was presented in our previous work [31]. Textures of mesh are designed and fabricated as the hydrophobic structure. The samples were treated with two different procedures to indicate the role of nano-sized structures to the wettability. One is merely rinsed the residual un-sintered ink slightly by deionized water (DI water) in ultrasonic bath (power: 160 W, frequency: 40 kHz) for 30 s, the other is rinsed in ultrasonic bath (power: 400 W, frequency: 40 kHz) for 20 min. Then the samples were modified by PFDTS to characterize the wettability of the structures.

2.3. Fabrication parameters and modification

Response to [1.3]: In SLM-IP Cu NPs process, the fabrication parameters were selected with a laser scanning velocity of 10 mm/s and laser power of 12 W. The texture surface modification was carried out by dipping the samples into an ethanol solution of 0.5 wt% PFDTS for 24 h at temperature of 30 °C, and followed by washing with ethanol and drying in an oven with 130 °C for 1 h.

2.4. Characterization and tests

The water CAs and SAs were measured with a water drop volume of 3 μL using an optical contact angle meter (Dataphysics-OCA20, made in Germany) at room temperature. The values reported in this paper are averages of five measurements made on different positions of the texture surface. SEM images were obtained on a scanning electron microscope (SEM, FEI, Quanta 200 FEG). The surface composition of surface structure was analyzed by X-ray diffractometer (XRD Rigaku D/Max-RB CuKa radiation). The height and morphology test was analyzed by confocal laser scanning microscope (CLSM, OLYMPUS, OLS-3000). The dynamic behavior of the water droplet dropped on the fabricated

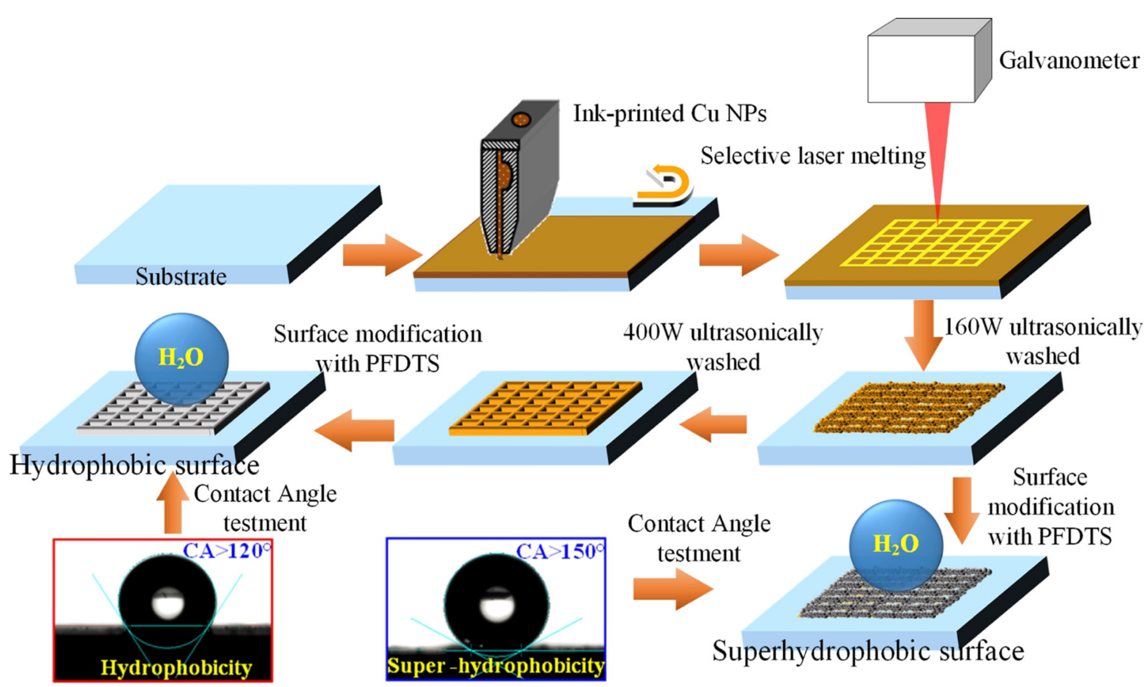

Fig. 1. Schematic of the sample preparation by SLM-IP Cu NPs: firstly, the solvent with Cu NPs is ink-printed on the substrate; secondly, the ink is scanned by a laser beam to form the structures of mesh; thirdly, the samples are rinsed in ultrasonic bath with a power of 160 W and 400 W respectively; finally, the wetting properties are tested after surface modification.