

Superhydrophilicity to superhydrophobicity transition of picosecond laser microstructured aluminum in ambient air



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ABSTRACT

Studies regarding the wettability transition of micro- and nano-structured metal surfaces over time are frequently reported, but there seems to be no generally accepted theory that explains this phenomenon. In this paper, we aim to clarify the mechanism underlying the transition of picosecond laser microstructured aluminum surfaces from a superhydrophilic nature to a superhydrophobic one under ambient conditions. The aluminum surface studied exhibited superhydrophilicity immediately after being irradiated by a picosecond laser. However, the contact angles on the surface increased over time, eventually becoming large enough to classify the surface as superhydrophobic. The storage conditions significantly affected this process. When the samples were stored in CO₂, O₂ and N₂ atmospheres, the wettability transition was restrained. However, the transition was accelerated in atmosphere that was rich with organic compounds. Moreover, the superhydrophobic surface could recover their original superhydrophilicity by low temperature annealing. A detailed XPS analysis indicated that this wettability transition process was mainly caused by the adsorption of organic compounds from the surrounding atmosphere onto the oxide surface.

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1. Introduction

Over the past few decades, many methods have been developed to fabricate metallic surfaces with special wettabilities because these surfaces are useful in several important applications such as anti-corrosion, oil–water separation, friction reduction, and liquid transportation [1]. Generally, metals and metal oxides tend to be hydrophilic owing to their high surface free energy [2]. Increasing the surface roughness of these materials further decreases the contact angle of water droplets on the surface. To obtain a hydrophobic metal or metal oxide surface, surface coatings are usually necessary for lowering the surface free energy.

Several studies have found that micro- and nano-structured metal oxide surfaces, which are initially hydrophilic, become hydrophobic and that some even become superhydrophobic in air with time [3–10]. Previously, this transition has been observed primarily for transition metal oxides, including the oxides of Cu [3–5], Fe [6], Ni [7], W [8], Ti [9] and Zn [10]. Moreover, the observed transition behavior is independent of the fabrication method. Micro- and nano-structures fabricated by methods such as thermal oxidation [11], laser nanostructuring [6], chemical vapor deposi-

tion [12] and plasma spray [13], for example, all show this transition behavior. Several mechanisms have been proposed to explain this phenomenon. Chang et al. [4] suggested that the change in the wettability of CuO nanowire films was attributed to the partial deoxidation of the topmost layer of the CuO wire surfaces into Cu₂O-like hydrophobic surfaces. Kietzig et al. [6] proposed the decomposition of CO₂ into carbon using active magnetite that was subjected to a laser nanostructuring process as a potential explanation for the observed wettability change. It can be seen that there is an obvious controversy about the mechanism of the wettability transition behavior.

In this paper, we studied the wettability transition of a picosecond laser micro-structured aluminum surface. Aluminum was chosen because its oxide is chemically stable in air; this inactivity avoids transition mechanisms that involve photocatalysis or the oxidation–reduction reaction. The picosecond laser micro-structured aluminum samples were stored in air, CO₂, O₂, and N₂ atmospheres and an atmosphere rich in organic compounds. We observed the wettability transition and analyzed their surface compositions to verify which component in air would be responsible for the wettability transition. Our results indicate that the adsorption of organic compounds from the air plays a key role in this process.

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2. Experimental section

2.1. Materials

Aluminum samples (99.9% purity) with a dimension of $10 \times 10 \times 2 \text{ mm}^3$ were mechanically polished to a mirror finish and cleaned ultrasonically with ethanol before laser treatment.

2.2. Laser irradiation

The as-prepared samples were irradiated with a linearly polarized Nd:YVO₄ picosecond laser with wavelength of 1064 nm, repetition rate of 101.8 kHz, and pulse width about 10 ps. A two mirror galvanometric scanner (hurrySCAN) with an F-Theta objective lens ($f = 100 \text{ mm}$) was used to focus and scan the laser beam in the x - y direction. The focused diameter of the Gaussian-profile laser beam at $1/e^2$ of its maximum intensity was approximately 25 μm . The laser processing experiments were performed in atmospheric environment under normal incidence of the laser beam. The laser scanning was performed line-by-line in the horizontal direction and then in the vertical direction. After irradiation, the samples were cleaned ultrasonically with ethanol and dried by compressed air came from a high purity cylinder.

2.3. Storage conditions

To investigate the transition mechanism, the laser structured samples were stored in various atmospheres, including CO₂, O₂ and N₂ atmospheres and an atmosphere rich in organic compounds. The device used for sample storage is shown in Fig. 1. The device was cleaned by ethanol and dried by compressed air before use. To create a CO₂, O₂ or N₂ atmosphere, an oil-free vacuum pump (avoiding the severe oil pollutions that are produced by common mechanical vacuum pumps) was used to evacuate the air in the transparent plastic container, and CO₂, O₂ or N₂ gas (99.999% purity) was flowed into the container from another valve at the same time. The pressure of the container was fixed at 50 kPa, and this process continued for 10 min to ensure that the environment was mainly composed of CO₂, O₂ or N₂. In the case of the organic-rich atmosphere, we placed 0.5 mL 4-Methyloctanoic acid (98%, J&K), which is naturally present in fruit and often be used as flavor additive for foods, in the 15 L container. All the containers were placed in our laboratory where our picosecond laser located, the temperature of the room was fixed at 25 °C.

2.4. Surface analysis

The morphologies of the surfaces were analyzed using a LEO-1530 scanning electron microscope (SEM), and topography measurements were taken using a SPM-9600 atomic force microscope (AFM) in contact mode and a 3D optical profilometer (MicroXAM-

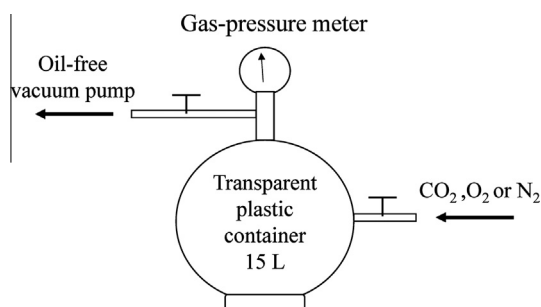


Fig. 1. Schematic diagram of the container used for sample storage.

3D, ADE technology) with a resolution of 1 nm in the vertical direction. X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical composition of the surfaces.

The wettability of the samples was evaluated by measuring the static contact angle (CA) using a video-based optical contact angle-measuring device (OCA 15 Plus from Data Physics Instruments) and the sessile drop technique in atmospheric environment. To avoid the surface pollution from the ambient environment during the CA measurement, two groups of samples were prepared for each condition. The first group samples were taken out from the container for CA measurement after being stored for 8 days. The second group samples were stored in the container for 30 days before the CA measurement. A 3 μL droplet of distilled deionized water was used for the CA measurement. The apparent CA of the water droplet on each sample surface was measured two times, and two samples were analyzed per group. Average CA value is reported in the text. All measurements were taken after the droplets stabilized (less than one minute after the water droplet reached the sample surface).

3. Results and discussion

3.1. Laser structured surfaces

Fig. 2 shows the aluminum surface after structuring using the picosecond laser under the laser fluence of 22.4 J/cm^2 , scanning speed of 100 mm/s and scanning interval of 30 μm . Because the laser fluence is high, its energy density is far beyond the ablation threshold, and the extra energy enables material removal from the surface. As a result, regular micro-pillars combined with micro-cavities were produced on the aluminum surface. In addition, some re-deposited molten metal and laser-induced nano-structures were found on these micro-structures. The average surface roughness (Ra) obtained in the 3D optical profilometer analysis was $5.237 \pm 0.536 \mu\text{m}$ (Fig. 2c). Fig. 2d shows the XPS spectra over the binding energy range from 69 to 90 eV of the aluminum surface after irradiation. Compared with that of the cleaned aluminum surface (being etched about 10 nm thick by argon ion to remove the natural oxide film), an oxidized Al peak about 74.2 eV binding energy (BE) only existed, which indicates that the surface was oxidized to form aluminum oxide [14]. The oxide film thickness should be more than 8 nm since the maximum penetration length of Al 2p photoelectrons in XPS measurement is 8 nm [15]. It is well known that aluminum is easy-oxide and its natural surface will be covered with a thin amorphous aluminum oxide film about 4 nm thick when exposed to air in very short time [16,17]. So the laser irradiation in fact increased the oxide film thickness.

As shown in Fig. 2e, this structured surface was initially superhydrophilic and had a contact angle of zero. Water droplets could spread quickly on the surface. The observed superhydrophilicity was attributed to the three-dimensional capillary effect [18]. However, when these samples were exposed to ambient air, the contact angle started to increase with time, reaching respectively to $96 \pm 3^\circ$ after 8 days, $136 \pm 4^\circ$ after 16 days, and $150 \pm 4^\circ$ after 30 days (Fig. 2f). The superhydrophilic surface became superhydrophobic in 30 days.

3.2. Surface wettability transitions in different atmospheres

To clarify the influence of the surrounding atmosphere on the wettability transition behavior, laser structured samples were kept in four different atmospheres, including CO₂, O₂ and N₂ atmospheres and an atmosphere rich in organic compounds immediately after the laser treatment. Fig. 3 shows the changes in the contact angle on these samples in 8 days and 30 days. The samples

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