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Reversibly switchable wettability between underwater superoleophobicity and oleophobicity of titanium surface via ethanol immersion and dark storage

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ABSTRACT

Herein, we report for the first time the use of ethanol for the switchable underwater wettability on a rough titanium dioxide (TiO_2) surface. The rough TiO_2 thin films on the titanium surfaces are fabricated by the high speed wire electrical discharge machining (HS-WEDM) processes, and the resultant surfaces show the switch between underwater superhydrophobicity and oleophobicity via ethanol immersion and dark storage. The underlying mechanism of the switch is depicted, and the result shows that during the ethanol immersion and dark storage, the change of hydroxyl groups leads to the switch. Considering that the use of ethanol is time-saving and low-cost, we anticipate that the use of ethanol will open up a new way of surface wettability change.

1. Introduction

Underwater superoleophobic surfaces, which display high oil contact angle (CA > 150°) and low oil sliding angle with different organic liquids in water [1], have recently attracted much attention due to their importance in various potential applications including self-cleaning [2], anti-platelet [3], oil droplet transportation [4] and oil/water separation [5,6]. Recently, smart interfaces of titanium dioxide (TiO_2) materials with tunable underwater-oil wettability are becoming a hot study because of their great value in potential applications such as anti-fouling, medical engineering, water industry components and so on, and experimental attempts have been made by researchers with the purpose of achieving the wettability. Miyake et al. reported the photoinduced underwater superoleophobicity of TiO_2 thin films on a glass slide prepared by a sol-gel method, and investigated the applicability of the TiO_2 mesh as an oil/water separation filter [7]. Guo et al. developed an underwater superoleophobic TiO_2 layer on fluorine-doped tin oxide substrate fabricated by a simple one-step hydrothermal method, and the layer can be reversibly switched between underwater oleophilicity and superoleophobicity by alternate ultraviolet (UV) irradiation and contamination treatment [8]. Chen et al. presented a one-step strategy for constructing a rough TiO_2 coating on a titanium (Ti) sheet formed by femtosecond laser irradiation [9]. As a result, a switchable underwater-oil wettability on the laser modified surface by alternation of UV irradiation and dark storage is achieved. These studies have all successfully demonstrated that UV irradiation could cause the conversion of TiO_2 layer. However, apart from the time-consuming and high-cost treatments with the UV techniques, it is still quite challengeable to deal with the complex shapes to achieve the switch. Therefore, a proper solution for the switchable underwater-oil wettability is highly expected to meet the requirements.

Herein, we present for the first time the use of ethanol for the switchable underwater wettability on a rough TiO_2 surface fabricated through the high speed wire electrical discharge machining (HS-WEDM) processes. HS-WEDM has the advantages of relative short process time and long working distance, which are suitable for low cost, high efficient and large-area 3D fabrication of microstructures on conductive materials. To the best of our knowledge, the reports about HS-WEDMed smart surfaces with switchable wetting are still limited until now.

2. Experiment

The rough TiO_2 layer was fabricated by a commercial HS-WEDM system (DK7732, China), and the details of the experimental setup are described in our previous work [10]. The pulse width was 12 μs, the wire speed was 50 Hz and the number of power tube was 3. To avoid the phenomenon of wire breaking in the machining process, the pulse width and pulse interval were fixed by a large ratio of 7:1. In the process of fabrication, molybdenum wire of 120 μm in diameter was loaded as an electrode, and aqueous solution of non-toxic line cut emulsion was used to improve the level of the processing technology. After machining, the fabricated surfaces were cleaned with acetone and distilled water to remove surface contamination using an ultrasonic cleaner.

The morphology and chemical composition of the surfaces were analyzed by scanning electron microscope (SEM, FEI Quanta 250, America), X-ray diffractometer system (XRD, D/Max-2500, Japan) and energy dispersive X-ray spectrometer (EDXS, X-Max, England). The CA values were measured with a contact angle analyzer (OCA20, Germany) by injecting 5 μL of liquid droplets, and the aver-

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age CA values were obtained at three different positions of the same sample. 1,2-dichloroethane ($(CH_2)_2Cl_2$, density = 1.25 g mL^{-1}, surface energy @25 °C = 31.86 mN m^{-1}) was employed to measure the oil wettability.

3. Results and discussion

Fig. 1 shows the SEM images of the polished and HS-WEDMed Ti surfaces and the CAs of water and oil droplets in an air system. As shown in Fig. 1a, the Ti surface before processing was relatively flat with few scratches generated by polishing, which was hydrophilic (67.1 ± 3.4°) and superoleophilic (6°). Correspondingly, as can be seen from the photograph (Fig. 1b), the HS-WEDMed Ti surface had rough microstructures including some craters and rice-shaped structures with the diameters ranged from 60 to 100 μm on the surface, and showed hydrophilicity (85.7 ± 3.1°) and superoleophilicity (0°). From the high magnification SEM image (Fig. 1c), it reveals that hierarchical structures existed due to aggregation of the rough TiO_2 layer.

Fig. 2a shows the X-ray diffraction pattern of the sample surfaces. For the fabricated Ti surface machined by HS-WEDM, there is no new peak comparing with the polished Ti surface. This disparity may be that the formed species by the HS-WEDM process are amorphous and cannot be detected by XRD. Figs. 2b and c show the EDXS spectra of the different surfaces were analyzed. Compared with the polished surfaces (Fig. 2b), elements O and C were present on the HS-WEDMed surface (Fig. 2c). The weight proportions of Ti decreased from 99.85% to 50.34%, while the weight proportions of oxygen and carbon increased to 35.36% and 9.23%, respectively. These results indicate that the fabricated Ti surface were oxidized, resulting in a rough TiO_2 layer on the surface. It has been recently demonstrated that WEDM machining formed TiO_2 during the formation of the rough microstructures [11].

We investigated the underwater-oil wettability of the HS-WEDMed surfaces. As shown in Fig. 3a, the oil CA to the HS-WEDMed surface was 80.5 ± 3.7° in water. However, after an ethanol immersion (5 s), the underwater oil CA of the surface was increased to 158.5 ± 1.8°, showing an interesting phenomenon on the underwater-oil wettability. More interestingly, the HS-WEDMed surface could recover underwater oleophobicity after keeping it in the dark for 2 days. Fig. 3b shows the photograph of an oil droplet on the polished Ti surface before and after the ethanol immersion in water. From it, we can see that the underwater oil CA of the polished surface increased from 132.1 ± 2.1 to 139 ± 1.7°, but still remained underwater oleophobicity. In addition, as shown in Fig. 3c, the HS-WEDMed surfaces were placed in water repeatedly several times to evaluate the durability of the switch. Hence, by employing ethanol to modify the HS-WEDMed Ti surface, we can achieve reversible underwater wettability between superoleophobicity and oleophobicity.

To study the effect of the parameters on the TiO_2 layer, the different pulse widths were used in the HS-WEDM process. Here, the wire speed (50 Hz) and the number of power tube (3) were fixed with the increase of pulse width (12, 24, and 48 μs). Fig. 4a shows O EDS maps of the HS-WEDMed Ti surfaces under the pulse widths of 12, 24, and 48 μs. The weight proportions of oxygen under the dif-

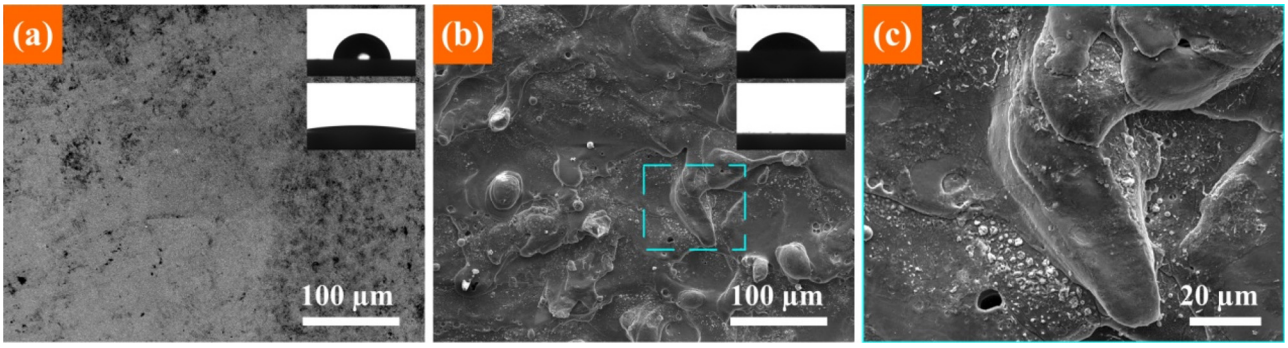

Fig. 1. SEM images of (a) polished and (b and c) HS-WEDMed Ti surfaces in low and high magnification, respectively. The insets (a and b) show the shape of water droplet (top) and oil droplet (bottom) on the surfaces.

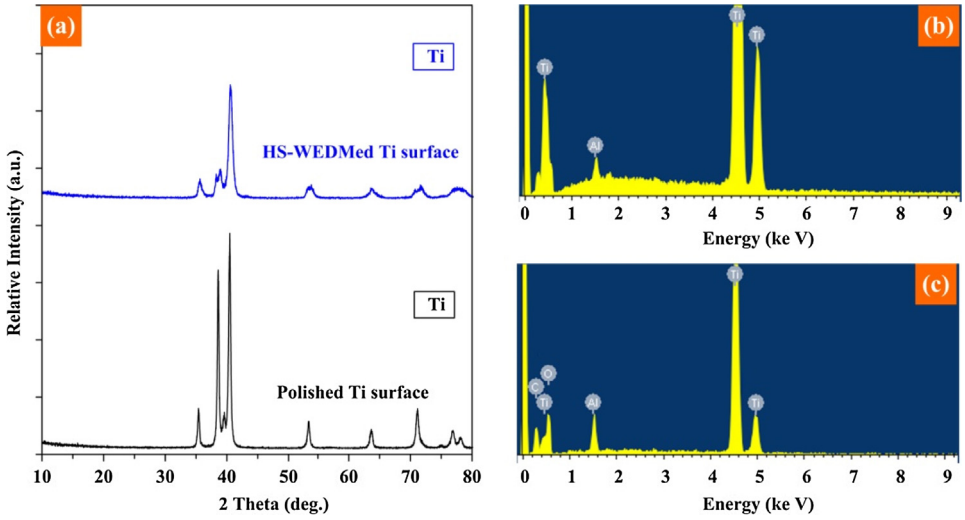

Fig. 2. XRD pattern (a) and EDXS spectra of the (b) polished and (c) HS-WEDMed Ti surfaces in low and high magnification.