Applied Surface Science 436 (2018) 263–267

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Anti-biofouling superhydrophobic surface fabricated by picosecond laser texturing of stainless steel

Ke Sun[a,1], Huan Yang[a,b,1], Wei Xue[a], An He[a], Dehua Zhu[a], Wenwen Liu[a], Kenneth Adeyemi[a], Yu Cao[a,*]

[a] *Zhejiang Key Laboratory of Laser Processing Robot, College of Mechanical & Electrical Engineering, Wenzhou University, Wenzhou, 325035, China*
[b] *International Collaborative Laboratory of 2D Materials for Optoelectronics Science and Technology of Ministry of Education, College of Optoelectronic Engineering, Shenzhen University, Shenzhen, 518060, China*

ARTICLE INFO

Article history:
Received 4 September 2017
Received in revised form
30 November 2017
Accepted 2 December 2017
Available online 7 December 2017

Keywords:
Anti-biofouling
Superhydrophobic surface
Laser ablation
Laser induced surface hierarchical micro-nano structures
Stainless steel

ABSTRACT

Anti-biofouling technology is based on specifically designed materials and coatings. This is an enduring goal in the maritime industries, such as shipping, offshore oil exploration, and aquaculture. Recently, research of the relationship between wettability and antifouling effectiveness has attracted considerable attention, due to the anti-biofouling properties of the lotus leaf and shark skin. In this study, super-hydrophobic surfaces (SHSs) with controllable periodic structures were fabricated on AISI304 stainless steel by a picosecond laser, and their anti-biofouling performance were investigated by seawater immersion for five weeks in summertime. The results showed that the specimens with SHS demonstrate significant anti-biofouling effect as compared with the bare stainless steel plate. We observed that nearly 50% decrease of the average microbe attachment area ratio (Avg. MAAR) could be obtained. The micro-groove SHS with more abundant hierarchical micro-nano structures showed better anti-biofouling performance than the micro-pit SHS.

1. Introduction

Biofouling is the accumulation of microorganisms, plants, algae, or animals on wetted surfaces. As commented by Salta et al. [1], whatever surface (natural or artificial) immersed in seawater, is affected by biofilm attachment. Marine biofouling has become a worldwide problem affecting maritime and aquatic industries such as marine vessels, underwater constructions, and desalination plants [2–4]. Biofouling on ship's hull can lead to increased hydrodynamic friction drag of up to 60%, which may require up to a 40% increase in fuel to compensate [3], in addition, it could cause significant increase in maintenance costs, the emissions of carbon dioxide, and sulfur dioxide [5].

Superhydrophobic surface (SHS) that mimics the lotus leaf and shark skin has been proved to be a promising technique for suppressing biofouling [6–8], and the artificial micro-nanoscale hierarchical structures with low wettability could effectively reduce the microbes attached to the material's surface. Spasova et al. [9] designed a low wettability plastic (Polyvinylidene Fluoride) which not only improved the thermal stability of nano-fibrous materials, but imparted the materials with anti-adhesive and antimicrobial properties. Liu et al. produced a SHS loaded by silver nanoparticles (Ag-NPs), which could effectively prevent corrosion of the Al substrate and bacterial absorption, as confirmed by electrochemical impedance spectroscopy [10]. Furthermore, polyelectrolyte multilayers [11,12], fiber glass [13], polymers [14] and hydrogels [15] were also used to form antimicrobial films on metal substrates. However, as to the above-mentioned methods, the disadvantages such as insecure metal-to-material adhesion [16], complex preparation steps and expensive materials requirements imposed restrictions on practical applications [17].

For metal materials, SHSs are usually achieved by creating a rough surface structure, and then combined with depositing a layer of low surface energy chemical molecules [18,19]. In this work, the SHSs with hierarchical structures on stainless steels were fabricated by a picosecond (ps) laser. The anti-fouling behaviors of the SHS specimens with different surface morphologies were investigated in seawater environments, and the effect of the surface

---

[*] Corresponding author.
E-mail address: yucao@wzu.edu.cn (Y. Cao).
[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.apsusc.2017.12.012
0169-4332/

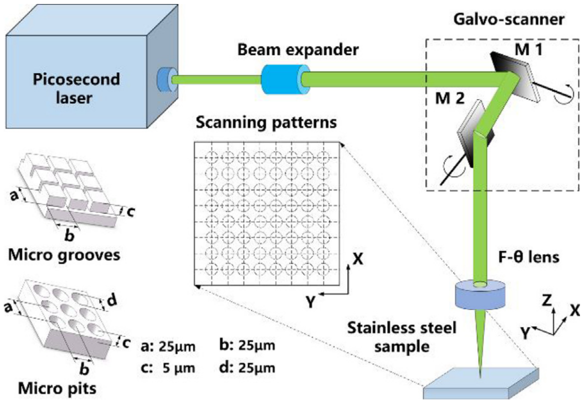

Fig. 1. Schematic diagram of the picosecond laser galvo-scanning system and the designed patterns of micro-groove/micro-pit array for the stainless steel SHSs.

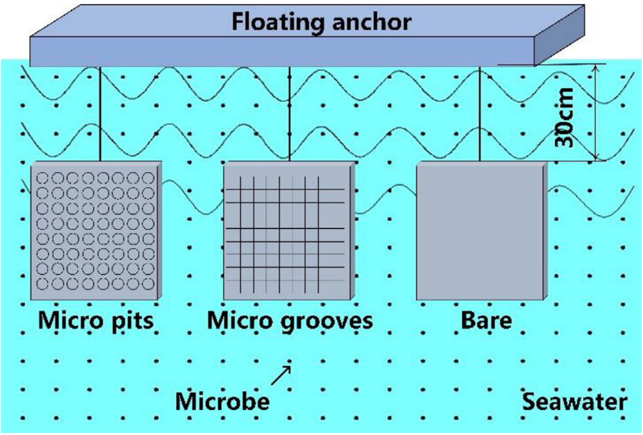

Fig. 2. Schematic diagram of the seawater immersion test.

topography on the anti-fouling characteristics of the SHSs was also presented in this paper.

2. Materials and methods

A 50 × 50 mm^2 AISI304 stainless steel sheet with thickness of 2 mm was used as the specimen substrate. The specimens were ultrasonically cleaned in an ethanol bath for 10 min before and after being textured by the ps laser. The ultrafast laser micro-machining system includes a 515 nm wavelength laser (TRUMPF, micro 5000) with pulse width of 10 ps at 400 kHz PRF (pulse repetition frequency) and a 2-D galvo-scanner system, as shown in Fig. 1. The focal plane was fixed on the specimen's surface and the focused laser beam was approximately 20 μm in diameter. Micro-groove and micro-pit array with the designed geometric profile are shown in Fig. 1, the designed depth of micro-groove and micro-pit was 5 μm and the line width/diameter was 25 μm, the spacing of micro-groove and micro-pit array was set at 25 μm. For fabricating the micro-pit array, a 2500 mm/s scanning speed was used with a PRF of 100 kHz, and the scanning time was 30 s. Because the distance between the adjacent pulses (25 μm) was bigger than the laser spot, the micro-pit was obtained by punching the pulses at the same location. A 400 mm/s scanning speed combined with a PRF of 400 kHz was chosen to fabricate the micro-groove.

The laser ablated specimens were chemically modified by spin coated with silicone sol (30 wt.% spherical silica NPs with the diameter ranges from 10 nm to 20 nm; provided by Aladdin Co.), then being heat treated at 270 ° in air for 30 min. Silica NPs are wide used for modifying metal surface to achieve superhydrophobicity [20]. The solution of silica nano particles (silicone sol) used in this paper is carried out with the reaction of the proportional mixture of tetraethoxysilane (TEOS), ammonium hydroxide, absolute ethanol and methyltriethoxysilane under certain conditions. The heat treatment promotes the hydrolysis and polycondensation reactions which leads to form $Si—CH_3$ groups on the silica NPs that contribute to lower the solid surface energy and achieve a firm adhesion between the substrate and the NPs [21]. Static contact angles (SCAs), advancing contact angles (θ_{adv}), receding contact angles (θ_{rec}) [inserted in Fig. 4(a)] and sliding angles (SAs) were measured five times at different tested area using a video optic CA instrument (Dataphysics, OCA15EC) equipped with a goniometer. The images of a 3 μL distilled water droplet placed on the specimen's surface were analyzed by a Low-Band Axisymmetric Drop Shape Analysis (LBADSA) software. The temperature and relative humidity in the experiment were 25 ° and 65% RH, respectively. The geometric profiles of the laser ablated surfaces were then measured by a profilometer, and the surface topographies were investigated using a scanning electron microscope (SEM, Zeiss, supra 55). As to describe the progress of biofouling on the specimen surfaces over time, a laser scanning confocal microscopy (OLYMPUS, OSL 4100) was used to detect and estimate the area of the attached microbes. In each round of the biofouling progress test, 5 rectangle areas with the same size of 1 mm^2 on the specimen surface were randomly selected to calculate the average microbe attachment area ratio (Avg. MAAR). The rate is defined as the following equation:

$$Avg.MAAR = A_f / A_t \tag{1}$$

where A_f is the total area of the attached microbes; A_t is the total sampling area, specifically 5 mm^2 in this study.

Seawater immersion tests were conducted for 36 days during summertime in the Dongtou island, Zhejiang province, China (27°51′N, 121°08′E, East China Sea), the location was selected in a small village close to the marine protected area, far away from the sources polluted by harbors and heavy anthropic activities. The natural conditions of the seawater is listed in Table 1. The specimens were installed on a plastic floating anchor which made the SHSs lie vertically at a depth of about 30cm, as shown in Fig. 2.

3. Results and discussions

Fig. 3 shows the effect of the laser fluence on the ablation depth and groove-width/ pit-diameter. When the laser fluence is lower than the threshold value of 0.9 J/cm^2, the surface gets very shallow laser marking traces. Along with the increasing laser fluence, a continuous increase of the ablation depth occurs, while the ablation width and pit diameter increase rapidly to the saturation values which is determined by the focused laser spot diameter and the Gaussian energy distribution [22]. Therefore, the optimized laser fluence for fabricating the micro-groove and micro-pit array were selected as 4 J/cm^2 and 9 J/cm^2, respectively.

Table 1
The natural conditions of seawater for immersion test.

Months	DIN (mg/L)	Phosphate (mg/L)	N/P	Water Temp. (°C)	pH Value	Salinity (‰)
JUNE	0.30	0.05	6.15	20.92	8.10	30.34
JULY	0.24	0.10	2.48	27.00	8.01	33.91