Surface & Coatings Technology 317 (2017) 95–102

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Controllable bidirectional wettability transition of impregnated graphite by laser treatment and transition mechanism analysis

Zhixiang Song, Fei Guo, Ying Liu, Songtao Hu, Xiangfeng Liu *, Yuming Wang

State Key Laboratory of Tribology, Tsinghua University, Beijing 100084, China

ARTICLE INFO

Article history:
Received 14 November 2016
Revised 19 March 2017
Accepted in revised form 21 March 2017
Available online 21 March 2017

Keywords:
Wettability
Laser treatment
Impregnated graphite
Surface morphology
Chemical composition

ABSTRACT

Controlling the wettability of surfaces is imperative for the tribology behavior during the friction and wear, especially in aqueous environment. In this work, fiber laser treatment of impregnated graphite was used to achieve a bidirectional wettability transition. The treated surfaces were characterized using scanning electron microscopy, 3D confocal surface topography analysis, Raman spectroscopy, and Fourier transform infrared (FTIR) spectroscopy. The surface treated by a low–energy laser became hydrophobic (increase of contact angle from 73.6° to 131.6°) and the surface treated by a high–energy laser became more hydrophilic (decrease of contact angle to 6.7°). Examination of the morphology indicated that with increasing laser energy, the roughness increased and the surface changed from a flocculent to scaly structure. Analysis of the energy spectra revealed an increase of oxygen content on the hydrophilic surface. In addition, Raman spectra analysis indicated a positive correlation between graphite ordering and the contact angle. The FTIR results demonstrated the existence of hydrocarbon on the hydrophobic surface. After ultraviolet/O_3 cleaning, the contact angle of the hydrophobic surface decreased to 37°; however, the contact angle of the surface which did not be treated by laser hardly changed. Based on these results, it was concluded that the wettability transition was caused by the changes in surface morphology and chemical composition.

1. Introduction

Graphite materials are widely used as ideal tribology materials because of their excellent self–lubricating performance and high thermal stability. In addition, graphite can be impregnated to improve its mechanical strength and electrical characteristics. The phenolic resin or furan resin impregnated graphite are used in applications of mechanical seals [1] and heavy–loaded thrust bearings [2], especially water–lubricated bearings; whereas silver impregnated graphite are used in electrical control systems and relays [3]. The surface characteristics, which mainly consist of surface topography and wettability, play an important role on the tribology behavior during the friction and wear [4,5], especially in aqueous environment. The control of interfacial energy and wettability is of prime importance in ensuring effective aqueous lubrication in interacting friction pairs [6]. The friction pair of hydrophilic-hydrophobic surfaces has a lower coefficient in aqueous environment [5]. Thus, efficient method of controlling the wettability is desired for impregnated graphite in water lubrication.

Numerous methods have been used to modify the surface wettability, such as laser treatment [7–14] and chemical modification [15,16]. Because laser treatment can be used to target specific areas and provide different treatments at different positions with higher precision than other methods [9], this approach has been implemented to modify the wettability of both non–metallic [8–13,17] and metallic [14,18,19] materials. A replication method using a laser–microtextured Si master was proposed by Sharad and Mool [17] to tailor the wettability of polycarbonate by changing the temperature. In addition, Ali et al. [18] controlled the wettability of a Mg alloy by adjusting the laser processing parameters using a pulsed fiber laser; however, only a hydrophilic surface was obtained.

The mechanism of the wettability transition is generally considered to involve the changes of surface energy and surface morphology, especially the microstructure or nanostructure. The microstructure affects the real contact area whereas the surface energy affects the cohesive forces between the solid and the liquid. Guo et al. [12], Cardoso et al. [13], and Luo et al. [14] focused on the effect of morphology changes. The hydrophobic transition is considered to be caused by the nanostructure and can be explained by the Cassie–Baxter model. Kozbial et al. [20] reported that the chemical composition was the main factor and proposed that airborne hydrocarbon contamination resulted in the hydrophobicity of the surface of highly ordered pyrolytic graphite (HOPG).

However, few studies reported a bidirectional wettability transition with high precision after the same type of treatment, which means that both of the hydrophilic surfaces and the hydrophobic surfaces can be obtained after the treatment. A bidirectional controlling method of wettability for impregnated graphite requires further exploration.

* Corresponding author.
E-mail addresses: songzx13@mails.tsinghua.edu.cn (Z. Song), guof2014@mail.tsinghua.edu.cn (F. Guo), liuying@mail.tsinghua.edu.cn (Y. Liu), hsttaotao@163.com (S. Hu), liuxf@tsinghua.edu.cn (X. Liu), yumingwang@tsinghua.edu.cn (Y. Wang).

http://dx.doi.org/10.1016/j.surfcoat.2017.03.047
0257-8972/

In this study, a laser–treatment method is presented to tailor the wettability of impregnated graphite; this method provides higher precision and simplicity than previously reported methods. A bidirectional wettability transition caused by different laser treatment parameters was achieved, and the transition mechanism was analyzed using Raman spectroscopy, attenuated total reflectance–Fourier–transform infrared (ATR–FTIR) spectroscopy, scanning electron microscopy (SEM), and 3D confocal surface topography analysis. In addition, an ultraviolet (UV)/O_3 cleaning process was applied to confirm the effect of hydrocarbon. The experimental results indicated that the hydrophobic transition was caused by the adsorption of hydrocarbon on the surface, whereas the hydrophilic transition was caused by the increasing real contact area and oxygen content. This bidirectional wettability transition can be applied to additional situations, e.g. self–cleaning surface or oil–water separation membrane, because of the simplicity of the method and wide contact angle range.

2. Experimental

2.1. Materials

Circular samples of impregnated graphite with dimensions of Φ54 mm × Φ38 mm × 11 mm supplied by Ningbo Vulcan Mechanical Seals Manufacturing Co. Ltd., China were used in this study. Compared with the non–impregnated graphite, the graphitic mechanical properties were enhanced by phenolic resin. The sample was grinded on a brass plate; polished on a nylon plate, and the roughness was 45.68 ± 2.37 nm.

2.2. Laser treatment

The laser treatment was performed using a fiber laser marking system (YLP–F50, Han's Laser Technology Industry Group Co., Ltd., China) with an output wavelength of 1.064 μm. The laser gain medium was a Yb^{3+}–doped fiber, and an F–Theta–Ronar lens with 254–mm focal length (SL–1064–174–254G) was also implemented. The laser pulse repetition frequency was fixed at 20 kHz, and the spot diameter was 50 μm. The distance between scan lines is 0.01 mm. The laser output power ranged from 5 to 15 W, and the scan speed ranged from 500 to 2000 mm/s. The linear energy F was proposed to describe the intensity of the laser per unit linear length: $F = P/vd_s$.

Here, P is the laser power, v is the scan speed, and d_s is the spot diameter. The implemented laser parameters of the different groups are listed in Table 1. Each of the treated areas was 4 × 4 mm^2. A schematic illustration of the laser marking system is presented in Fig. 1.

Table 1
Parameters of laser treatment in different groups.

Group	Scan speed (mm/s)	Power (W)	Linear energy (J/cm^2)	Assist gas
0	–	0	0	None
1	2000	5	5	None
2	2000	7.5	7.5	None
3	2000	10	10	None
4	2000	12.5	12.5	None
5	2000	15	15	None
6	1000	5	10	None
7	1000	7.5	15	None
8	1000	10	20	None
9	1000	12.5	25	None
10	1000	15	30	None
11	500	5	20	None
12	500	7.5	30	None
13	500	10	40	None
14	500	12.5	50	None
15	500	15	60	None

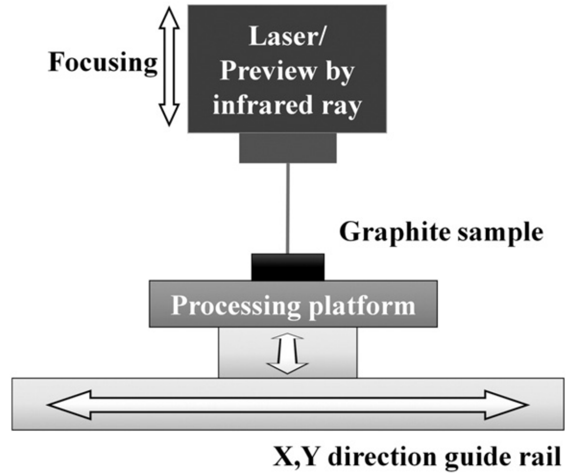

Fig. 1. Schematic of the laser marking system.

2.3. Contact angle measurement

The wettability is described by the contact angle, which is defined as the angle at the triple point of the gas, liquid, and solid phases. In this study, the static contact angle of a 2–μl droplet of deionized water was determined using a surface tension meter (DCAT21, Data Physics, Germany) at 24.9 ± 0.5 °C and 65% ± 5% relative humidity based on the sessile drop method. The dynamic contact angle was measured using OCA25, Data Physics, Germany by increasing and reducing the volume of a sessile drop during drop shape analysis.

2.4. Surface characterization

The surface morphology was examined using SEM (Tescan LYRA3 SEM–focused ion beam (FIB) system, Chech) at 500–10000× magnification and 3D confocal surface topography analysis (Nexview 3D optical surface profiler, Zygo Corp., America) using a 10× objective lens and 1× ocular lens. Raman spectroscopy (LabRAM HR Evolution, HORIBA Jobin Yvon, France) was performed using a 532–nm laser in the range of 800–3500 cm^{-1}. A spot size of 1.25 μm and laser power of 1.1 mW were used to avoid thermal damage to the graphite surface, the number of passes was 1, and the integration time was 30 s. Curve fitting was performed using the software package Labspec 5 (HORIBA Jobin Yvon). FTIR spectroscopy (Bruker Hyperion IR–Microscope, Germany) was performed using an ATR objective lens in the range of 650–4000 cm^{-1} with a resolution of 4 cm^{-1}.

2.5. UV/O_3 treatment

UV/O_3 treatment of the impregnated graphite was performed for 10 min using a UV/O_3 cleaner (BZS250GF–TC, Shenzhen HuiWo Technology Co., Ltd., China).

3. Results and discussion

3.1. Laser treatment and contact angle

Smoke was observed during the laser processing, especially during the high–energy processing, because of the thermal decomposition of the phenolic resin and oxidizing reaction of graphite.

Fig. 2 shows the effect of laser treatment on the water contact angle and two dynamic parameters, namely the advancing and receding contact angles. The contact angles on impregnated graphite varied widely for the different groups. The water contact angle of Group 15 (laser power of 15 W, scan speed of 500 mm/s, and linear energy of