Fabrication and tribological properties of superhydrophobic nickel films with positive and negative biomimetic microtextures

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Abstract: Nickel (Ni) films with positive and negative textured surfaces of lotus and rice leaf patterns were fabricated through an inexpensive and effective method. The as-prepared Ni films were superhydrophobic and exhibited excellent tribological properties after chemical treatment. Experimental results indicated that the water contact angles (WCAs) on the surfaces of biomimetic textured Ni films (approximately 120°) were far greater than those on smooth films (65°). The biomimetic textured surfaces became superhydrophobic (WCA of approximately 150°) after perfluoropolyether (PFPE) treatment, which could be due to the combined effects of the special texture and the PFPE. The as-prepared biomimetic-textured Ni films modified with PFPE were improved with a low friction coefficient and excellent antiwear properties, which were due to the combination of the effective lubrication of PFPE and the special textures that served as a good lubricant and a debris reservoir. Moreover, the antiwear properties of the as-prepared Ni films with negative biomimetic microtextures modified with PFPE were much better than those of films with positive biomimetic microtextures modified with PFPE.

Keywords: nickel; positive; negative; bio-mimicking; superhydrophobic; friction

1 Introduction

Owing to the outstanding properties of Ni films, such as hardness, chemical inertness, and wear and corrosion resistance, they have been widely used in microelectromechanical systems (MEMS) and magnetic storage systems [1–6]. As the dimensions of components in MEMS and magnetic storage systems decrease toward the microscale and even the nanoscale, the small size and close spacing of the components can cause serious problems in MEMS operations related to adhesion and friction [7]. Surface chemical modification [8–12] and topographical modification [13–15] are two main approaches to alleviate the problems of adhesion and friction. Recently, a great deal of attention has been paid to perfluoropolyether (PFPE) as an ideal molecular lubricant for MEMS because it has been shown to solve the problem of friction in MEMS devices [10, 16, 17]. Therefore, PFPE was chosen as the chemical modifier in this study.

Functional surfaces with biomimetic microtextures have drawn much interest because of the advantages they offer in many applications, such as their hydrophobic properties, anti-adhesion characteristics, and ability to control friction [17–21]. The natural world offers multiple examples of surfaces that are optimized to control friction through a combination of surface...
texture, orientation, and flexibility, such as the surfaces of a gecko’s thumbs and sharkskin [20–24]. Our previous reports found that diamond-like carbon films with lotus-leaf-like biomimetic microtextures exhibited improved tribological behavior [17]. Shafiei and Alpas demonstrated that bio-textured nickel films could reduce friction [20, 21]. Therefore, enhancing surface properties against friction by fabricating surfaces that mimic biotextures will provide a promising technological trend in the future.

This paper reports in detail the development of a simple replication technique that allows specific biotextures to be fabricated in the form of self-sustaining Ni films. For this purpose, the biotextures of lotus leaves and rice leaves were replicated to create Ni surface features that reduce and control frictional forces. The Ni films with positive and negative textures of lotus and rice leaves on the surface were obtained through a combination of replication techniques and electroplating methods.

2 Experimental

2.1 Materials

The starting materials included biological originals (rice and lotus leaves), polydimethylsiloxane (PDMS; Sylgard 184 Silicone Elastomer Kit, Dow-Corning, USA), PFPE (HOCH_{2}CF_{2}O–(CF_{2}–CF_{2}O)_{m–n}–CF_{2}CH_{2}OH, where m and n are integers; molecular weight = 3,800; commercial name Zdol 3800, Johnson Matthey, USA), and Ni boards (Jiangsu JCMATERIALS Technology Co. Ltd, China). Acetone, nickel sulfate hexahydrate, nickel chloride hexahydrate, boric acid, and sodium dodecyl sulfate, all of which were analytically pure, were used as received. The Ni boards were cleaned with dilute hydrochloric acid solution and deionized water before use. The original locations of the rice and lotus leaves, as well as their corresponding habitats, are shown in Table 1.

| Species       | Locality          | Habitat         |
|---------------|-------------------|-----------------|
| Rice leaf     | Changzhou city,   | Paddy field,    |
|               | Jiangsu province  | hydrophily      |
| Lotus leaf    | Changzhou city,   | Pond, hydrophily|
|               | Jiangsu province  |                 |

Table 1 List of the biological originals examined in this study

2.2 Sample preparation

The fabrication of a Ni film with biomimetic textures is schematically illustrated in Fig. 1.

2.2.1 Duplication

The fresh lotus and rice leaves were placed on a clean glass dish. A mixture of 90.9 wt% sylgard silicone elastomer 184 and 9.1 wt% curing agent was poured over the leaves to obtain negative impressions of the textures. The dish containing the covered leaves was left at room temperature for 2 h to remove bubbles in the solution. It was then placed in an oven at 65 °C for 10 h and air cooled at room temperature. After cooling, the textured PDMS film was peeled off of the original template. Negative replicas were obtained on the surfaces of the PDMS films (Fig. 1(c)). Next using the same process, the negative replicas were used as templates to produce positive replicas on the PDMS surfaces (Fig. 1(g)). Finally, all of the PDMS samples with positive and negative biomimetic textures were sputter-coated with a thin layer of gold that had a thickness of approximately 100 nm to enhance their conductivity for electroplating.

2.2.2 Electroplating

Each as-prepared textured polymer with gold film was placed in a Ni electroplating bath to form a biomimetic metallic layer, following the same procedure.

Fig. 1 Schematic illustration for fabricating Ni surfaces with positive or negative surface topographies of biological templates.
described in our earlier work [19]. The plating time was 2 h and the current density was 2 A/dm². The pH value of the baths was 4.5–5.5. The plating experiments were conducted at 39 ± 2 °C. After the electroplating, the PDMS films were peeled off to obtain Ni layers that were approximately 100 μm thick with positive or negative impressions of the biomimetic textures (Fig. 1(e) and 1(i)). The Ni films were then rinsed with de-ionized water and dried under a flow of N₂. For convenience, we use N to denote textured Ni film, L to denote lotus leaf, and R to denote rice leaf. Hereafter, the textured Ni films with positive lotus leaf-like microtexture, negative lotus leaf-like microtexture, positive rice leaf-like microtexture, and negative rice leaf-like microtexture are abbreviated as positive-LN, negative-LN, positive-RN, and negative-RN, respectively.

2.2.3 Surface chemical modification

The Ni coatings with positive or negative biomimetic textures were immersed in a dilute solution of 1 mM PFPE in methoxyperfluorobutane (HFE 7100, Sigma-Aldrich) and kept for 24 h. The samples were then removed from the coating solution and placed in an oven that was kept at 120 °C for 3 h. Finally, the samples were ultrasonicated in HFE 7100 for 10 min to remove the physically adsorbed molecules, rinsed with HFE 7100, and dried under a flow of N₂. Hereafter, the textured Ni films modified with PFPE are referred to as NP for convenience. The corresponding textured Ni films with positive lotus leaf-like microtexture, negative lotus leaf-like microtexture, positive rice leaf-like microtexture, and negative rice leaf-like microtexture that were modified with PFPE are referred to as positive-LNP, negative-LNP, positive-RNP, and negative-RNP, respectively.

2.3 Surface characterization

The surface morphologies of the biological originals and as-prepared biomimetic textured Ni films were observed on a JSM-5600LV scanning electron microscope (SEM; JEOL, Japan) at 20 kV. The surface chemical compositions were examined with a PHI-5702 multifunctional X-ray photoelectron spectroscope (XPS; Perkin-Elmer, USA) using Mg Kα radiation as the excitation source. Water contact angles (WCAs) were determined using a contact angle system (HARKE-SPCA; Beijing Harke, China). A 5-μL droplet was used for the WCA measurements, and average values of at least three repeat measurements for each sample were recorded. Tribological properties were measured using a UMT-2MT tribometer (CETR, USA) under ambient conditions (20–25 °C, relative humidity = 40–50%) and a load of 60 mN, at a sliding speed of 30 mm/s in the reciprocating–sliding mode. The upper counterparts used here were commercially available 440-C stainless steel balls (diameter = 6 mm). Plots of the friction coefficient (COF) versus time were recorded automatically, and at least three repeat measurements were performed. The images of worn surfaces were obtained using a Contour GT non-contact 3D profilometer (Bruker, Germany).

3 Results and discussion

3.1 Ni films with positive or negative biomimetic surface morphologies

Typical SEM images of Ni surfaces with positive or negative biomimetic textures are shown in Fig. 2. Figure 2(a) shows an SEM image of positive-LN. It is obvious that the positive surface structures were replicated from the original lotus leaf. Biomimetic textures on the Ni surface were highly uniform: Many micropapillae with diameters ranging from 5 to 10 μm were distributed randomly on the surface. An SEM image of negative-LN is depicted in Fig. 2(b). Contrary to the surface of positive-LN, a roughly complementary structure composed of countless micro-orifices with diameters ranging from 6 to 10 μm was found on the surface. As seen in Fig. 2(c), the papillae with diameters of approximately 2–50 μm were distributed randomly on the surface. An SEM image of negative-LN is depicted in Fig. 2(b). Contrary to the surface of positive-LN, a roughly complementary structure composed of countless micro-orifices with diameters ranging from 6 to 10 μm was found on the surface. As seen in Fig. 2(d), the micro-orifices had diameters of approximately 2–50 μm.
3.2 Chemical characterization

To obtain insight into the chemical composition of the Ni surface modified with PFPE, XPS investigation was performed on the surface, the results of which are shown in Fig. 3. The scan survey spectrum of PFPE shows three elements: fluorine (F\(_{1s}\)), carbon (C\(_{1s}\)), and oxygen (O\(_{1s}\)), the existence of which provides solid evidence that PFPE was adsorbed successfully on the textured surface.

3.3 Surface hydrophobicity

The static WCA is a primary parameter that provides a convenient means to assess the relative hydrophobicity of a solid surface. The results measured in this work are shown in Fig. 4. Here the WCAs of the Ni surfaces with rice leaf-like microstructures were the maximum measured values and were measured in the transverse direction, since the droplets could be pinned between the longitudinal grooves [25–27]. Obviously, compared with the WCA of the smooth Ni surface (65°), Ni surfaces with positive biomimetic textures showed much larger WCAs. In particular, after chemical modification with PFPE under a 5-μL water droplet, the Ni surfaces with positive biomimetic textures exhibited improved superhydrophobicity (WCA = 151.2° on positive-LNP; WCA = 153.2° on positive-RNP). In addition, the same pattern of change occurred on Ni surfaces with negative biomimetic structures (WCA = 147.9° on negative-LNP; WCA = 152.7° on negative-RNP).

It is well known that the WCA of a solid surface depends on several factors, such as surface topography, surface roughness, and surface chemistry. Generally, greater roughness and lower surface energy lead to higher WCAs and higher hydrophobicity. When water droplets are released on a textured sample, air is trapped in the cavities of the rough surface, resulting in a composite solid–air–liquid interface, which leads to a higher contact angle [28]. When the surface energy was decreased by chemical modification in our experiments, PFPE with terminal hydrophobic groups (–CF\(_3\)) led to a higher WCA. It can be clearly seen that the difference in contact angles induced by PFPE treatment was much larger for the textured Ni films than the smooth film. This was due to the combination effects of a textured surface and the low surface energy of the material, which could yield a contact angle above 150° and lead to a larger change.
in contact angle as a result [29, 30]. However, chemical modification of the smooth films using PFPE did not produce WCAs above 120°.

3.4 Tribological and wear properties

The microtribological properties of the films were investigated with a ball-on-plate tribometer at a load of 60 mN and a sliding rate of 30 mm/s, and the results are shown in Figs. 5 and 6. The tribological tests were performed on the surfaces of rice leaf-like microtextured samples in both the transverse and longitudinal directions. However, when a load of 60 mN was set, the actual contact load repeatedly changed from nearly 0 mN to more than 400 mN during sliding in the transverse direction. This large error may have been due to the significant change of structures in the transverse direction, which resulted from the longitudinal grooves. Conversely, the actual contact load remained at approximately 60 mN during sliding in the longitudinal direction. Thus, the tribological results of the rice leaf-like structured samples are presented only in the longitudinal direction. It was observed that the COFs of the textured Ni films were lower than that of the flat film, which could be explained by the fact that the textured Ni films with protrusions and hollows of lotus and rice leaves had smaller contact areas [20].

The wear resistance of the as-prepared textured Ni coatings (positive-LN, negative-LN, positive-RN, and negative-RN) was still poor. They displayed heavy wear as soon as the counterpart balls began to slide on them, and the COF continued to increase to an average value of approximately 0.7. However, it was clearly seen that the antiwear abilities of the as-prepared Ni coatings with biomimetic microtextures modified with PFPE (positive-LNP, negative-LNP, positive-RNP, and negative-RNP) were significantly improved. The PFPE remained as an effective lubricant layer for more than 600 s at a load of 60 mN and a sliding rate of 30 mm/s. This was due to the combined effects of the lubrication of PFPE and the textured surfaces acting as reservoirs for the lubricant and the wear debris. Moreover, the COFs of the as-prepared Ni coatings with negative biomimetic microtextures modified with PFPE (negative-LNP and negative-RNP) were lower than those of the films with positive biomimetic microtextures modified with PFPE (positive-LNP and positive-RNP). In order to evaluate the endurance of the PFPE-deposited samples, loads of 100–300 mN and a sliding rate of 30 mm/s were applied for 1 h. The result of the negative-LNP is shown in Fig. 7 as an example. It was found that the endurance of the negative-LNP was much better than that of the samples without PFPE treatment (Figs. 5 and 7). The PFPE remained as an effective lubricant layer for more than 3,600 s at a load of 100 mN. When the load increased to 300 mN, the friction coefficient of the lubricant film increased slowly to approximately 0.6, indicating the breakdown of the lubricant film.

A 3D non-contact profilometer was used to observe the worn surfaces of the different samples at an applied load of 60 mN and a constant sliding velocity.
Fig. 7  Variation of Negative-LNP in COF with time at normal loads of 100–300 mN and a sliding rate of 30 mm/s for 1 h.

of 30 mm/s for 10 min (Fig. 8). The results showed that the surface textures could trap wear debris from the interface, reducing the plowing and deformation components of friction [31]. On the other hand, the wear particles on the surface of the smooth sample could produce severe scratches, resulting in poor frictional properties.

Among the eight as-prepared textured samples, the unmodified ones exhibited the poorest wear resistance. However, the antiwear performance of the modified samples, which produced less wear debris at the interface, was significantly higher. This obvious difference indicates that PFPE, which has excellent lubricating properties, reduced the contact surface wear for the biotextured films and the textured surfaces could store lubricants and trap wear debris from the interface [20, 32]. In other words, the combination of the effective lubrication of PFPE and the textured surfaces resulted in the best tribological behavior. It can also be clearly seen that the antiwear performances of the as-prepared Ni coatings with negative biomimetic microtextures modified with PFPE (negative-LNP and negative-RNP), which produced less wear debris at the interface, were better than those of coatings with positive biomimetic microtextures modified with PFPE (positive-LNP and positive-RNP). The trend was in accordance with the results of the variation in COF with time, possibly because the negative replicas could store more lubricants and debris than those of the positive replicas.

4 Conclusions

Ni films with biomimetic microtextures were obtained through a simple and effective method. Combined with PFPE chemical modification, the as-prepared biomimetic textured Ni films exhibited superhydrophobic properties. The as-prepared biomimetic textured Ni films modified with PFPE showed improved

Fig. 8  3D images of different worn surfaces: (a) positive-LNP, (b) negative-LNP, (c) positive-RNP, (d) negative-RNP, (e) positive-LN, (f) negative-LN, (g) positive-RN, (h) negative-RN, (i) smooth nickel film.
performance with low COF and excellent antiwear properties, which resulted from the combination of the effective lubrication of PFPE and the biomimetic textures that acted as reservoirs to store lubricant and wear debris. These surfaces with special microtextures are of great importance for both fundamental research and practical applications that require properties such as superhydrophobicity and antiwear.

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