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Tribological and magnetic characterization of fluorosilanes on cobalt surface

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ABSTRACT

In this paper, we present a study of tribological properties of fluorosilane monolayer on magnetic surface. The used fluorosilane was 1H, 1H, 2H, 2H perfluorodecyltrichlorosilane (FDTS), and the used magnetic material was a cobalt film. The effectiveness of modification of the cobalt surface by FDTS was monitored by the measurement of the wetting contact angle and the surface free energy. The increase of surface hydrophobicity was observed upon the modification by reducing the surface free energy and increasing the wetting contact angle. The nanotribological properties were characterized by means of adhesion, friction and wear, using atomic force microscopy (AFM). The cobalt surface modified by FDTS exhibits lower values of adhesion and the coefficient of friction in comparison with those for the unmodified surface. It was also found that FDTS effectively reduces wear of the system.

We also investigated the magnetic structure of the cobalt film before and after modification by FDTS. The magnetic structure was composed of maze stripe domains magnetized perpendicular to the film surface, as revealed by magnetic force microscopy (MFM). The domain structure of the modified cobalt film was practically the same (in character and in size) as that observed for the bare cobalt film.

1. Introduction

The tribological properties of organic thin films like fluorosilane have been extensively studied in recent years because of their potential applications in many technological fields. Their applications include antistiction coatings and orientation layers in nanofabrication of microelectromechanical systems (MEMS). They are also used as ultrathin lubricant which minimizes adhesion, friction and wear.

One of the most attractive surfaces in these applications are cobalt and its alloys. These materials have been used in the military, aerospace industry and also in biomedical applications, including the therapy of cardiovascular diseases, orthopedics and dentistry [1]. The widespread use of cobalt alloys is associated with their good resistance to corrosion and wear, and their tolerance in an environment of tissues and body fluids [2]. Depending on the specimen thickness, cobalt and cobalt-based systems possess various magnetic properties, and especially various magnetic domain structures [3–5]. From the practical point of view, cobalt-based thin films and multilayers are used in high-density magnetic media, in magneto-optic recording media and as magnetic sensors [6–9], cobalt-based alloys are used as high-performance permanent magnet materials [10,11].

To achieve better mechanical and nanotribological properties of cobalt or cobalt alloys, they are subjected to modification by compounds such as fluorosilanes. In this paper, we report a study of tribological properties of cobalt films before and after modification by 1H, 1H, 2H, 2H perfluorodecyltrichlorosilane (FDTS). Basic research performed by the authors showed that FDTS has larger water contact angle, lower surface free energy and lower coefficient of friction in nano- and microscale than other silanes with fluorocarbon and methyl terminal groups. For this reason we chose FDTS for the coating of cobalt films. Some properties of the investigated surfaces, like hydrophobicity, were evaluated by contact angle measurements (CAM), while the adhesion and friction were measured using atomic force microscopy (AFM). We also present a study of the magnetic structure of the unmodified and modified cobalt films, using magnetic force microscopy (MFM). To the authors' knowledge, the mentioned studies have been made for the first time.

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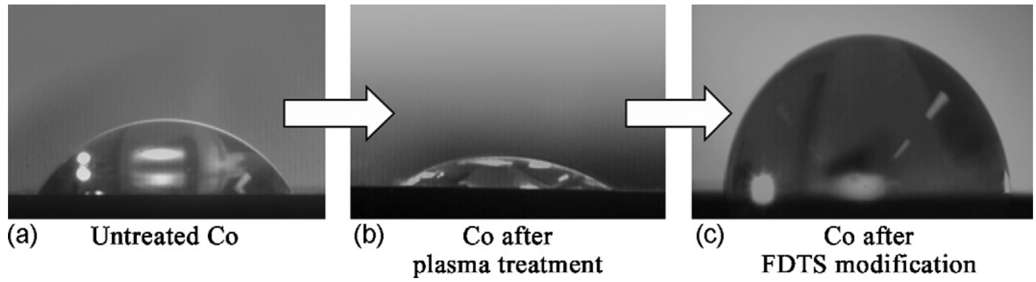

Fig. 1. Water droplets on cobalt surface (a), surface after plasma treatment (b), and surface subsequently covered by FDTS (c).

2. Experimental

Cobalt films 100-nm-thick were deposited on oxidized Si(1 0 0) substrates by thermal evaporation in a system maintained at a base pressure of about 10^{-3} Pa. The cobalt surface activated by oxygen plasma was placed into a vapor phase deposition (VPD) system and kept under low pressure (0.1 Pa). Then the specimen was kept in the modifier vapor for 20 min at room temperature and finally outgassed at low pressure for 1 h at 40 °C to remove any excess of physisorbed and unreacted molecules [12–14]. As a result, FDTS monolayer (1.65 nm in thickness) was grown on the cobalt surface. The FDTS compound was ordered from the ABCR, GmbH & Co. KG, Karlsruhe.

Some properties of the studied surfaces, such as hydrophobicity and surface free energy, were evaluated by CAM. The static contact angle was measured in air by the use of a sessile-drop method using a contact angle goniometer. A drop of proper liquid (water, glycerine and diiodomethane) was deposited on the surface with the use of microsyringe. The image of the droplet was recorded by a digital camera. The surface free energies of cobalt and cobalt surface modified by FDTS were calculated using the Van Oss–Chaudhury–Good method [15].

The morphological and magnetic structures were made visible with a NT-MDT instrument, using AFM and MFM respectively, operating in air under ambient conditions. Nanotribological measurements were performed with AFM using a rectangular Si_3N_4 cantilever with a spring constant calibrated by the Sader method (k = 0.62 N/m) [16,17]. The adhesive force was obtained from the force–distance curve after reckoning the pull-off force [18–20]. The friction force was calibrated using the method described by Ruan and Bhushan [21]. The coefficient of friction was obtained from the slope of the friction force versus normal load plots. Normal loads typically ranged from 5 to 100 nN.

Wear tests were performed with AFM using Budget Sensors (diamond coating on the tip) with a cantilever spring constant of 50 N/m. Wear tests were performed on a 1 μm × 1 μm area. After wear test the scan area was increased to 5 μm × 5 μm, the microscope was switched to operate in tapping mode, and topography image was taken at the same place at the resonance frequency of 320 kHz. The wear result was observed by the change in height between place without and with wear marker. Each measurement was repeated three times.

Morphological and magnetic images were taken using the two-pass method [4,22,23]. For each raster line, the first pass was made very close to the specimen surface and yielded knowledge of the surface morphology (AFM). The second pass then followed the recorded morphology but at an increased scan height (large enough to eliminate the short-range van der Waals forces that provided the morphological contrast) and yielded knowledge of the magnetic structure of the specimen (MFM). We used MikroMasch silicon cantilevers with tips magnetized along the tip axis. The tips used were coated with a FeCoNi film about 60 nm thick. MFM images were recorded with a tip-specimen separation of 50 nm.

3. Results and discussion

Fig. 1 presents contact angle measurement for the unmodified and modified surfaces. The measured value of the water contact angle was about $(59 \pm 2)^\circ$ for bare cobalt surface, it was about $(24 \pm 2)^\circ$ after plasma treatment, and it was about $(90 \pm 2)^\circ$ after FDTS coating. These experimental data provide information that plasma treatment makes the surface hydrophilic. The modification of the surface by FDTS leads to an increased contact angle, and consequently to an increased hydrophobic character of the surface. In the case of silicon, the literature data show that –CF3 terminated monolayer has a water contact angle of around 108–110° [13]. Nevertheless, in the case of the study made by us the main roles are played by a large number of defects, the layers packing as well as the magnitude of roughness. This is supported by the fact that the authors obtained in the preliminary study for the Si and Cu substrates modified by FDTS contact angles of 111° and 123°, respectively.

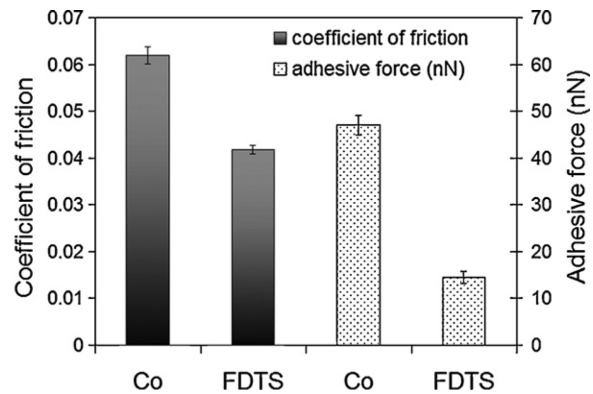

Fig. 2. The coefficient of friction and adhesion measured by AFM.

The contact angle gives information about the surface energy, and also allows to predict the strength of capillary forces and in consequence adhesion forces. For the surface modified by FDTS, the free energy is lower because the contact angle is higher. The obtained value of the surface free energy was about 72.2 mJ/m^2 for bare cobalt surface and it was about 31.5 mJ/m^2 after FDTS coating.

In the nanoscale, adhesion force is due to several components such as capillary force, van der Waals force, electrostatic force, and other chemical and physical interactions. The adhesion measurements performed in ambient conditions, so as in our case, show that the dominant force is the capillary force. The van der Waals force also contributes [24,25], but its magnitude is small when compared to that of the capillary force [26–28].

The capillary force causes the occurrence of the meniscus bridge between the AFM tip and the surface. The force between a tip and a solid surface can be represented by the reduced equation:

$$F_c = 4\pi\gamma_{LV}R\ \cos\Theta \qquad (1)$$

where γ_{LV} is the liquid–vapor surface tension, Θ is the solid–liquid contact angle and R is the radius of solid sphere.

For hydrophilic surface the capillary force is higher than for hydrophobic surface. Therefore on the hydrophilic cobalt surface water film is easily formed and consequently for the unmodified cobalt surface the adhesion force is increased as compared with that for the surface modified by FDTS (Fig. 2).

The variations of the coefficient of friction are also due to the change in the nature of the surface from hydrophilic to hydrophobic. For more hydrophilic cobalt surface the coefficient of friction has a higher value, and the obtained value is 0.062 (Fig. 2). This is attributed to the high surface energy related to the formation of hydrogen bonds between the AFM tip and hydroxylated cobalt surface. The break of these hydrogen bonds causes an increase of the coefficient of friction [29,30]. In the case of the surface modified by FDTS this effect does not occur and the coefficient of friction is

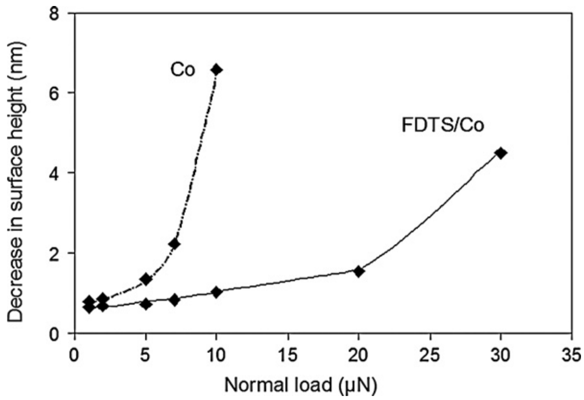

Fig. 3. Dependence of the decrease in surface height on the normal load.

lower, and the obtained value is 0.041. In other words, the coefficient of friction decreases with increasing hydrophobicity.

To determine mechanical properties, the surfaces were subjected to antiwear investigation. Fig. 3 shows the relationship between the decrease of surface height and the normal load for bare cobalt and the surface modified by FDTS. The bare cobalt surface and the surface modified by FDTS showed the critical load of 5 and 20 μN, respectively. When the normal load is smaller than the critical load, the height of FDTS monolayer changes only slightly. Whereas above the value of the critical load, the monolayer of FDTS is removed from the surface and the wear of this surface increases rapidly. In other words, the modified surface shows better wear resistance and higher critical load than the unmodified surface. This is due to the existence of strong covalent bound Si–O (242.7 kJ/mole) between the surface and the modifying agent [31].

Fig. 4a presents MFM image of a bare cobalt film. The magnetic domain structure is in the form of a maze stripe pattern. The magnetic domains are of the order of 100 nm in width. The domain pattern shows no directionality, i.e. the stripe domains run in random directions in the film plane. The observed structure is characteristic of materials with sufficiently high perpendicular magnetic anisotropy [3,4,32–35]. The bright and dark areas in the MFM image correspond to the domains of opposite magnetization in the direction perpendicular to the film plane. The reason for the undulation of the domains (the maze structure) is the reduction in the magnetostatic energy at the cost of a larger total domain wall area.

Fig. 4b shows MFM image of the cobalt film modified by FDTS. It is seen that in this case the magnetic domain structure is practically the same in character and in size as that for the bare cobalt film. In other words, the FDTS film was too thin (one monolayer, 1.65 nm in thickness) to modify the domain structure of the cobalt film in a noticeable way. It is worth noting, however, that in general the magnetic domains became larger with increasing thickness of the FDTS film. This effect can in fact be caused by an increasing degree of mixing at the FDTS/cobalt interface and by an increasing geometric alignment of the agglomerates of the FDTS film (the shape anisotropy) [36].

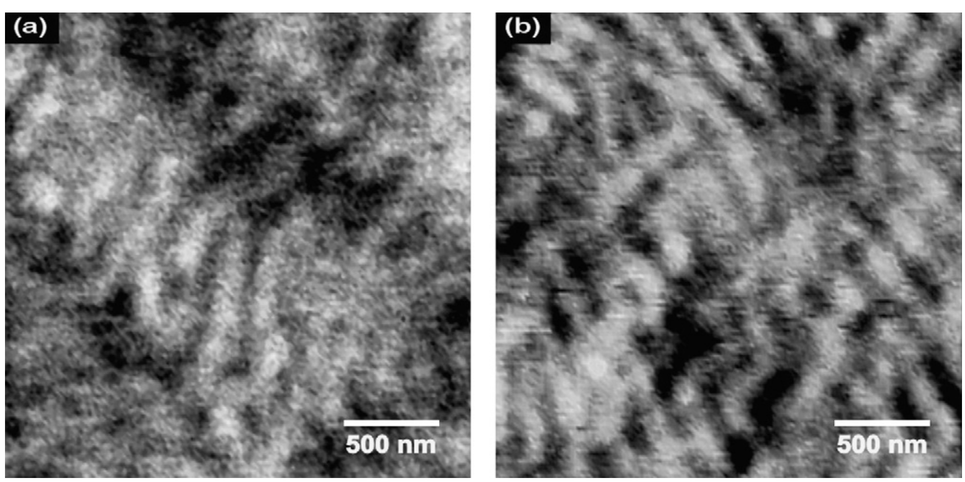

Fig. 4. MFM images of the domain structure of cobalt films before (a) and after modification by FDTS (b).

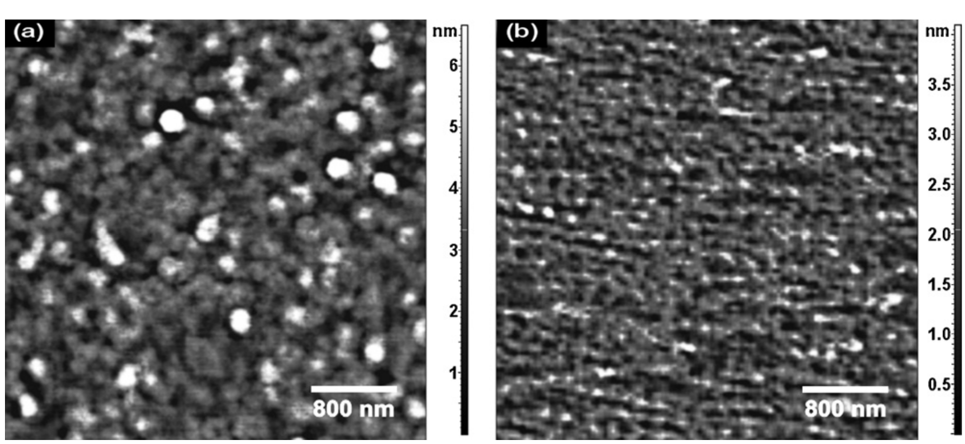

Fig. 5. AFM images of the surface of a bare cobalt film (a) and after modification by FDTS (b).

The used cobalt films with magnetization perpendicular to the film surface exhibit a relatively strong stray magnetic field in close proximity to the surface, of the order of a few hundred kA/m. In this context, it is worth noting some influence of this magnetic field (perpendicular to the sliding contact surface) on wear and friction processes, as reported in Refs. [37–39]. In general, the presence of a magnetic field can increase or decrease wear and friction, depending on the nature of the materials in contact, on the sliding velocity and on the other experimental conditions [37,38].

Fig. 5a and b presents AFM images of the surface of a bare cobalt film and the surface of the cobalt film modified by FDTS, respectively. The morphological structure of the bare cobalt film is composed of rough grains. The grains are packed closely, i.e. the bare cobalt film is seen to be practically continuous. The surface of the cobalt film modified by FDTS is imaged as composed of small grains forming one monolayer of this compound.

4. Conclusions

In summary, the cobalt surface modified by fluorosilane (FDTS) has higher water contact angle and lower surface free energy than the unmodified cobalt surface. Nanotribological investigations have shown that the modified surface has lower adhesion and coefficient of friction than the unmodified surface. The variations of nanotribological properties are due to the change in the nature of the surface from hydrophilic to hydrophobic. The modification of the cobalt surface by fluorosilane also leads to better wear resistance and higher critical load. From the nanotribological point of view, fluorosilane exhibits good antifrictional and antiwear properties and can be used for potential applications.

The magnetic domain structure exhibited a maze stripe pattern. The domains had their magnetizations perpendicular to the film surface. The domain structure of the cobalt film modified by fluorosilane was practically the same (in character and in size) as that observed for the bare cobalt film. This in turn means that the used fluorosilane film was too thin (one monolayer, 1.65 nm in thickness) to modify the domain structure of the cobalt film in a noticeable way.

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