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Tribological properties of nano-porous anodic aluminum oxide template

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Abstract: A highly ordered porous alumina template with pores of 45 nm in diameter was synthesized by a two-step electrochemical anodizing process. The influence of pore-enlargement treatment on the porous structure and tribological properties of the film was investigated, and ultrasonic impregnation technology was applied on it to form self-lubricating surface. The structure of the self-lubricating film and its tribological properties were investigated in detail. It can be concluded that the optimum time of pore-enlargement treatment is 20 min. The diameter of the pores and the surface porosity of the film are about 70 nm and 30%, respectively, while the film maintains the property of its high hardness. Under the same friction condition, the frictional coefficient of the self-lubricating film is 0.18, much lower than that of the anodic aluminum oxide template, which is 0.52. In comparison with the lubricating surface of non-porous dense anodic aluminum oxide template, the lubricating surface fabricated by the ultrasonic impregnation method on the porous anodic aluminum oxide template keeps longer period with low friction coefficient. SEM examination shows that some C_{60} particles have been embedded in the nanoholes of the anodic aluminum oxide template by the ultrasonic impregnation technology.

Key words: anodization; self-lubricating; ultrasonic impregnation; C_{60}; pore-enlargement

1 Introduction

The anodic aluminum oxide (AAO) template formed in oxalic acid solution is generally considered to have a porous structure and to mainly consist of amorphous Al_2O_3 [1], and the film has the merits of high hardness, good wear resistance and excellent corrosion resistance [2−5]. However, the tribological properties of AAO template are not good enough for practical applications because of its high friction coefficient. Filling the pores with lubricating materials is an easy way to reduce the friction coefficient, which can be developed to produce new types of self-lubricating anodized aluminum material. Various methods have been studied in order to improve the friction performance of aluminum anodic oxide coating, such as physical impregnation, duplex anodization, sputter-deposition [6−8]. The methods of physical impregnation have been used widely for their convenient and economic characteristics. However, its filling efficiency is low. Duplex anodization is the method to deposit solid lubricant, such as MoS_2, in the pores of anodized film on aluminum by reanodizing in $(NH_4)_2MoS_4$ solution. Some researchers think that the deposited products were sulphides of Mo rather than single MoS_2, which decrease the self-lubricating properties of the materials [9−10]. Recently, the excellent tribological properties of C_{60} have been widely studied because of its potential applications as solid lubricant [11−13]. In tribology, it has been considered as a super lubricator due to its spherical molecular structure, good stress resistance and stiffness, much lower surface energy and good chemical stability, etc [14]. BHUSHAN et al [15] introduced fullerene as a new solid lubricant, described the fundamentals of its crystal structure and properties, proposed a mechanism for its lubrication action, and presented friction and wear data on the fullerene films. So, this work aims to make C_{60} particles enter deeply into the porous structure of AAO. Since the pores of the films are too small to be filled with solid lubricant, and the surface porosity of the films is quite small [16−17]. It is necessary to enlarge the pores of AAO before the self-lubricating treatment.

In this work, the structure and composition of the anodized films were analyzed. The influence of pore-enlargement treatment on the porous structure and tribological properties of AAO formed in oxalic acid solution was investigated. After the pore-enlargement treatment, the method of ultrasonic impregnation technology was proposed to prepare self-lubricating surface, and the tribological property is also measured with a pin-on-disk type wear tester.

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2 Experimental

2.1 Anodization

The high-purity aluminum plate (thickness of 0.25 mm, purity of 99.999%) was cut into pieces with 28 mm in diameter, and annealed for 3 h in vacuum. Then, they were washed in acetone by ultrasonic. To decrease the surface roughness, they were immerged into a mixture of perchloric acid and ethanol absolute (1/4 perchloric acid + 3/4 ethanol absolute), and polished for 2 min under 8 V voltage by electrochemical method.

The two-step oxidation of high purity aluminum wafer was carried on in 0.3 mol/L oxalate acid solution for 4 h, with 40 V voltage provided by a stable electrical source. The samples were immersed in 5% (mass fraction) phosphoric acid solution at 30 °C for 20, 30 and 40 min, respectively. After pore-enlargement treatment, each specimen was washed with ionic water to remove the residual acid and dried in a cold air stream.

2.2 Self-lubrication treatment

One of the specimens was immersed into the boiling water with pH=6.2 for 20 min and a dense non-porous film was obtained. The templates with porous film and non-porous film were immersed in C_{60}-toluol solution at room temperature in the environment of ultrasonic for 10 min. Then it was put in the solution for 2 h, and dried in baking box at 120 °C for 30 min.

3 Tribological test and analysis

The tribological behaviors of the samples were evaluated on a UMT-2 type CETR tribological tester with a self-made pin-on-disk geometry in 40%−50% (relative humidity) atmosphere at ambient temperature under oscillating sliding and dry friction conditions.

The steel pin was made of GCr15 bearing steel (HRC 59−61) with a diameter of 4 mm, and the pin was carefully ground and polished with a roughness smaller than 0.025 μm. The reciprocated stroke magnitude was 10 mm and the average travel speed was 20 mm/s. The normal load was 5 N. The wear tests were run for 30 min corresponding to a sliding distance of 36 m.

Hardness test was carried out on a micro-hardness tester, with a load of 0.98 N and a holding time of 15 s. The micro-morphologies of self-lubricating surfaces were measured with a high resolution scanning electron microscope (SEM). The wear volumes of the films were measured with an optical surface profilometer.

3.1 Analysis of AAO template

Figure 1 shows that the microhardness of each AAO template is Hv475.6, Hv394.9, Hv285.9 and Hv164.3 when the duration of pore-enlargement treatment is 0, 20, 30 and 40 min, respectively. The hardness of the AAO template decreases with the duration of pore enlargement.

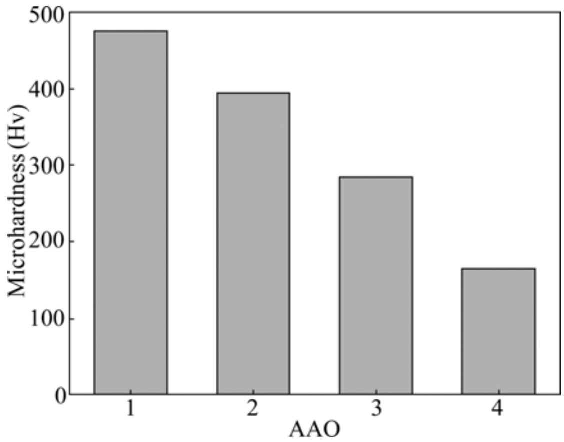

Fig.1 Hardness of AAO template with and without pore-enlargement treatment: 1—AAO; 2—AAO with 20 min pore enlargement treatment; 3—AAO with 30 min pore enlargement treatment; 4—AAO with 40 min pore enlargement treatment

The SEM images show the effect of the pore-enlargement treatment on the porous structure of the film. The diameter of the pores increases with the duration of pore-enlargement treatment. The shape of the pores changes from irregular round to regular round. The surface porosity of the films increases from 13% to 30%, 50% and 70% when the duration increases from zero to 20, 30 and 40 min, respectively. After pore-enlargement treatment for 40 min, the pores changes from round to hexagonal, and the diameter of the pores increases to 90 nm.

As the tester is of on pin-on-disk geometry, after the test wear scar of each film was observed with a surface profilometer, the depths of wear scar for four surfaces are shown in Fig.3. The depth of wear scar increases as the duration of pore-enlargement treatment increases from 0 to 40 min, with a rapid increase at 30 min, but there is almost no increase when the duration of pore-enlargement treatment is 20 min.

Figure 4 shows the effect of frictional coefficient of the films, when the pores are enlarged for 20 min. The frictional coefficient decreases and the shape of the pores changes from irregular round to regular round, and surface with regular round pores owns better tribological properties. After pore-enlargement treatment for 30 min and 40 min, both frictional coefficients are increased evidently. It has been examined from Fig.2 that extended pore- enlargement treatment makes the cell wall thinned, so the capacity of wall to support normal pressure wall becomes weak. Further enlarging the pores will destroy the porous structure of AAO completely. Thus, AAO with 20 min pore enlargement possesses the regular

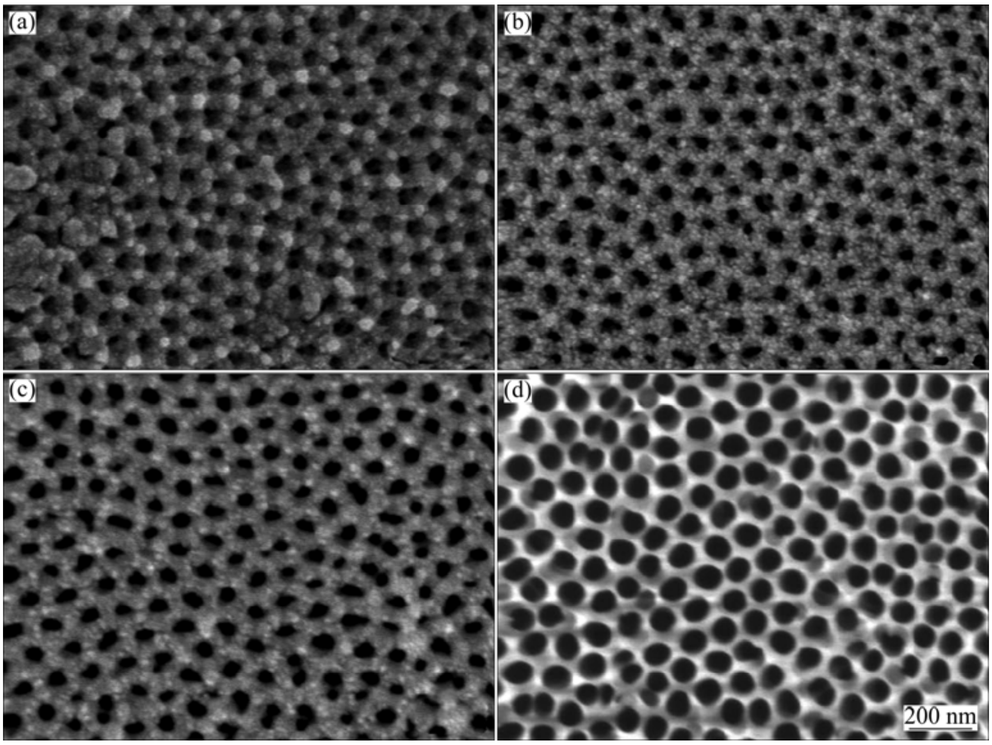

Fig.2 SEM images of pore-enlargement treatment for AAO template surface: (a) 0 min; (b) 20 min; (c) 30 min; (d) 40 min

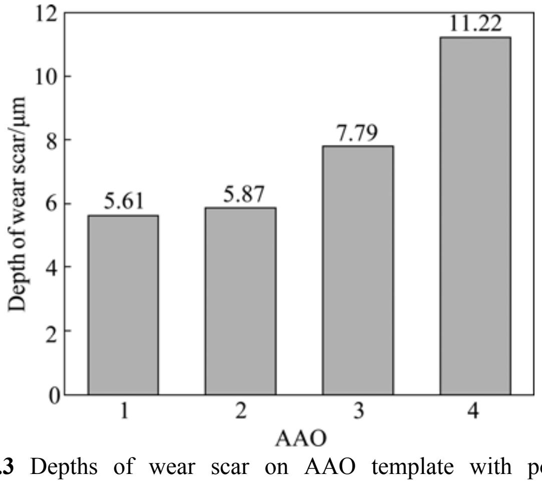

Fig.3 Depths of wear scar on AAO template with pore-enlargement treatment: (a) 0 min; (b) 20 min; (c) 30 min; (d) 40 min

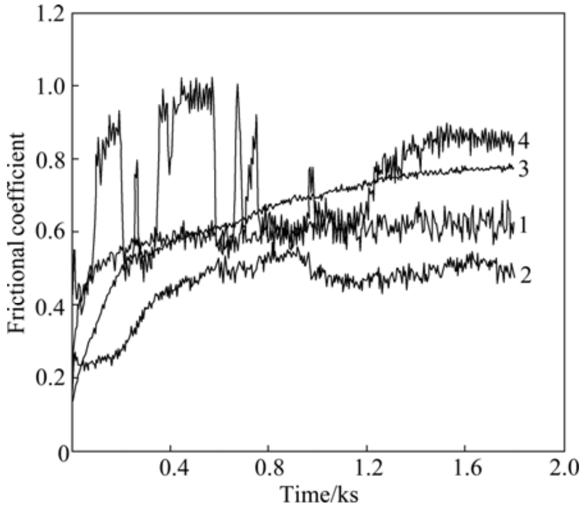

Fig.4 Frictional coefficients of AAO template with pore-enlargement treatment: 1—AAO; 2—AAO with 20 min pore enlargement treatment; 3—AAO with 30 min pore enlargement treatment; 4—AAO with 40 min pore enlargement treatment

surface texture and fine tribological properties. In order to maintain a good tribological property of AAO, 20 min should be the optimum duration time for pore-enlargement under our experimental conditions. The diameter of the pores and the surface porosity of the film are about 70 nm and 30%, respectively. At the same time, AAO still retains relatively high hardness and good wear resistance.

3.2 Analysis of self-lubricating porous aluminum films

Because of the excellent hardness of C_{60}, the microhardness of self-lubricating porous aluminum films reaches Hv630.7. Figure 5 shows the SEM image of porous AAO template impregnated with C_{60}. The part directed by arrow shows that some nanoholes have been filled up by nano-like material. Figure 6 gives the frictional coefficient of porous AAO template, porous AAO template ultrasonic impregnated with C_{60} particles and non-porous AAO template ultrasonic impregnated with C_{60} particles. It is shown that the frictional coefficient of AAO is 0.52, and the lower frictional coefficients are obtained after self-lubricating treatment by the ultrasonic impregnation method. The frictional coefficient of non-porous membrane by ultrasonic impregnation is very low at the first stage of friction, but soon after it increases to a higher level than that for ultrasonic impregnated porous template and closes to that of anodic oxide coating. However, the frictional coefficient of ultrasonic impregnation coating of porous AAO is more uniform in the whole friction processing and its average value (about 0.18) becomes the lowest of the present tests.

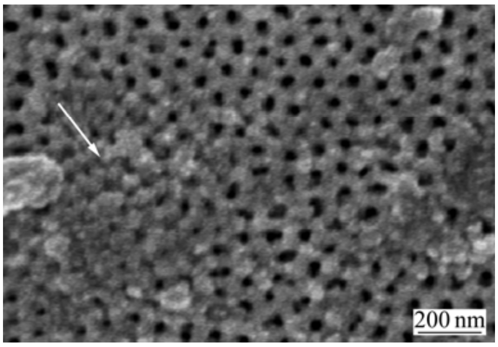

Fig.5 SEM image of porous AAO template impregnated with C_{60}

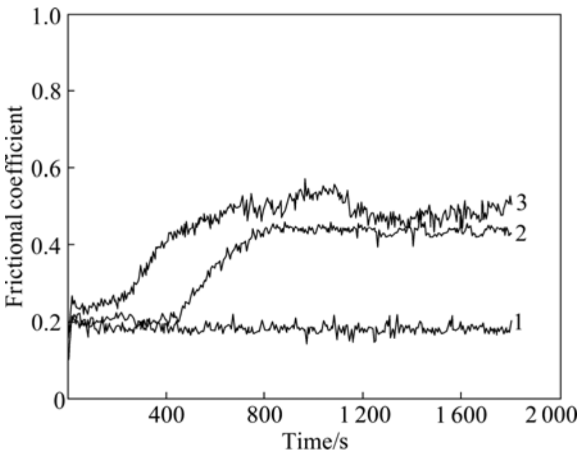

Fig.6 Frictional coefficients of self-lubricating treatment on AAO template surface: 1—Ultrasonic impregnation film/porous AAO; 2—Ultrasonic impregnation film/boiling seal AAO; 3—Porous AAO

It is believed that C_{60} nanoparticles will be embedded in the nanopores during friction and wear by compressive stress. Thus, the C_{60} nanoparticles play a role of decreasing the friction coefficient. As shown in Fig.6, the ultrasonic impregnation lubricating treatment to porous and non-porous AAO templates decreases the frictional coefficient. For the non-porous AAO template, there is only a small fraction of C_{60} on the surface of membrane; therefore, its frictional coefficient is low at the initial stage, but increases rapidly after 400 s because the C_{60} particles on the surface of AAO have been exhausted almost by matched surface completely. For the porous AAO template, the C_{60} particles move randomly under the effect of ultrasonic wave and some are embedded deeply into the holes. During sliding, the AAO surface with embedded C_{60} particles in the numerous nanoholes become possible to form transfer film between the AAO and the steel pin; a low friction coefficient can, therefore, be kept till 1 800 cycles. It is considered that the nanopores on the surface can serve as the reservoirs for the C_{60} nanoparticles.

It is shown from the present experiments that the abrasion of self-lubricating porous film is quite light, and the depth of wear scar is only 4.82 μm. In Fig.7, the SEM images of worn surface on the counterpart show that the worn surface becomes smooth after the self-lubrication treatment. This indicates that the C_{60} particles with porous AAO are beneficial to reducing the counterpart wear.

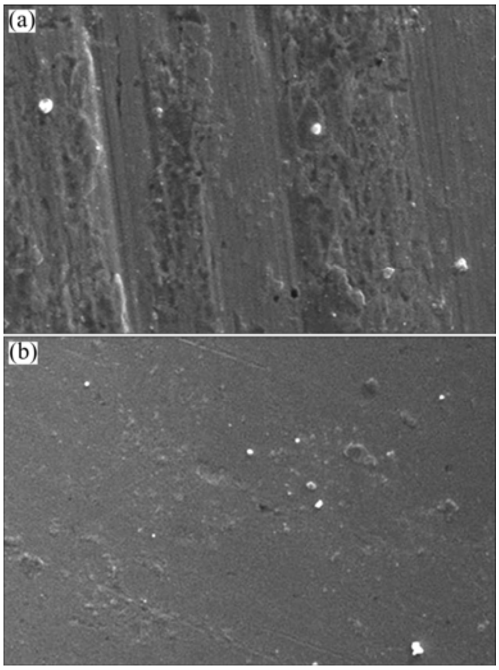

Fig.7 SEM images of worn surface for steel pin: (a) Before self-lubricating treatment; (b) After self-lubricating treatment

4 Conclusions

1) In the pore enlargement treatment, the shape of the pores changes from irregular round to regular round, then from regular round to hexagonal with the duration increases from 0 to 40 min. AAO with 20 min pore enlargement treatment retains relatively high hardness and good wear resistance, and possesses regular round surface texture and fine tribological properties.

2) The sphere-like C_{60} nanoparticles can be embedded into the nanoholes of anodic oxide film by using ultrasonic impregnation, which can decrease the friction between the AAO template and the steel pin. Its frictional coefficient is decreased to 0.18, which is lower than that of the anodic aluminum oxide template. As well,

the porous AAO template impregnated with C_{60} nanoparticles is beneficial to reducing the counterpart wear.

3) The nanopores on the anodic oxide film surface can serve as the reservoirs for the C_{60} nanoparticles, thus the porous anodic oxide film can hold the low frictional coefficient for much longer period compared with the non-porous film.

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