FRICTION PROPERTIES OF ARRAY FILMS OF AMORPHOUS CARBON NANORODS PREPARED BY DUAL-CATALYST GROWTH ON POROUS AAO MEMBRANE

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ABSTRACT
The array films of amorphous carbon nanorods were prepared by thermal catalytic pyrolysis of acetylene at 650°C on a porous anodic aluminum oxide (AAO) membrane with Co-Ni catalysts. The morphology and microstructure of the array films were examined by scanning electron microscopy (SEM) and Raman spectroscopy. The friction properties of array films of amorphous carbon nanorods were investigated using a ball-on-disk tribometer and a friction force microscopy (FFM) in ambient air. The friction coefficients of the array films were influenced by the graphitization degree of the amorphous carbon nanorods. The amorphous carbon film with high graphitization degree showed low friction coefficient.

INTRODUCTION
Aluminum and its alloys are promising candidates for engineering application in many aspects. However, high friction coefficient, poor wear resistance and low seizure load of aluminum alloys are a major drawback for applications that require sliding contact. Recently, a technique of forming self-lubricating aluminum alloys using porous anodic aluminum oxide (AAO) as lubricant reservoirs has attracted more interests. The incorporation of solid lubricants, such as MoS₂ particles, and carbon nanotubes or nanofibers, into the pores of AAO membrane on aluminum substrate reduced friction significantly under dry sliding conditions.

Amorphous carbon (a-C) film can have chemical inertness and extraordinary mechanical properties, making it useful for protecting metal objects from scratching and mechanical attack. The graphitization degree of the amorphous carbon has an effect on the friction properties. In this present work, the array films of amorphous carbon nanorods with different degrees of graphitization were synthesized by thermal catalytic pyrolysis of acetylene on porous AAO membrane through adjusting the atomic ratio of Co and Ni in dual catalysts. The friction properties of the array films in ambient air were examined using a ball-on-disk tribometer and a friction force microscopy (FFM).

1. EXPERIMENTAL
Specimens of 99.999 % purity aluminum, with 30 mm in diameter and 2 mm in thickness, were cleaned by ultrasonic oscillation and electropolished. The specimens were then anodized at a constant cell potential 40 V at 15°C in a solution of 0.3 M H₂C₂O₄ for 40 min. The specimens were re-anodized at the same potential and temperature for 3 h, and then immerged into H₃PO₄ to enlarge the pore diameter.

Co-Ni dual catalysts were electrodeposited in the ordered nanopores of the AAO membrane in an aqueous solution of CoSO₄·7H₂O and NiCl₂·6H₂O, stabilized with H₃BO₃ in ac 15 V. The array films of amorphous carbon nanorods were synthesized by catalytic pyrolysis of acetylene on the AAO membrane in an acetylene-nitrogen mixture (1: 1) at 650°C for 30 min in a quartz tube reactor.

The friction properties of array film of amorphous carbon nanorods were investigated by a ball-on-disk tribometer and a friction force microscopy (FFM) in air (RH 45%) at room temperature. For the ball-on-disk tribotester, the as-deposited film specimens served as the disk, and the match ball fabricated by quenched-and-tempered steel was 3 mm in diameter. The tests were performed at an applied load of 490 mN and a sliding velocity of 0.1 m·s⁻¹. For the FFM measurements, the micro-friction force signals were obtained by scanning the tip at a constant tip velocity of 1.5 µm·s⁻¹ and at normal loads of 8 nN-50 nN.

2. RESULTS AND DISCUSSION
A typical SEM image of AAO membrane after pore-enlargement is shown in Figure 1. These pores on the AAO membrane are uniform size and take an ordered arrangement with honeycomb structure. The diameter of pore was about 90 nm, and the thickness of AAO membrane was about 4 µm.

Figure 2 shows a cross-sectional SEM image of carbon nanorod arrays synthesized with the dual catalyst (Co to Ni ratio of 1: 4) on AAO membrane. The carbon nanorods on AAO membrane are vertically aligned, and the thickness of the array film is about 3 µm. The same morphologies of array films were also observed after synthesized with other dual catalysts.
A typical Raman spectrum of array film of carbon nanorods synthesized with the dual catalyst was composed of two peaks around 1340 cm\(^{-1}\) (D-peak) and 1580 cm\(^{-1}\) (G-peak). In general, the relative intensity of the D band to G band could be used to evaluate the degree of graphitization, and was inverse proportion relation. The ratio of \(I_D/I_G\) in the Raman spectrum was about 1.216, which indicated that the carbon nanorods presented mainly amorphous structure. The decrease in the ratio of \(I_D/I_G\) was observed with increasing the atomic ratio of Co to Ni in the dual catalysts.

Measured by the ball-on-disk tribotester, the mean friction coefficients of the aligned films synthesized with dual catalysts with the Co to Ni ratios of 1: 4, 1: 1 and 4: 1, were 0.26, 0.24 and 0.23 in turn. The aligned amorphous carbon nanorods were squeezed and formed a smooth superficial layer with low interfacial shear strength on the Al substrate during sliding.

The micro-friction force signals of the array films versus load obtained by FFM measurements are shown in Figure 3. The micro-friction force signals increase almost linearly with the load within the applied normal load of 8 nN-50 nN. According to the principle of FFM, the slope of the friction force plot is referred to the friction coefficient factor, equivalent of the friction coefficient. The friction coefficients of the array films synthesized with dual catalysts containing the Co to Ni ratios of 1: 4, 1: 1 and 4: 1 are approximately 0.135, 0.127 and 0.116, respectively. It is evident that the array film of amorphous carbon nanorods with high graphitization degree shows low friction coefficient.

Figure 4 shows a FFM image obtained on the array film synthesized with dual catalyst containing Co to Ni ratio of 4: 1 at a normal load of 35 nN. The view of FFM image is highly smooth, indicating that the friction force on the array film of amorphous carbon nanorods is uniform. There were no obvious detached carbon nanorods observed when the maximum load was used during the micro-friction tests. It is believed that the array films of amorphous carbon nanorods have a high wear resistance under relatively lightly-loaded conditions. These results indicate that the amorphous carbon nanorods produce the lubricating layer on the surface of aluminum substrate.

3. CONCLUSIONS

(1) The array films of amorphous carbon nanorods with different degrees of graphitization were synthesized by thermal catalytic pyrolysis of acetylene on AAO membrane through Co-Ni dual catalysts. The friction properties of array films were influenced by the graphitization degrees of amorphous carbon nanorods. The aligned film with high graphitization degree showed low friction coefficient.

(2) The array films had low friction coefficient and high wear resistance under relatively lightly-loaded conditions due to the self-lubricated effect.

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