Tribology International 103 (2016) 388–393

Contents lists available at ScienceDirect

Tribology International

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

Ultra-low friction properties of carbon nitride tantalum coatings in the atmosphere

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ARTICLE INFO

Article history:
Received 6 April 2016
Received in revised form
15 July 2016
Accepted 20 July 2016
Available online 28 July 2016

Keywords:
CNx
Tantalum
In atmosphere
XPS

ABSTRACT

In this research, a tantalum (Ta) addition to the Carbon Nitride (CNx) coating was focused on to obtain its high hardness and a low-friction coefficient by varying the graphite-like structure at the topmost surface. A CNx:Ta coating was synthesized by a co-sputtering technique with tantalum set on a carbon target, and then XPS analysis was conducted for a better understanding of chemical bonding. The friction test was conducted in the atmosphere, and basic mechanical property of hardness was measured by Nanoindentation hardness tester. The XPS analysis revealed that TaC and TaNx in the coating bonded with some sort of oxygen and also TaC and TaNx did not strongly interact with the carbon structure. The friction coefficient of $CN_{0.22}$:Ta was observed to be 0.01–0.02 with a built-up transfer layer on the counter material's surface.

1. Introduction

Low friction-coefficient materials are in demand in the automobile industry to reduce energy loss. Reducing energy consumption is one of the most important factors in the development of a passenger car [1]. Many automobile parts are lubricated by oil, which is circulated by a pumping system to prevent wear of points of contact, and to reduce friction or frictional heat. However, elimination of this pumping system can reduce the vehicle's weight and increase the room in the engine compartment. Diamond-related materials such as diamond-like carbon (DLC) have the potential to offer low surface roughness, high hardness, chemical inertness, low friction without lubrication, and so on. Several researchers reported ultra- or super-low friction coefficients. Hydrogenated amorphous carbon (a-C:H) showed a friction coefficient on the order of 0.01 in dry nitrogen [2,3]; in high vacuum [4,5], amorphous carbon nitride (CNx) also achieved this friction coefficient [6]. These low friction mechanisms are still under discussion; topics have included repulsive-force generation at the interface of an a-C:H/a-C:H contact [2,3], the role of hydrogen atoms in terminating the dangling bond of a-C:H [5], and the construction of a graphite-like layer on the topmost surface of the coating owing to friction [7,8]. Although these carbon materials have desirable low-friction properties, almost all of them still show a relatively high friction coefficient in atmosphere [9,10]. The factors obstructing low friction included the existence of dangling bonds without termination by hydrogen atoms [11], lesser passivation of the DLC surface by gas or water molecules in atmosphere than in vacuum [12], a tribofilm formation with a small amount of hydrogen [13], or oxygen/water molecules playing an important role in reacting with the transfer layer on the counter pair [14]. Conversely, DLC that uses oxygen from the atmosphere to hydrate-Si–O–Si-chains to reduce the friction coefficient has been newly developed [15]. From the view point of gaining a low friction coefficient in the atmosphere, it is necessary to prevent chemical reactions between DLC and oxygen or water molecules beneath the contact. One of the strategies for obtaining such truly chemically inert DLC is to use tetrahedral amorphous carbon (ta-C) because of its high hardness and its C–C single bond, which is also known as a sigma bond. The other strategy is to alloy DLC with some element [16–21]. Previously, the authors conducted friction tests on tantalum-containing a-C coatings (TaC/aC) under atmospheric conditions [22]. The TaC coating showed a friction coefficient of approximately 0.05 in atmosphere. This result indicates that the added element reduced the friction coefficient.

From the view point of a solid lubricant, the hardness of a material is important for reducing the contact area between a ball specimen and a disk specimen under an elastic contact situation. A low-friction coefficient was provided by a thin soft layer on the disk specimen [23]. Therefore, if some elements are added to gain

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http://dx.doi.org/10.1016/j.triboint.2016.07.015
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a low friction coefficient, it is necessary to maintain the material's hardness; moreover, the thin film of low shearing strength at the topmost surface plays an important role. The previous result for carbon nitride (CNx) indicated that nitrogen atom desorption occurred when the CNx slid against the silicon nitride (Si_3N_4) ball because of a weak bonding between C and N, approximately 10 nm from the surface, which was a graphite-like structure, and it provided a low-friction property [24]. In this study, we focused on a tantalum addition to the CNx coating (forming so-called CNx:Ta) to obtain hardness [25,26] and a low-friction coefficient by varying the graphite-like structure at the topmost surface.

2. Experimental

2.1. Materials and deposition process

Electron cyclotron resonance sputtering equipment (Elionix, EIS-200) was used to alloy a CNx:Ta coating onto a silicon wafer (Si (100), 50 mm diameter, and 0.35 mm thickness) by a co-sputtered technique of carbon and tantalum. A schematic image of the sputtering system is shown in Fig. 1(a), and carbon target (the ash is less than 20 ppm) and the tantalum (Ta) target of 1.0 mm thickness (99.99% purity, separated from foil by cutting) are shown in Fig. 1(b) and (c). An argon and nitrogen gas mixture was introduced to the vacuum chamber as ionization gas exited by microwaves (2.45 GHz) from the power source, and the Ar/N_2 plasma was extracted by an electrode set at in front of the target, forming an ion beam. The Ar and N_2 gas flow was set to 8.4×10^{-9} m^3/s. The Ta content varied by the target area, which was set to 0, 5.0 and 7.5 mm^2 on the carbon target. The deposition process time was 120 min. The applied ion beam acceleration voltage was 2.0 kV. The microwave power was 100 W. Before the deposition process, the vacuum chamber was evacuated to 1.5×10^{-2} Pa, whereas the Si(100) substrate was heated to 260 °C starting 15 min before deposition began and lasting until end of deposition to reduce the adsorption of water molecules on the surface. The CNx:Ta coating thickness was approximately 200 nm.

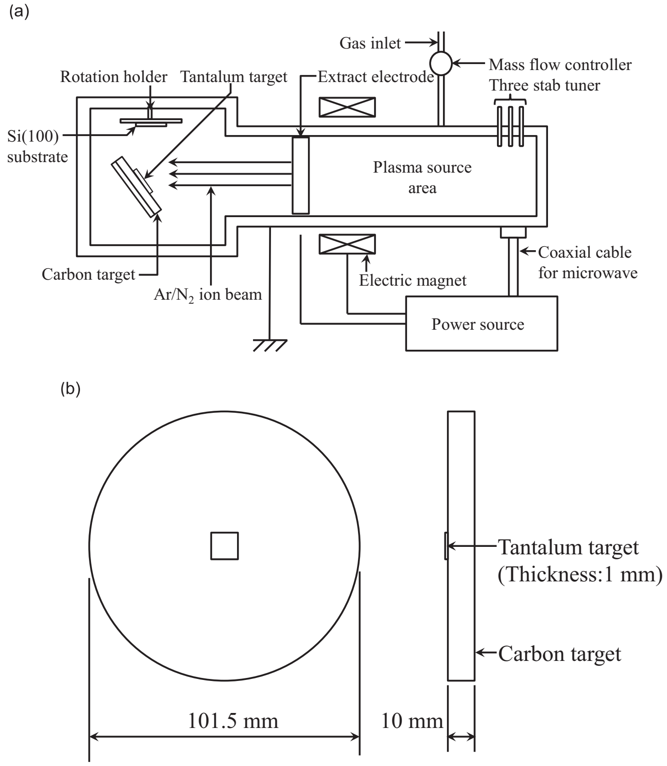

Fig. 1. Schematic images of (a) sputtering equipment of the electron cyclotron resonance system and (b) target size and shape of carbon and tantalum.

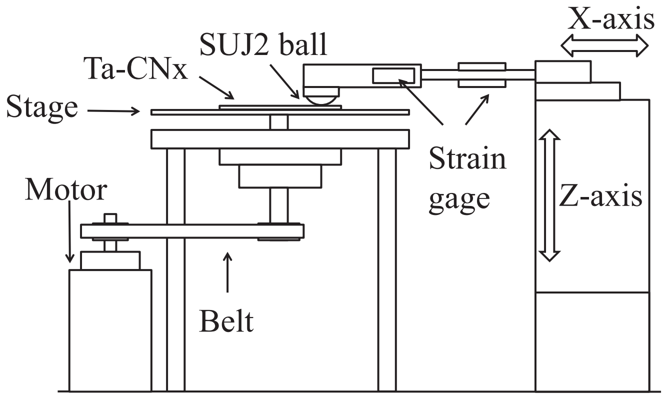

Fig. 2. Schematic image of the ball-on-disk type friction tester.

2.2. Ball-on-disk friction test and counter material

A friction test was performed by a ball-on-disk (BoD) friction tester whose schematic image is shown in Fig. 2. The CNx:Ta specimen was set on a rotatable specimen holder. The holder was connected to a rotating shaft, belt, and motor. The motor was put on a separated area to reduce the effect of its vibration on the friction results. The counter material was a stainless steel (SUJ2) ball with an 8 mm diameter. The ball was held by a ball holder, which was connected to leaf spring-type force measurement equipment. The force was measured by elastic deformation of these leaf springs (on which strain gauges were equipped), and the strain value was transformed into a voltage value at the amplifier. In this study, a normal load was applied at 8 N, and the sliding speed was set to 62.8 mm/s. Also, a friction test was conducted in air from 8% to 15% humidity and a temperature of 23 °C. The friction test was continued for 15,000 cycles and then completed. After the friction tests, the balls and CNx:Ta specimens were observed by optical microscopy and auger electron spectroscopy.

2.3. XPS, AES analysis, and nanoindentation hardness

The chemical bonding of carbon, nitrogen, and tantalum was analyzed by X-ray photoelectron spectroscopy (XPS, ULVAC-PHI, Quantum 2000) before the friction tests. The incident X-ray was Al-Kα, 15 kV, and 25 W with 0.1 eV step acquisition. The XPS analysis was only conducted on the as-deposited area because its spatial resolution was wider than the wear track. Therefore, auger electron spectroscopy (AES, Perkin-Elmer, PHI-650) analysis was conducted because it had the SEM observation ability to distinguish between the inside and the outside of the wear track. The acceleration voltage was 5 kV, and the current was 100 nA. Before the XPS analysis, presputtering was conducted to clean the surface using an Ar ion beam equipped with the XPS.

The nanoindentation hardness was measured by ENT-1000a (Elionix, with Berkovich-type indenter) with an indentation load of 200 μN, and 20 measurement points were selected with a distance of at least 30 μm from each indentation position to eliminate the plastic deformation effect. The highest and lowest hardness values and noisiest data were removed from these 20 points, and then the measurement values were averaged.