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Nanomechanical and boundary lubrication properties of titanium carbide and diamond-like carbon nanoperiod multilayer and nanocomposite films

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ABSTRACT

To develop a new low friction and wear resistant coating, nanometer period TiC and DLC multilayer films composed of titanium carbide and hydrogen-free diamond-like carbon (DLC) layers were deposited by bias rf sputtering. Nanoperiod multilayer films were deposited by controlling the opposing time of the substrate to each of the titanium carbide and graphite targets. Below the 6-nm target layer period, nanocomposite films with nm-scale particles were deposited. Above the 12-nm target layer period, multilayer films were deposited. The nanoindentation hardness and nanowear resistance of the nanoperiod multilayer (TiC/DLC)n films change with the layer period. The 12-nm-target-period (TiC/DLC)n film shows higher hardness and nanowear resistance. The dependence of boundary lubrication properties on target period under poly (alpha-olefin) (PAO), PAO with glycerol monooleate (GMO) and water was investigated by an oscillating tribotest. The boundary lubrication properties of the (TiC/DLC)n films are significantly improved compared with those of the DLC monolayer film. Moreover, the hard and nanowear-resistant 12-nm-target-period multilayer film shows the lowest friction coefficient and a small damage depth under boundary lubrication using PAO, PAO with GMO and water. It is deduced that the 12-nm-target-period multilayer (TiC/DLC)n film has the shortest period and the largest number of interfaces that prevent damage elongation, and it is hard and shows superior nanowear resistance.

1. Introduction

A wear-resistant, lubricating film is desired to reduce wear and friction force fluctuations. One candidate is a carbonaceous film such as a diamond or diamond-like carbon (DLC) film, which has wear resistance and lubrication properties [1,2]. DLC films show an extremely low friction owing to a tribochemical reaction layer [3]. The addition of other elements to DLC films is considered to compensate for the deficiencies of DLC films. The fabrication of DLC films containing silicon and other elements at the interface between substrates and films has been proposed. The tribological properties of these DLC films were investigated [2–7].

As additive materials in DLC films, metals, such as tungsten (W), titanium (Ti), zirconium, hafnium, and molybdenum, which can form high-strength carbides in DLC films, are considered. The use of such methods is expected to improve tribological properties, such as film strength, if high-strength carbide can be formed in the defective parts of the carbon network [4]. Metals, such as W, Ti and ferrous (Fe) in DLC films, can improve boundary lubrication properties [5,6]. Furthermore, the boundary lubrication properties of various films were also evaluated [7–10]. For instance, in an attempt at the fuel-efficiency minimization of automobile engines by decreasing friction, the coating of DLC films on the shim of a follower series has been investigated [11–13]. In engine oil, the effect of friction decrease has been observed on shims coated with DLC films, and the lubrication properties of these films were compared with those of other coatings such as titanium nitride films; an excellent advantage of coating with hydrogen-free DLC films was obtained [11–14].

On the other hand, lubricants, such as poly (alpha-olefin) (PAO) with glycerol monooleate (GMO), are capable of providing a significant reduction in friction, through the improvement in the lubrication property of hydrogen-free DLC films under boundary lubrication [13]. Hydrogen-free DLC films containing metals, such as cobalt (Co), cerium (Ce), magnesium (Mg), nickel (Ni), and Ti, which are expected to react with PAO and GMO additives, were deposited. The boundary lubrication properties of these metal-containing DLC films were investigated to clarify the effect of metal addition to hydrogen-free DLC films [12,14].

Research on the development of nanoperiod multilayer and nanocomposite films has recently been carried out to improve the mechanical properties of the films [15,16]. For example, it was found that the hardness of these multilayer films was significantly improved compared with that of monolayer films. The hardness enhancement mechanism of a superlattice film is based on the restriction of dislocation movement within and between layers in the superlattice film [15]. In our previous study, a nanoperiod (CN/BN)n multilayer film was deposited in order to improve mechanical properties [17]. The dependence of

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wear properties on the number of sliding cycles indicates that wear resistance increased at the interface between the CN and BN layers of the multilayer films [18].

Generally, the friction coefficient μ is approximately proportional to the ratio of the shearing strength S to the hardness H [19]. To realize low-friction boundary lubrication, the hardness H must be increased and the shearing strength S must be decreased. To apply these multilayer films in the field of solid lubricants, we proposed nanoperiod multilayer solid lubricant films, whose friction should be lower than that of conventional solid lubricants since the hardness and Young's modulus increase in the laminating direction and the shear resistance remains low in the sliding direction [20–22]. Therefore, it is considered that the friction coefficient will decrease with the increases in hardness and Young's modulus, if the shear resistance can be maintained approximately parallel to the substrate. For this reason, our research is focused on the deposition of solid lubricant films that have a lower friction coefficient than monolayer films. It has been clarified that nanometer-period multilayer $(C/BN)_n$ films with carbon and BN layers [20] and $(WS_2/MoS_2)_n$ films with WS_2 and MoS_2 layers [21] have much better tribological properties than monolayer films. $(DLC/Au)_n$ multilayer films composed of hydrogen-free DLC and gold layers have superior boundary lubrication properties under water and PAO both with and without GMO [22].

Nanoperiod multilayer films composed of TiC and DLC are expected to have a higher hardness and a lower shearing strength due to a tribochemical reaction layer. The TiC top layer tribochemically is expected to react with the lubricant additives and produced a tribochemical reaction layer under boundary lubrication.

In this study, to realize low friction and long lifetimes under boundary lubrication, the titanium carbide and hydrogen-free DLC nanoperiod multilayer films are deposited, and their nanomechanical and boundary lubrication properties are evaluated.

2. Experimental methods

2.1. Deposition and analysis of films

Multilayer films composed of TiC and DLC were deposited by rf bias sputtering, which supplied high-frequency powers to both the target and the substrate. 13.56 MHz RF powers of substrate and target were nearly 45 and 400 W, respectively. Ar gas pressure is 2 Pa. Substrate bias voltage is −150 V. Two semicircular targets, graphite and titanium carbide, were used. A film was deposited by rotating a substrate, and two semicircular targets were set to alternately face the substrate in an Ar gas atmosphere. TiC and DLC layers were deposited on the Si surfaces that were opposite the titanium carbide and graphite targets, respectively. In the case of multilayer film deposition, the substrate was first set opposite the graphite target, and then rotated until the substrate was opposite the TiC target. The DLC layer was deposited first, and then the titanium carbide layer was deposited. A TiC layer was deposited as the topmost layer of the (TiC/DLC)n film to improve the boundary lubrication properties and to make the site on the surface react with the lubricant additives.

In this study, 3-, 6-, 12-, 18-, 24- and 30-nm-target-period multilayer films were deposited by controlling the deposition time. The total thickness of the DLC and TiC monolayer and (TiC/DLC)n multilayer films was set to be nearly 250 nm. Before the deposition of the DLC and TiC film, a substrate was pretreated by Ar sputtering in order to clean its surface. To control the thickness of each TiC and DLC layer, the deposition rate of each material was evaluated by examining the difference between the steps with and without coverage. The time period in which a substrate was held facing each target was determined by the deposition rate. The sputtering deposition rate of the TiC film is nearly twice that of the DLC monolayer film. Therefore, to obtain the proper Ti concentration, we deposit three times thicker DLC, because the TiC monolayer film showed higher friction. Therefore, to obtain a DLC layer with a thickness that is three times that of a TiC layer, the time for which the substrate was controlled to be opposite the graphite target was nearly six times that for the TiC target.

The structure and composition of deposited multilayer films were evaluated by transmission electron microscopy (Hitachi HD-2000 STEM, accelerating voltage; 200 kV) and Raman spectroscopy (JASCO NRS-1000DT Raman spectrophotometer, 532 nm) The composition of these films was analyzed by Auger microscopy (JEOL JAMP 7800 F).

2.2. Evaluation method

2.2.1. Nanoindentation test

To evaluate the nanoindentation hardness of the thin (TiC/DLC)n multilayer films, the nanoindentation properties of these films were investigated using an AFM device (Digital Instruments Nanoscope III) together with a nanoindentation measurement system (Hysitron Inc.) [15,23]. The radius of the Bercovich diamond indenter (a three-sided pyramid) is approximately 100 nm. The diamond indenter is regularly checked using a quartz standard sample. The nanoindentation hardness of the films was measured under 20–25 °C and 30–50% humidity conditions.

The hardness was derived from load–indentation curves. These films were as thin as 250 nm. The test was performed with a loading time of 20 s at 100 μN load. Here, the hardness was evaluated from the plastic deformation depth. The plastic deformation depth was evaluated from the intersection point of the x-axis and the straight line fitting from the appropriate unloading curve [17,18].

2.2.2. Nanowear test

The nanowear test was carried out to evaluate the nanometer-scale wear resistance of multilayer and DLC monolayer films using the AFM device, as shown in Fig. 1(a). The diamond tip was slid against the specimen surface by a Piezoelectric ceramic materials (lead zirconate titanate; PZT) scanner. The PZT scanner moved the sample for contact, loading and scanning [17,18]. The test conditions used were as follows: the radius of the Berkovich diamond indenter tip was nearly 200 nm, the applied loads ranged from 20 to 50 μN, the scan area was $500 \times 500\ nm^2$, and the friction speed was 4.0 μm/s. The nanowear was measured using the AFM device from the change in surface profile measured at a load of less than 1 μN after the nanowear test. To avoid the change of the tip profile, the surface profiles are evaluated by standard specimen before and after the nanowear test. To remove adhesion material, the tip slid with DLC monolayer films after each nanowear test. To carry out this measurement, the average depth of nanowear was evaluated.

2.2.3. Evaluation of boundary lubrication properties

An oscillating friction tester (Optimol Instruments SRV4) was used to investigate boundary lubrication properties, as shown in Fig. 1(b). To evaluate the boundary lubrication properties of the deposited (TiC/DLC)n nanoperiod multilayer films, an oscillating sample was pressed on a 6-mm-diameter ball. We used the ball made of martensitic stainless steel (SUS440C), the hardness is 58 HRC, and the centerline average area roughness, Sa, and maximum area roughness, Sy is 5.7 nmSa and 83 nmSy, respectively. We tested DLC coated sample and uncoated SUS440C ball, to obtain the good boundary lubrication [9]. We measured the friction force using a friction sensor. The dependence of friction on the number of oscillation cycles was evaluated. Tests were performed under the boundary lubrication of PAO with or without 1 mass% GMO additive, and distilled water besides them. 2 ml lubricant was supplied to the surface. The test conditions used were as follows: load, 10 N; amplitude of oscillation, 500 μm; sliding speed, 50 Hz; total number of oscillation cycles, 30,000; temperature, nearly 20 °C. The friction coefficients were evaluated