Influence of carbon content on the microstructure and tribological properties of TiN(C) coatings in water lubrication

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ABSTRACT

TiN(C) coatings with different carbon content were deposited on Si(100) wafers and 316L stainless steel disks using unbalance magnetron sputtering (UMS) from Ti and C targets in a mixture of N_2 and Ar gases. The microstructure and phase of TiN(C) coatings were observed and analyzed using field emission scanning electron microscope (FE-SEM) and X-ray diffraction (XRD), and the bonding structures of TiN(C) coatings were analyzed using Raman spectroscopy, X-ray photoelectron spectroscopy (XPS). The friction and wear properties of TiN(C) coatings sliding against SiC balls in water were investigated using ball-on-disk tribometer, and the wear tracks of the TiN(C) coatings were observed using 3D-profilometer and FE-SEM. The results showed that the orientation of TiN (111) changed to TiN(100) with an increase in the C target current while the peak of TiC(400) was observed at the C target current beyond 2 A. When the C target current varied in the range of 1–3 A, the Ti−C, Ti−(C,N),C≡N bonds were observed, whereas the DLC-rich area with C≡C bonds was detected as the C target current higher than 2 A. The hardness of TiN(C) coatings first increased to 32 GPa at the C target current of 1 A, and then decreased gradually with further increment in the C target current. The lowest friction coefficient of 0.24 and the lowest specific wear rate of 3.3×10^{-6} mm^3/Nm were obtained simultaneously as the TiN(C) coatings were deposited at the C target current of 3 A.

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1. Introduction

Currently, the water lubrication systems as a substitute for conventional oil lubrication systems are promising method to resolve the environment pollution of oil lubricant. However, due to the low viscosity of water, the estimated water lubrication films thickness of 70 nm is as thin as 1/100–1/1000 thickness of oil hydrodynamic films [1]. Furthermore, the corrosion induced by water will limit the application of metallic materials in the water lubrication systems. An alternative approach is to take advantage of the metallic materials modified via depositing hard coatings with good lubricity in water environment. As is known, the carbon-based coatings and transition metal nitride coatings are the promising candidates for the sliding parts in water hydraulic systems [2]. In comparison to the transition metal nitride coatings (e.g. CrN [3–5], CrSiN [3], TiCN [5,6] and TiAlN [6]), the carbon-based coatings (such as Diamond [7], DLC

[8–10] and a-CN$_x$ [11–15]) exhibit the lower friction coefficient and lower wear rate as sliding against ceramic and steel balls in water. However, the adhesion of carbon-based coatings on steels was too weak. Actually, the transition metal nitride coatings are widely used as protective coatings against wear and corrosion due to their high hardness, low friction coefficient and high corrosion resistance [16–20]. Among them, the TiCN coatings are very interesting coatings that combine the high hardness and low friction coefficient of the TiC or DLC phases and the high toughness of the TiN phases [21]. Recently, Wang et al. [6] reported that the friction coefficient of 0.17 and the low specific wear rate of 2.3×10^{-6} mm^3/Nm for TiCN coatings were obtained when they slid against SiC balls in water. Actually, the bonding structure and mechanical properties of the TiCN coatings are strongly dependent on the C content in the coatings [21–24]. However, the influence of C content on the tribological properties of TiCN coatings sliding against SiC balls in water has not been studied systematically.

In there, the TiN(C) coatings with varying C content were deposited on Si(100) wafers and 316L stainless steel disks using unbalanced magnetron sputtering (UMS) from Ti and C targets at different C target currents in a mixture of N_2 and Ar gases. The influence of carbon

content on the structure and mechanical properties of TiN(C) coatings was investigated systematically. Optimum deposition parameters for the TiN(C) coatings with excellent tribological properties in water were outlined.

2. Experimental procedures

2.1. Deposition method

Because the TiN(C) coatings deposited on Si(100) wafers were used for the experiments of Raman analysis, XPS analysis, SEM observation and Nano-indentation tests, while those on 316L disks were used for the samples of XRD analysis and friction tests in water. Thus, the TiN(C) coatings were deposited onto both Si(100) wafers and 316L stainless steel substrates simultaneously by closed-field unbalanced magnetron sputtering system (UDP-650, Teer Coatings Limited, UK), in which two pure titanium (Ti) and two graphite (C) rectangular targets were installed. The Si(100) wafers were directly introduced into the deposition chamber without further cleaning whereas the 316L stainless steel disks with dimension of $\Phi30$ mm $\times 4$ mm were ground and polished to a surface roughness of $R_a = 30$ nm using a metallographic polishing machine (UNIPOL-820), and then cleaned ultrasonically in ethanol for 20 min and dried before loading into the deposition chamber. After loading the substrates on substrate holder, the deposition chamber was vacuumed to less than 4×10^{-4} Pa. Before deposition the substrate surface was bombarded for 30 min by Ar plasma generated by glow discharge at a bias voltage of -450 V, and then a pure Ti adhesive layer (~ 0.2 μm) was first deposited onto the substrates for 10 min, followed by the deposition of TiN(C) coatings in a mixture gas of N_2(15 sccm) and Ar(50 sccm) gases. During deposition, the chamber pressure maintained at 0.227 Pa. The substrate holder was rotated at a speed of 10 rpm and the bias voltage applied to the holder was -60 V. The relative concentration of elements in the TiN(C) coatings was controlled via adjusting the target current. The Ti target current was kept at 8 A while the C target current varied in the range of 0–4 A. The total thickness of the TiN(C) coatings was about 1.0 μm.

2.2. Characterization of TiN(C) coatings

The crystal phases of TiN(C) coatings were measured using D8-Advance X-ray diffraction (XRD) (Bruker, Germany) with Cu K$_\alpha$ radiation ($\lambda = 0.15404$ nm). A continuous scan mode was used to collect 2θ data from 10° to 100° at the sampling pitch of 0.02 and the scan rate of 2°/min. The X-ray tube voltage and current were set at 40 kV and 40 mA, respectively and the incident angle of X-ray beam was 0.25°. Besides, the bonding structure and microstructure of TiN(C) coatings were analyzed using Raman spectroscopy (Invia RENSHAW 2000) and X-ray photoelectron spectroscopy (XPS, VG ESCALAB 220i-XL) and observed using a field emission scanning electron microscope (FE-SEM) (Philips FEG-XL30). The elements' content of TiN(C) coatings was determined using X-ray photoelectron spectroscopy (XPS, VG ESCALAB 220i-XL).

The hardness and reduced Young's modulus of TiN(C) coatings were measured using Nano Indenter XP (Nano Instruments, Inc., Oak Ridge, Tennessee). The indentation penetration depth obtained for the TiN(C) coatings was set as 160 nm. The friction behaviors of TiN(C) coatings were investigated using ball-on-disk tribometer in deionized water. The normal load and sliding speed were kept at 2 N and 0.1 m/s, and the total sliding distance was 500 m. The SiC balls with a diameter of 8 mm were used as mating balls, and their hardness, elastic modulus and surface roughness were 22 GPa, 430 GPa and 88.5 nm, respectively. The friction forces were detected by a LMA-A-10N load cell (Kyowa Co. Ltd., Japan). The load cell voltage was measured by a DPM-700B strain amplifier (Kyowa Co. Ltd.,

Japan) and recorded by NR-110/150 data collection system (Keyence Co. Ltd., Japan) with a compatible personal computer. The diameter of balls' wear scar was measured using optical microscope (XJZ-6, China). The cross-section area of wear track for coatings was measured using a Micro-XAM^{TM} non-contact optical profilometer (ADE Phase-Shift, USA). Thus, the specific wear rates for balls and coatings were calculated [11]. The wear tests were repeated for three times to obtain the mean value of wear rates. In order to understand the wear mechanism of the TiN(C) coatings sliding against SiC balls in water, the wear tracks on the TiN(C) coatings were observed using optical microscope and a field emission scanning electron microscope (SEM) (JEOL-JSM-7001F) equipped with EDS (Inca Energy 350, Oxford, UK).

3. Results and discussion

3.1. Composition, chemical bonding and microstructure of TiN(C) coatings

Fig. 1 showed the variation of Ti, C and N concentration with the C target current. With an increase in the C target current, the C content in the TiN(C) coatings increased from 0.99 at.% to 8 at.%, while the N concentration decreased linearly from 53.58 at.% to 41.6 at.%. However, the Ti concentration first increased from 46.4 at.% to 48.5 at.% when the C target current increased from 1 to 3 A, and then decreased to 45.6 at.% at the higher C target current of 4 A. This indicated that the TiN(C) coatings deposited at the higher C target current contained higher C concentration, but the higher C content would hinder the incorporation of N element. Furthermore, the increment of Ti concentration in the TiN(C) coatings deposited at the C target current below 3 A showed that the C atoms promoted the activity of Ti atoms and reacted with Ti atoms more easily than the N atoms did. But the positive effect was circumscribed when the C concentration exceeded a critical value. When the C target current was 4 A, the Ti atoms concentration decreased due to the following reasons: (1) the lower concentration of N atoms resulted in the formation of limited Ti–N bonds; and (2) a large portion of C atoms existed as the amorphous carbon or C≡N bonds rather than the Ti–C bonds [21–23]. These could be proved by the following analysis of Raman and XPS.

Fig. 2 showed the influence of C target current on the Raman spectra of TiN(C) coatings. It is clear that the Raman spectra of TiN(C) coatings could be divided into two regions. One from 100 to 800 cm^{-1} corresponded to titanium carbide/nitride while another from 1200 to 1700 cm^{-1} corresponded to amorphous carbon as the carbon content varied from low to high. When the C target current was below 2 A, there were two peaks in the range of Raman shift from 100 to 800 cm^{-1}. The peak in the acoustical range (150 to
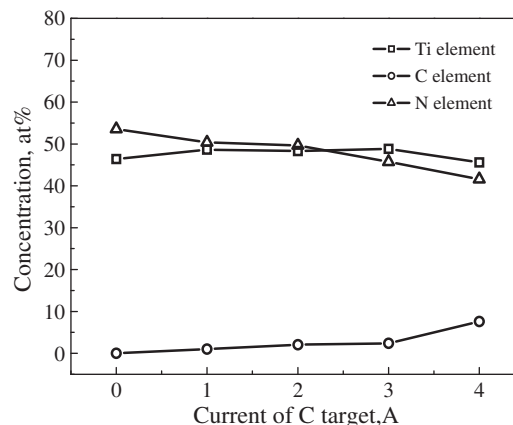

Fig. 1. Variation of Ti, C and N element concentrations with C target current.