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Influence of the C_2H_2 flow rate on gradient TiCN films deposited by multi-arc ion plating

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ABSTRACT

Gradient TiCN films were deposited in the arc ion plating system with Cr and Ti targets under the mixed Ar, C_2H_2 and N_2 gases at a temperature of 480 °C. In this study, the effect of the C_2H_2 flow rate on composition, microstructure, bonding energy, hardness, modulus, elasticity, plasticity, adhesion and tribological behaviors of the deposited TiCN films were systematically investigated. The XRD result showed that all the films exhibited a highly textured growth with the (1 1 1) as the preferred orientation along the surface normal. By increasing the flow rate of C_2H_2, the contents of TiC and TiCN decreased and increased, respectively, which led to a significant decrease in hardness from 62 GPa to 31 GPa. The adhesion strength increased and wear rate decreased due to the decrease of the brittle TiC phase in the films.

1. Introduction

In order to improve the wear resistance of the tools and mechanical components, a number of films have been developed. The two main objectives of surface engineering for tribological applications in components and tooling are: increase wear resistance and modify friction behavior [1]. For tribological applications, it is critical to decrease the coefficient of friction while maintaining the strength and hardness of the films. Hard transition metal nitride and carbide film has long been proven an effective way to improve the tribological properties of the tools due to their high hardness and excellent wear resistance [2–4]. TiC and TiN films have been studied and extensively used as protective layers in the past years, but they can hardly satisfy the requirements when used in some severe conditions. TiCN films are a solid solution of TiN and TiC phases with high hardness, thermal stability, low friction coefficient, excellent wear resistance [5–7], which combines the properties of TiC and TiN, and have been used in many industries.

TiCN films were formed when C atoms added into the TiN crystal lattice, the C atoms can substitute for N atoms in the face-centered cubic structure in any proportion [8,9], so the composition range of TiCN films is rather broad, and the C content has a significant influence on the properties and microstructure of TiCN films. Karlsson et al. [10] synthesized $TiC_{1-x}N_x$ films by arc evaporation and discovered that the intrinsic stress and hardness have a maximum when x was between 0.4 and 0.7. Huang et al. [11] deposited $TiC_{1-x}N_x$ on 316 austenitic stainless steel by a filtered arc deposition system, found that the films showed highly textured growth with the (1 1 1) as the preferred orientation, and the peak center shifts to lower Bragg angles with the increase of C content, they also found that the coefficient of friction was decrease with increasing the content. Cheng et al. [12] showed that for the TiCN films deposited with a large area filtered arc deposition technique, there was an increase in hardness with C content up to maximum at 2.8 at.%, then decreased rapidly. It was predicted that the formation of an optimized TiCN film would have considerable potential in providing an excellent combination of high hardness, thermal stability, and low friction coefficient. Therefore, it has great significance to investigate the influence of the carbon content on TiCN in detail.

In this paper TiCN films were deposited by arc ion plating under various $Ar/N_2/C_2H_2$ gas mixtures, and the N_2, C_2H_2 flow rate was increased during the deposition. Consequently, the films have continuously varying volume fractions and mechanical properties. The composition, bonding ennergy, crystalline structure of the film was characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD). Hardness, elastic modulus, adhesion properties were tested by nanoindentation measurement, Rockwell adhesion, and scratch adhesion tests, respectively. The influence of carbon content on crystalline structure, chemical composition and mechanical properties of TiCN films was systematically studied.

2. Experiment details

2.1. Deposition conditions

TiCN films were deposited in a computer automation ion plating machine model AS700. The machine consists of 12 sets of standard

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Table 1
Synthesis conditions for gradient TiCN layer.

Sample	N_2 flow rate (sccm)	C_2H_2 flow rate (sccm)	Temperature (°C)	Turn (r.p.m.)	DC-bias (V)	Pressure (Pa)
C1	700	35–100	480	3	−150	0.8
C2	700	35–230	480	3	−150	0.8
C3	700	35–350	480	3	−150	0.8

cathodic arc ion evaporators (CAE: 3 groups), auxiliary anodes, vacuum system, heating system, and substrate bias system. The deposition zone is approximately 700 mm in diameter × 300 mm high. In the experiment, the cathodic arc ion evaporators were equipped with 6 titanium targets and 3 chromium targets (all 99.95% purity). High purity argon (99.99%) was used as the sputtering gas, and mixtures of high purity nitrogen (99.99%) and acetylene (99.99%) were used as reactive gases for all the TiCN films.

All the TiCN films were deposited on polished cemented carbide (12 mm × 12 mm × 3 mm, WC 92 wt%, Co 8 wt%) and HSS specimen (12 mm × 12 mm × 3 mm, WC 92 wt%, W6Mo5Cr4V2Al). The samples with HSS substrate were used to investigate the adhesion of the films. Before loading into the deposition chamber, all the substrates were ultrasonically cleaned in acetone, methanol, and dried. After that, the substrates were loaded at a circle planetary substrate holder in the midpoint of the chamber, and the holder typically rotated at a speed of 3 rpm. The distance between the target and the rotating substrate holder was held constant at 250 mm. Prior to deposition, the chamber was pumped down to a base pressure below 4×10^{-3} Pa, and the substrates were heated to 450 °C, then the specimen were subjected to Ar and Ti plasma cleaning under a high substrate bias voltage of −800 V for 17 min. To initiate the film process, the substrate bias voltage was reduced to −150 V, and the temperature was increased to 480 °C. In order to improve the adhesion of the TiCN films, all the specimen were deposited with CrN and TiN gradient layer for 11 min and 33 min, respectively. Both CrN and TiN gradient layers were deposited in a N_2 atmosphere, the mass flow of N_2 was increased from 380 sccm to 400 sccm in the first 11 min, then increased from 400 sccm to 700 sccm when deposited TiN layer. After the deposition of the compositional gradient bonding layer, TiCN films were deposited. In order to acquire films with different C contents, the flow of C_2H_2 was varied, and the films were denotes as C1, C2, and C3. The TiCN layer for C1, C2, C3 was deposited by gradually increasing C_2H_2 flow in a mixed C_2H_2 and N_2 atmosphere from 35 sccm to 100 sccm, 230 sccm, 350 sccm, respectively, and the deposition time of all the TiCN layers was kept fixed at 56 min. Synthesis conditions for gradient TiCN layer are shown in Table 1.

2.2. Films characterization

The surface morphology of films was examined using a 5XB-PC optical microscopy (OM) and a FEINANOSEM 430 field emission scanning electron microscope (FESEM). The optical microscopy was employed to measure the surface feature of films, and images of representative areas of the films were captured by a CCD camera to calculate the density of particles. FESEM with an EDS were used to determine the composition of the particles on the surface.

The thickness and cross-sectional microstructure of the TiCN films were investigated by a Calo test. The phase structure and preferred orientation of the films were characterized by grazing incidence X-ray diffraction (GIXRD, Philips X'Pert PRO) and Bragg–Brentano X-ray diffraction (BBXRD, Bruker D8 Advance), and all the GIXRD patterns were taken at an incident angle of 2°.

The composition and bonding energy of the films were investigated using a X-ray photoelectron spectroscopy instrument (XPS, Thermo VG ESCALAB250), operating with a monochromated Al-Kα X-ray radiation source. In the measurement, an argon ion beam of 3 kV was used with a current of 2 μA, and high-resolution spectra were acquired. The conditions were as follows: pass energy, 50.0 eV; energy step size, 0.1 eV; spot size, 500 μm. In order to characterize the chemical composition of the gradient films in different depth, the XPS spectra of Ti 2p, N 1s and C 1s for different etch levels were compared.

The hardness and elastic modulus of the films were measured by nanoindentation using continuous stiffness measurements (CSM) by a nanoindenter (Agilent technologies, G-200) with a Berkovich diamond indenter.

The adhesion was carried out using the Rockwell and scratching tests. Standard Rockwell tests measured with a diamond tip at a load of 1470 N. The scratching tests were done with a multifunctional scratch tester (HT-3001) equipped with an acoustic emission detector. The parameters of scratch test were as follows: load rate, 60 N/min; scratch speed, 2 mm/min, and the load increased from 5 N to 150 N.

The wear rate and the friction were carried out using a ball-on-disk tribometer (HT-2005) with WC ball. The tests were performed with load of 5 N. All the tests were performed with a total time of 3600 s under dry sliding condition at ambient temperature and humidity, and the wearing diameter and the rotational speed was 6 mm, 637 r.p.m., respectively.

3. Results and discussion

3.1. Microstructure of gradient TiCN films

The chemical compositions of the TiCN films are showed in Fig. 1, and all the relative atomic concentrations were acquired by XPS. In order to investigate the composition of gradient layer, all samples were etched by Ar ion for two levels, and each level corresponding to different etch time. The presence of oxygen was observed, and the content declined sharply after sputtering by Ar ions for 50 s. This may imply that there is a serious contamination on the film surface, the bombardment of Ar ion could sweep the contamination away, and the residual oxygen less than 10 at.% may result from the contaminations containing O which trapped by the defects on the surface of the films. Without Ar ion bombardment, the C content of C1, C2, C3 was 49.5 at.%, 55.7 at.%, 63.9 at.%, respectively, which showed an steady increasing, as the peak value of C_2H_2 flow rate increased from 100 sccm to 350 sccm. The figure also presents a decrease of C concentration for each sample while the etching process was carried out for 50 s, which suggested that there is a gradual increase in carbon content from the interface to the surface of the film. It's worth noting that the Ti and N content decreased with the increase of the peak value of C_2H_2 flow rate. The reason may be stated as: with the increase of C_2H_2 flow rate, the C_2H_2 was ionized to CH_x^{n+} effectively, and more carbon was incorporated into the film effectively, so it showed a relatively decreasing of Ti and N content.

Fig. 2 shows the XRD spectra of all the films. In order to investigate the preferred orientation (PO) of the films detailedly, both Bragg–Brentano X-ray diffraction (BB-XRD) and Grazing incidence X-ray diffraction patterns were presented in Fig. 2. The peak at 43.5° can be assigned to CrN, which origin from the CrN bonding layer. It