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Influences of bias voltage on mechanical and tribological properties of Ti–Al–C films synthesized by magnetron sputtering

Xianjuan Pang [a,b], Lei Shi [a], Peng Wang [a], Guangan Zhang [a], Weimin Liu [a,*]

[a] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China
[b] Graduate School of Chinese Academy of Sciences, Beijing, 100039, PR China

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ABSTRACT

Ti–Al–C films were deposited on silicon (100) substrates using magnetron sputtering TiAl target and graphite target in argon atmosphere at various substrate negative bias voltages. The composition, surface morphology, hardness and friction coefficient of the resulting films were characterized using x-ray photoelectron spectroscope, energy dispersive spectrometry, atomic force microscopy, nanoindentation and tribological tester. Results show that the structure and properties of the deposited films strongly depend on the applied substrate negative bias voltage. The Ti–Al–C films deposited at high substrate negative bias voltage show high surface roughness, low hardness and short wear life. In contrast, the Ti–Al–C films deposited without negative bias voltage exhibit uniform and smooth surface, a high hardness of approximately 37 GPa and low friction coefficient and long wear life. Excellent friction and wear behaviors of the Ti–Al–C films deposited without negative bias may be attributed to the dense structure and high hardness.

1. Introduction

Ceramic films with high hardness, high elastic modulus and good wear resistance, are widely used to increase the cutting efficiency and operational life of cutting tools and maintain the dimensional tolerances of components used in applications such as molds and dies, where wear can often occur. TiC is characterized by short bonds, relatively low density (4.91 g/cm^3), very high melting point (Tm = 3340 K), high modulus (410–510 GPa), and good thermal stability, high thermal conductivity, high hardness (HV = 28–35 GPa) and strength [1–6]. And TiC films also exhibit high strength, hardness, thermal stability and chemical inertness, which are used on ball bearings for improving their hardness, smoothening surface and decreasing friction coefficient or acting as protective layers for cutting and milling tools and inserts. However, TiC films have low oxidation resistance, relatively high stress and brittleness, which greatly restrict their wide applications in industry [7]. Many studies have been conducted to resolve these problems. It is found that the addition of a ductile metal (Cu, Al, Ag, Au, etc.) into ceramic films is often used to effectively modify their mechanical properties with the aim to reduce the stress, improve their adhesion to substrates and reduce their brittleness [7–11]. Combinations of WC as a hard phase and Co or Ni (6–12 wt.%) as a binder phase are often used in cutting tool industry [12]. The ratio of binder to carbide phase is of key importance and would influence the hardness and toughness of materials. Jan Soldán et al. [7,8] reported the additions of Cu and Al into TiC film. It was found that the addition of Cu or Al into the TiC film resulted in a remarkable reduction of stress while its hardness was decreased only slightly. However, few have been reported on the effect of Al addition on the tribological behaviors of the TiC films.

Metal containing-TiC films have been usually achieved by magnetron sputtering technique which can be carried out at reduced temperatures where the diffusion rates of the elements are low [8,10,11]. As for the sputtering deposition techniques, the properties of deposited films could be influenced by such plasma parameters as applied bias voltage and current density. The detailed investigation on the effect of these parameters on the characteristics of deposited films is vital for the deposition of metal containing-TiC films with desired properties.

This article reports on the preparation, mechanical properties and tribological behaviors of Ti–Al–C films deposited using magnetron sputtering techniques. The main attention is devoted to investigating the effect of applied negative bias voltage on the structure, mechanical properties and tribological behaviors of Ti–Al–C films.

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* Corresponding author. Tel./fax: +86 931 4968166.
E-mail address: wmliu@lzb.ac.cn (W. Liu).

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2. Experimental details

2.1. Film deposition

Ti–Al–C films were deposited on silicon (100) substrates using magnetron sputtering TiAl target (TiAl (50/50 at.)) and graphite target in argon atmosphere. Prior to deposition, the Si substrates were firstly ultrasonically cleaned in acetone and alcohol for 10 min. After drying with dried gas, the samples were put into the depositing chamber. The substrate-target distance was controlled to about 100 mm. The depositing chamber was evacuated to a vacuum of 4.0×10^{-3} Pa, and backfilled with argon gas (Ar) to a pressure of about 0.7 Pa. Then, the substrates were cleaned using Ar^+ bombardment for 10 min at a pulsed substrate negative bias voltage of −700 V, to remove some adhering impurities on substrates. Subsequently, the films were deposited under 120 sccm Ar gas flow rate and varied pulsed bias on the substrate. During deposition, the substrate was heated to 250 °C and the medium frequency (20 kHz) magnetron sputtering target was kept at constant current of 2.5 A to deposit Ti–Al–C films. The thickness of all the films is controlled between 1 and 2 μm.

2.2. Film characterization

The film thickness was measured using a surface profilometre and the growth rate was calibrated with the measured film thickness and the corresponding deposition time. The surface morphology and surface roughness of the films were observed on an SPM (Nano IIIa) atomic force microscope (AFM). FESEM (JSM-6701F) was utilized to observe the cross-sectional structure and thickness of the deposited films. X-ray diffraction (XRD) was performed on Philips X'perts diffractometer at CuKα wavelength. To obtain the diffraction peak profiles of the thin films along the vertical direction, grazing angle X-ray diffraction (GAXAD) with a grazing angle of 1° was applied for phase identification and qualitative texture characterization. The chemical bond states on the surfaces of the Ti–Al–C films were analyzed on a PHI-5702 x-ray photoelectron spectroscope (XPS) operating with monochromated Al Kα irradiation at pass energy of 29.4 eV. And the compositions of the films were determined with energy dispersive x-ray spectroscopy (EDS) (KEVEX SIGMA, USA). The hardness of the Ti–Al–C films was determined on a nano-indenter (Nanotest 600) using a Berkovich diamond tip and continuous stiffness option, with the maximum indentation depth being kept at 100 nm to minimize the substrate contribution. Five replicate indentations were made for each film sample and the hardness was calculated from the load–unloading curves. The adhesion strength between the film and the substrate was further studied using a WS-92 acoustic emission scratch tester.

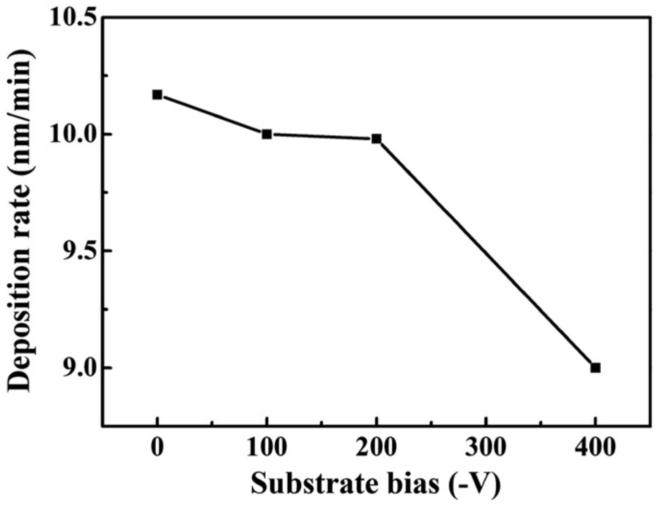

Fig. 1. Deposition rate of the films as a function of applied negative bias voltage.

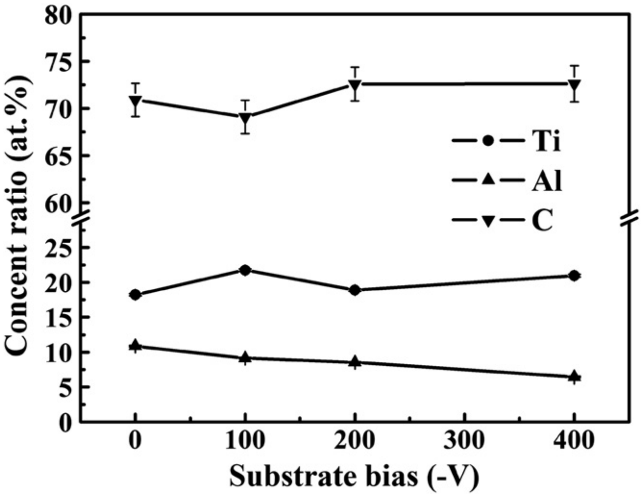

Fig. 2. The composition of the films as a function of applied negative bias voltage.

The friction and wear behaviors of the as-deposited samples were evaluated on the UMT-2MT tribometer (Center for Tribology, Inc., CA, USA) by sliding the films on silicon substrate against a steel ball (Ø = 3 mm, HRC = 64, Ra = 0.02 μm) at a sliding frequency of 3 Hz, 5 Hz and 10 Hz, respectively, a sliding distance of 5 mm, and a load of 3 N. The friction test rig provides a reciprocating-sliding configuration. All the tests were performed at room temperature and a relative humidity of 30%–40%. The sliding time and the friction coefficient were recorded automatically during the test. The tribological properties of all samples are evaluated within 30 min. Combined with X-ray energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM) was utilized to analyze the wear scar and debris on steel balls after sliding on deposited films.

3. Results and discussion

3.1. Growth rate

Fig. 1 shows the dependence of the deposition rate on the applied substrate bias voltage for the Ti–Al–C films grown on Si substrate. It is seen that the deposition rate (film thickness over deposition time) decreases gradually from 10.2 to 8.3 nm/min when the bias voltage increases from 0 to −400 V. The drop of deposition rate is caused by re-sputtering of the as-deposited film, i.e., kicking off the adatoms or growing surface by the incoming ions [13].

3.2. Composition

Figs. 2 and 3 plot the variation of the Ti, Al and C atomic ratios measured by EDS versus the applied negative bias voltage during the deposition. It is seen that the contents of Ti, Al, C and C/(Ti + Al) atomic ratio change slightly as the bias voltage increases. During the co-sputtering process, co-sputtering of titanium-aluminum and graphite does not significantly influence the composition when substrate bias voltage varies, which is similar to the research results of H. L. Wang et al. [13]. However, the increase of the negative bias voltage from 0 to −400 V resulted in a relative increase in Ti/Al atomic ratio from about 1.67 to 3.25. This trend can be rationally understood if one notices the growth mechanism of films prepared by magnetron sputtering. Firstly, the binding between C–C bonds is stronger than that of Me–C bonds. As the bias voltage increases, the sputtering of the film by Ar ion is stronger. And with the sputtering of the high energy ion, the metallic atoms may be re-sputtered from the surface of films. Consequently,