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Deposition, structure and hardness of Ti–Cu–N hard films prepared by pulse biased arc ion plating

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ABSTRACT

In this work, Ti–Cu–N hard nanocomposite films were deposited on 304 stainless steel (SS) substrate by using pulse biased arc ion plating system with Ti–Cu alloy target. The effects of negative substrate pulse bias voltages on chemical composition, structure, morphology and mechanical properties were investigated. The composition and structure of these films was found to be dependent on the pulse bias, whereas the pulse biases put little influence on hardness of these films. The XPS spectra of Cu 2p showed that obtained peak values correspond to pure metallic Cu. Cu content in Ti–Cu–N nanocomposite films changed with pulse bias voltage. In addition, X-ray diffraction analysis showed that a pronounced TiN (111) texture is observed under low pulse bias voltage while it changed to TiN (220) orientation under high pulse bias voltage. Surface roughness of the Ti–Cu–N nanocomposite films achieved to the minimum value of 0.11 μm with the negative pulse bias voltage of −600 V. The average grain size of TiN was less than 17 nm. The mechanical properties of Ti–Cu–N hard films investigated by nanoindentation revealed that the hardness was about 22–24 GPa and the hardness enhancement was not obtained.

1. Introduction

Over the past decades, hard coatings have been successfully applied to cutting tools, moulds and other metal components, greatly improving their performances and lifetime. With ever-increased requirement of hardness and other mechanical or tribological properties of tools or machine parts, only TiN hard film doesn't meet these requirements of modern industry [1,2], so great interests are paid much attention to hard nanocomposite films [3–7]. Comparing with TiN film, hard nanocomposite films represent the new generation of hard films, which had higher hardness (up to 50–70 GPa) and smaller grain size than those of the conventional hard films such as TiN [8–13]. Hard nanocomposite films can be divided into two groups. The first group represents nc-MeN/hard phase nanocomposite films with a-Si_3N_4 and a-TiB_2 etc. as hard phase. This concept of nc-MeN/hard phase hard nanocomposite films was proposed by Veprek et al. [4–7] and the nc-TiN/a-Si_3N_4 films with extremely high hardness was reported; here nc- and a- denote the nanocrystalline and amorphous phase, respectively. The second group of hard nanocomposite films represents nc-MeN/soft phase nanocomposite films with Cu, Ni, Y, Ag, etc. [14–17] as a soft phase and this concept was proposed by Musil et al. [3,10]. The elements Me = Ti, W, Zr, Cr, Mo, Al, etc. form hard nanocrystalline nitrides in both groups of nanocomposites.

According to the nc-MeN/soft phase nanocomposite films, Ti–Cu–N hard nanocomposite films have been widely investigated and prepared by d.c. reactive magnetron co-sputtering [18,19], magnetron sputtering with low energy ion flux irradiation [20], arc ion plating [21,22] and arc ion plating and magnetron sputtering hybrid method [23,24]. It has been reported that hardness of Ti–Cu–N films deposited by d.c. magnetron co-sputtering can reach 30 GPa [18]. Hyung et al. [23] showed that the maximum value of hardness of Ti–Cu–N nanocomposite films reaches 45 GPa by using a reactive arc ion plating and magnetron sputtering hybrid system. The hardness of Ti–Cu–N nanocomposite films deposited by magnetron sputtering with low energy ion flux irradiation [20] can be influenced by Cu content and the maximum value of hardness 42 GPa is obtained with Cu content of 2 at.%. And the hardness of Ti–Cu–N films deposited by arc ion plating reached 40.8 GPa and the grain size of TiN is less than 15 nm [25].

Arc ion plating is a widely used industrial hard coatings deposition technique, greatly improving the wear-resistant properties and usage life of cutting tools, moulds and other mechanical components. In order to improve film qualities, d.c. biases are generally used, but continuous ion bombardment causes substrates temperature increasing and large residual stresses. Moreover,

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macroparticles (MPs) are always present in the coatings so that this technique has not been considered suitable for synthesis of fine coatings such as optical films. In 1991, Olbrich et al. [26,27] introduced pulse bias into arc ion plating. In comparison to conventional d.c. biased arc ion plating, pulse biased arc ion plating (PBAIP) is featured with low substrate deposition temperature, low residual stress, macroparticle cleaning, fine grain size and high film/substrate adhesion, while keeping all the advantages of arc deposition [26–28]. Therefore, PBAIP has all the virtues for fine films such as nanocomposite film. It could be specified that the microstructure and grain size of Ti–Cu–N nanocomposite films prepared by PBAIP will be different from those reported in references [26–28] and will be investigated.

In this study, Ti–Cu–N nanocomposite films were deposited on HSS substrates by PBAIP. The effects of pulse bias voltages on the composition, structure, and hardness of these nanocomposite Ti–Cu–N films were investigated.

2. Experimental

2.1. Thin film deposition

Ti–Cu–N hard films grown on 304 stainless steel (SS) substrates by pulse biased arc ion plating were prepared with the change of negative substrate pulse bias voltage from −100 to −900 V with an alloy target (Ti:88, Cu:12 at.%). The schematic diagram of this system is shown in Fig. 1. Before placing the substrates in vacuum chamber, they were polished and pre-cleaned with acetone in an ultrasonic bath for 20 min. When the chamber was evacuated to approximately 5×10^{-3} Pa, argon gas was introduced and with the partial pressure 0.4 Pa. In order to remove any oxide or contaminant on the surface, the TiCu alloy target was used to bombard and to sputter the substrate surface with a constant target arc current of 80 A, a d.c. bias of −900 V was used to clean the substrate surface, and bombardment time 5 min. In order to ensure film adhesion, a thin layer of TiCu (~50 nm) was coated firstly on the samples. For the formation of nitrides, nitrogen reactive gas was continuously introduced into the deposition chamber during film deposition. During deposition, a pulsed power source superimposes a negative pulse bias to the substrates with the following parameters: pulse bias magnitude $U_p = -100$, -300, -600 and -900 V, respectively, and constant pulse frequency $f = 40$ kHz and duty ratio $D = 30\%$. The current density used in the negative bias voltage application was about 0.6–1.1 mA/cm^2. During the deposition, the following parameters were maintained constant: the arc source currents $I_{TiCu} = 80$ A, N_2 partial pressure $P_{N2} = 0.3$ Pa, the distance between samples and cathode arc targets 400 mm, and the total deposition time 60 min. During deposition, substrate temperature T_s was in the range of 380–430 °C. The thicknesses of the deposited films were in the range of 3.1–4.0 μm.

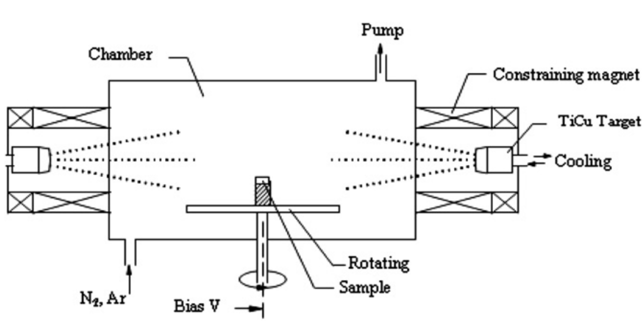

Fig. 1. A schematic diagram of pulse biased arc ion plating system.

2.2. Film characterization

Film composition was measured by electron probe microanalysis (EPMA) using an EPMA-1610 (SHIMADZU, JAPAN) system. Structural characterization of the deposited films was carried out by X-ray diffraction (XRD, *D*/max2400 with Cu K$\alpha = 0.154056$ nm) with $\theta - 2\theta$ mode. X-ray photoelectron spectroscopy (XPS) was used to examine chemical state of Ti–Cu–N films. The surface morphology and surface roughness were measured by scanning electron microscopy (SEM) and contacting surface morphology analyzer (Alpha-Step IQ), respectively. The average grain size was calculated by equation of Scherrer [29]:

$$D = \frac{0.9\lambda}{B\cos\theta} \quad (1)$$

where D is the average grain size, λ is X-ray' wave length, it is known as $\lambda = 0.154156$ nm. θ is Bragg diffraction angle,B is peak width at half height (FWHM) of the film diffraction peak. The crystal structural of Ti–Cu–N hard films was analyzed by XRD (X-ray diffraction). Film hardness and Young's modulus were measured by a nanoindentation system (Triboscope, Hysitron Inc.) with an impression depth lower than 10% of film thickness and the load of indenter used in this present experiments was 3 mN. In order to diminish non-uniformity of the films, the results were averaged over more than 10 measurements.

3. Results and discussion

3.1. Chemical composition and chemical bonding

The atomic content in the films was shown in Fig. 2. It can seen that the content of Cu appeared to decrease from 3.90 to 3.00 at.%, and then suddenly increase to a maximum value of 5.5 at.% with negative pulse bias voltage increasing from 100 to 900 V. With negative pulse bias voltage increasing, the content of Ti and N appeared to increase and decrease, respectively. Sundgren et al. [30] investigated the effect of substrate bias on the composition of TiN and TiC films and showed that the energy of the species impinging on the substrate increased as the bias voltage increased. Since the sputtering yield increased with energy, more materials were resputtered with the increase of bias voltage. In addition, the sputtering yield of Cu is larger than Ti [31]. It implied that the Ti has the lowest sputtering yield of all three elements. Therefore, the

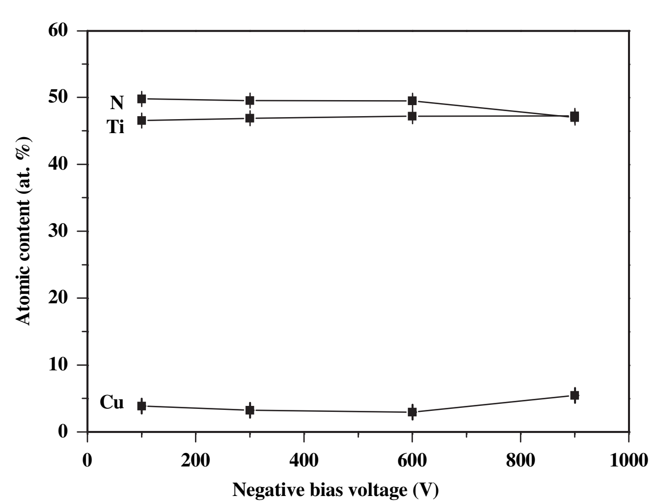

Fig. 2. The atomic content of the Ti–Cu–N films as a function of negative bias voltage.