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Mechanical and tribological properties of multicomponent Ti–B–C–N thin films with varied C contents

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ABSTRACT

Multicomponent thin films of Ti–B–C–N with different C contents (C target current ranging from 0.0 to 4.0 A) were deposited onto unheated Si(100) wafers (for mechanical analyses) and M42 tool steels (for tribological measurements) by reactive close-field unbalanced dc-magnetron sputtering in an Ar–N_2 gas mixture. These films were characterized and analyzed in terms of their microstructure by X-ray diffraction, their hardness by microindentation measurements, their surface root-mean-square roughness by atomic force microscopy, and their friction and wear behaviors by Rockwell-C testing, microscratch testing, dynamic impact testing and pin-on-disc tribometer. It was found that the mechanical and tribological properties of multicomponent films (typically 1.6 ± 0.2 μm in thickness) were closely related to the C content (varied from 4.4 at.% to 42.0 at.%). For the best multicomponent film with 12.4 at.% C content, a high hardness of 27 GPa was achieved and the best cohesive and adhesive strength was evidenced in terms of critical load values of L_{C1} (~37 N), L_{C2} (>75 N), and the highest adhesive strength (HF1). Moreover, by dynamic impact testing the multicomponent film could endure impact cycles up to 2×10^5 without adhesive failure. However, when the C content was further increased up to 42.0 at.%, the hardness, cohesive and adhesive strength were decreased due to the formation of amorphous structure. It was also found that the pin-on-disc test under dry conditions showed that the frictional coefficients decreased with C content. The frictional coefficients obtained at a load of 2 N were kept at ~0.57 without C incorporation and decreased to ~0.18 at C current of 4.0 A. The tribological properties of the Ti–B–C–N films with different C contents are also explained in terms of mechanical properties and wear mechanisms.

1. Introduction

Currently, there is a worldwide extensive research in the development of novel engineering materials, especially in the form of thin films. Nanostructured multiphase composites and multicomponent materials in which the dimensions of the individual phases or components are in the range from 3 to 20 nm represent a new class of engineering materials [1–3]. These materials are formed by a mixture of phases and/or components, which typically consist of nanometer sized crystals embedded in a preferable matrix which may be either amorphous or nanocrystalline [4,5]. For example, binary transition metal nitrides and carbides such as TiN and TiC, and ternary Ti–C–N and Ti–B–N systems are attractive materials because of their high hardness, high melting point, chemical inertness, good wear and corrosion resistance, and thermodynamical stability [6–8]. For these reasons, they have been used for hard wear-resistant coatings in machining industry, diffusion barriers in microelectronics, and electrodes in semiconductor devices. The demand for advanced coatings with further increased mechanical and tribological properties has very recently led to more complex coatings as compared to binary and ternary alloyed coatings, resulting in quaternary systems like Ti–B–C–N [9,10]. However, no comprehensive work has been reported on Ti–B–C–N thin films in literature. These multicomponent nanocomposite hard coatings are at the beginning of their development [11].

In the present study, multicomponent Ti–B–C–N thin films were prepared onto unheated Si(100) wafers (for mechanical analyses) and M42 tool steels (for tribological measurements) by reactive close-field unbalanced dc-magnetron sputtering in an Ar–N_2 gas mixture. The effects of C target currents in the range from $I_C = 0.0$ to 4.0 A (corresponding to the C content from 0 to 42.0 at.% in multicomponent Ti–B–C–N thin films) on mechanical and tribological properties were investigated. These films were characterized and analyzed by X-ray Diffraction(XRD), X-ray photoelectron spectroscopy (XPS), microindentation measurements, atomic force microscope (AFM), scanning electron microscopy (SEM), Rockwell-C testing, micro-scratch testing, dynamic impact testing, and pin-on-disc tribometer.

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2. Experimental

2.1. Multicomponent film deposition

Multicomponent film deposition was performed in a reactive close-field unbalanced dc-magnetron sputtering system (UDP450, Teer Coating Limited) on unheated both Si(100) wafers and M42 high-speed-steel substrates. Two C, one Ti, and one TiB_2 targets were used for depositing multicomponent Ti–B–C–N thin films. The sputtering was carried out in an Ar–N_2 gas mixture at a pulsed ($f=250$ kHz) bias voltage of −60 V with a substrate rotation speed of 15 rpm and a working pressure of ~0.26 Pa. The substrates were mounted on a turn-table in the middle of the chamber. Before sputtering the background pressure was pumped down to $\leq 5.0\times10^{-5}$ Pa. The amount of nitrogen introduced into chamber was monitored and controlled by a computer-controlled optical emission spectroscopy system, whose value was set at 80% in this study. The Ti and TiB_2 target currents were fixed at 6.0 and 3.0 A respectively, while the C target currents (I_C) ranging from 0.0 to 4.0 A to obtain multicomponent films with different C contents. The substrate surface was pre-sputtered with Ar plasma at a negative bias voltage of 500 V for 30 min prior to film deposition, followed by deposition of a thin Ti buffer layer (~100 nm in thickness) in order to improve adhesion and reduce stress at the interface with the substrate. During deposition the substrate temperature was estimated to be ~200 °C due to plasma heating. The deposition parameters are shown in Table 1.

2.2. Multicomponent film characterization

The elemental concentration of Ti, B, C and N in the films were determined by X-ray photoelectron microscopy (XPS, PHI 5802 system) with a monochromatic Al Kα X-ray source ($h\nu=$ 1486.6 eV). The phase composition of an amorphous (B_2N, CN_x) matrix was determined by XPS [12,13]. Crystallographic structure of the films was determined by XRD using a Rigaku MiniFlex diffractometer with a Cu tube operated at 40 kV and 30 mA. The measurements were carried out using Cu Kα radiation with a Ni filter to remove Cu Kβ reflections. The surface topography of the films was acquired by scanning the samples in air with AFM (Auto-Probe CP, Park Scientific Instruments) operated in a contact mode. The scan areas are $1\times1\ \mu m^2$ with a resolution of 256×256 pixels. The total thicknesses of Ti–B–C–N films were measured by a stylus profilometer (Form Talysurf) and confirmed by cross-sectional scanning electron microscopy (SEM, JEOL, JSM 5600).

The hardness and elastic modulus were analyzed by microhardness indentor H100C (Fisher) using a Berkovich diamond tip with a maximum load of 20 mN. The calibration of the hardness value was frequently checked by measuring on a standard fused silica sample. In order to minimize the substrate effect, the maximum indentation depth was kept less than 10% of the total film thickness. Ten separate measurements were taken for each sample in order to get a mean value. The cohesive and adhesive strength of the films was qualitatively assessed by a Rockwell-C tester under a load of 150 kg. It was also quantitatively tested using a Teer 3001 scratch tester. A diamond indenter with 0.2 mm radius was drawn across the films at a sliding velocity of 10 mm/min with a loading rate of 100 N/min. MTS-810 impact tester was used for testing the impact resistance of the films with a Rockwell-C diamond stylus of 0.2 mm radius. During the test, each sample was subjected to five tests with 2×10^3, 8×10^3, 2×10^4, 8×10^4 and 2×10^5 impact cycles in unlubricated conditions. The impact tester was set in load control mode in sinusoidal form. The impact force was set to 300 N with 50 Hz impact frequency. A preload of 5 N was applied to ensure that the diamond stylus was in good contact with the sample surface. Before each test, the surface of sample and the tip of the indenter were cleaned using acetone. The wear behaviors of the films were evaluated by a conventional pin-on-disc tribometer. Wear tests were carried out by a tungsten carbide (WC) ball with a 5 mm diameter having surface roughness 0.1 μm. During the tests on all the films, the ball and the disc were cleaned with alcohol to get rid of dust and other contaminants to keep the surface conditions as identical as possible. The friction and wear tests were carried out at room temperature in dry conditions. The loads used in this experiment were 2 N with fixed sliding speed of 0.0565 m/s for 4500 revolutions.

Table 1
Deposition parameters, film thickness, and elemental composition of the multicomponent Ti–B–C–N films.

Sample	Target current I_C (A)			Bias (V)	Thickness (μm)	Composition (at.%)			
	Ti	TiB_2	C			Ti	B	C	N
TBCN01	6.0	3.0	0.0	−60	1.58	38.8	12.5	0.0	48.7
TBCN02	6.0	3.0	0.5	−60	1.64	35.3	14.4	4.4	45.9
TBCN03	6.0	3.0	1.0	−60	1.67	37.7	10.8	12.4	39.1
TBCN04	6.0	3.0	1.5	−60	1.71	33.4	11.3	19.2	36.1
TBCN05	6.0	3.0	2.0	−60	1.75	31.4	10.5	24.4	33.7
TBCN06	6.0	3.0	2.5	−60	1.73	29.8	8.1	28.4	33.7
TBCN07	6.0	3.0	3.0	−60	1.79	27.5	8.6	32.3	31.6
TBCN08	6.0	3.0	3.5	−60	1.77	23.5	11.3	37.5	27.7
TBCN09	6.0	3.0	4.0	−60	1.82	22.3	8.8	42.0	26.9

The concentration data were derived by XPS from a series of films from the area under each elemental spectrum. Uncertainties of the data were estimated to be within 15%.

3. Results

The concentration of all the elements in Ti–B–C–N films was controlled by changing the C target current (I_C) and keeping the Ti and TiB_2 target currents constant. We have first performed an XPS analysis of nine Ti–B–C–N films. Although the Si(100) substrates were conventionally cleaned before deposition, they were exposed to air prior to the XPS measurement and therefore contained surface oxide contamination. Overview spectra from these films revealed that, in addition to the dominant Ti, B, C, and N related peaks, a very small O 1s peak was also present and disappeared after the sample was irradiated with a small Ar ion dose.

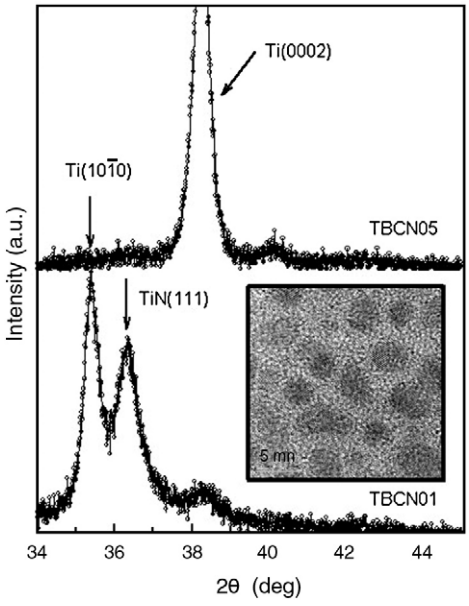

Fig. 1. Typical XRD θ–2θ scan patterns obtained from samples TBCN01 and TBCN05. Note that Ti(1010) and Ti(0002) diffraction peaks are from ~100-nm-thick Ti buffer layers. The inset shows that the C-free Ti–B–N film has two-phase nanocomposite microstructures comprising of nanocrystalline TiN phase surrounded by an amorphous TiB_2 matrix.