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Microstructure and phase composition dependent tribological properties of TiC/a-C nanocomposite thin films

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ABSTRACT

TiC/a-C nanocomposite films were deposited by rf magnetron sputtering on silicon substrates. A thin Cr inter-layer was interposed to enhance the interfacial adhesive strength. At a low deposition power of 25 W, the formation of TiC phase with (200) orientation was observed. Cross sectional scanning electron microscopy (SEM) image of this film showed growth with columnar microstructure. However, at higher deposition powers, 75 W and 125 W, several XRD peaks related to TiC were observed including prominent TiC (111) orientation. These films were found to be composed of fine spherical grains embedded in an amorphous carbon (a-C) matrix. Weak tribological performance and poor film/substrate adhesive resistance were observed in the 25 W deposited columnar structured film. However, films deposited at higher power exhibited superior tribological and scratch resistant properties such as low friction coefficient and high wear resistance. Such a large discrepancy in friction and wear behavior of these films could be explained in terms of microstructure and phase composition. Films with columnar microstructure possess residual compressive stress, low hardness and reduced fracture toughness. In contrast, spherical shaped TiC nanograins embedded in a-C matrix exhibited superior hardness and high fracture toughness.

1. Introduction

The development of multilayered and nanocomposite thin films is based on tailoring of material properties through the control of growth morphology that involves the modification of grain and grain boundaries [1–3]. Grain size refinement has emerged as an essential step for designing nanocomposite thin films suitable for protective applications in several mechanical components [4–7]. Especially, for tribological components, some of the basic material properties such as high hardness, high toughness, low friction coefficients and high wear resistance are essential [4,8,9]. Such a requirement of multi-functionality can be obtained in multi-layer and nanocomposite coatings [10–13]. In nanocomposite coating, hard and soft phases are often mixed to obtain improved mechanical and tribological properties [10]. In addition, synergetic effects like improvement in hardness and toughness can be obtained from appropriate mixture of various phases at nano-scale [1]. In this regard, carbides/nitrides embedded in amorphous hydrogenated (a-C:H) and un-hydrogenated amorphous carbon (a-C) matrixes have revealed superior tribological performance [5,10,14,15]. Specifically, nanocomposite coatings based on the dispersion of transition metal (TM) carbide nanocrystallites in a-C matrix show low friction coefficient and high wear resistance [10]. This is consistent with the fact that improvement in wear resistance is related to less friction coefficient. The wear in this process is confined to the generation of cracks which propagate towards the interface. Mitigation of this deleterious aspect leads to the improvement in load bearing capacity, which in turn, prevents brittle fracture and delamination of the coating [10]. The toughness of a composite is vastly enhanced through the dispersion of a hard nanocrystalline phase inside a soft matrix [1,10]. In addition, such a configuration is known to resist crack nucleation and their migration. The presence of an amorphous phase facilitates grain boundary sliding that introduces ductility and prevents fracture and surface fatigue. Such a characteristic leads to the improvement in wear resistance. Moreover, a-C matrix phase associated with TiC nanocrystallites acts as a lubricant under humid environment [7,14]. Therefore, the modification of grain/grain boundary morphology and microstructure is a topic of importance to improve the tribo-mechanical properties of TiC/a-C coatings [5,7,10,14].

The present paper investigates tribo-mechanical properties of rf sputtered nanocomposite TiC/a-C coating deposited on silicon substrates. For the improvement in tribological properties, the influence of sputtering power was considered to modify the microstructure and chemical composition of film. Hardness, elastic modulus and fracture toughness of nanocomposite coatings depend on grain/grain boundary microstructure that can be manipulated by sputtering power. More

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importantly carbon content in the film was found to vary with sputtering power which is crucial to improve wear resistance including low friction coefficient.

2. Experimental

TiC films were deposited on silicon substrates by rf magnetron sputtering using a 2 inch circular TiC target in argon atmosphere. The substrate was cleaned by acetone before deposition to remove surface contamination. Target to substrate distance, gas flow rate and deposition pressure were kept constant at each power level. A table is given which includes all important deposition parameters and conditions (Table 1).

For the deposition of Cr inter layer, a Cr metallic target was used and the deposition pressure was kept at 5×10^{-3} Torr. Magnetron was rf powered at 50 W to achieve an approximately 110 ± 10 nm thick Cr inter-layer over a 9 minute time duration. This inter-layer was used to enhance the interface adhesion between the substrate and TiC coating. For TiC deposition, discharge powers were 25, 75 and 125 W and the deposition times were calibrated to achieve a thickness of ~500 nm for all the discharge powers. Surface morphology and cross section imaging were carried out using a Zeiss Supra Field Emission Scanning Electron Microscope (FESEM). The FESEM analysis was carried out at a beam voltage of 3 kV. Carbon resonance RBS spectra of the TiC nanocomposite films were acquired with an incident He^{++} energy of 4.259 MeV. The backscattering signals from C in the TiC film could be clearly observed using C resonance RBS. A RUMP simulation for the RBS analysis revealed a carbon to titanium (C/Ti) ratio in the TiC film and chromium to titanium (Cr/Ti) ratio in the Cr inter-layer. X-ray diffraction was used in a grazing incidence mode at an angle 1° with a Bruker D8 diffractometer where CuKα radiation was used in XRD. Cr interlayer diffraction peak is measured at a grazing incidence angle of 5°. Raman spectra were recorded in back scattering geometry with a Renishaw micro-Raman spectrometer (Model INVIA) equipped with an Ar-ion laser operating at a wavelength of 514.5 nm. Raman imaging based on color contrast was carried out in the wear track to investigate sliding induced chemical changes. Spectral resolution of $1\ cm^{-1}$ could be achieved using a 20× objective and 1800/mm grating. In all these measurements, 100% laser power was used for 60 s of exposure time. Contact angle (CA) measurements were carried out using a contact angle meter equipped with a CCD camera (Holmarc, HO-IAD-CAM-01, and India). Volume of water droplet used for CA measurement was ~3.5 mm^3. These measurements were carried out at room temperature and atmospheric pressure with a relative humidity of ~65 ± 3%. The tests were repeated 3 times and standard deviations were typically ±2°. Surface roughness was measured by Dektak 6M-stylus profiler in which a diamond tip having a radius of curvature of 12.5 μm and a load of 5 mg is linearly scanned with a speed of 10 μm/s. On each sample, the test is carried out 5 times and average value is reported. Nanoindentation measurements (Hysitron) were performed with a diamond Berkovich indenter with a loading–unloading rate of 2 mN/min. This was performed up to a maximum load of 2 mN. Oliver and Pharr method was used to calculate the elastic modulus and hardness of the specimen [16]. For each film, five times loading–unloading hysteresis curves were obtained from different locations which nearly overlap with each other indicating homogeneous characteristics of films. Linear reciprocating mode of a ball on the disk micro-tribometer (CSM Instruments, Switzerland) was used to carry out friction measurements. In all these measurements, the normal loads and sliding speeds were kept constant at 1 N and 4 cm/s, respectively. The diameter of the sliding Al_2O_3 ball was 6 mm with a surface roughness of 0.04 μm. Tribology experiments were conducted in ambient atmospheric and unlubricated conditions where the relative humidity level was 75%. Each tribology experiment was repeated three times and the trend of the friction curves were found to be nearly similar. The dimension of wear profile after the test was measured by a Dektak 6M-stylus profiler using a 5 mg load and 30 μm/s scanning speed. In this method, the tip of the diamond stylus with a radius of curvature of 12.5 μm was scanned across the wear track. Scratch resistance of the film was measured by a scratch tester (CSM Instruments, Switzerland) coupled to a Rockwell spherical diamond indenter with a tip radius of 200 μm. These tests were performed using progressive loads from 1 to 20 N for a transverse scratch length of 3 mm with a loading rate of 5 N/min. The tests were carried out in ambient atmospheric conditions and scratch tracks were examined by an optical microscope.

Table 1
Deposition parameters and conditions at various discharge power levels.

Power (W)	Deposition time (min)	Deposition rate (nm/min)	Target to substrate distance (mm)	Gas flow rate (sccm)	Deposition pressure (Torr)
25	395	1.3	65	72	5×10^{-3}
75	96	5.2	65	72	5×10^{-3}
125	55	9.1	65	72	5×10^{-3}

3. Results and discussion

3.1. Surface and cross-section morphology of films

Surface roughness is less 12 nm in the 25 W deposited film which increases to 40 and 30 nm in 75 and 125 W deposited films. Fig. 1 shows planar and corresponding cross-sectional SEM images of TiC films deposited at three different deposition powers of 25, 75 and 125 W. In the cross sectional image, Cr inter-layer is distinctly shown in the bottom of the TiC film. This layer is introduced to enhance the interface bonding by imparting ductility to improve adhesion and toughness. Galvan et al. investigated that TiC/a-C:H coating exhibits high toughness and adhesion when Cr inter-layer is used [17]. In this study, all the films are of similar thicknesses. This was acquired through the control of power and deposition times for avoiding the thickness effect on film properties. At a lower deposition power of 25 W, elongated, columnar microstructure exists in the film [Fig. 1(a)]. However, at high deposition power, a fine nanostructured granular morphology is observed [Fig. 1(b) and (c)]. It is studied that the transition from a columnar to a glassy microstructure is a consequence of an increase of the intensity of ion bombardment or increasing the C content in the films [17,18]. It was shown that when carbon concentration is low, the coating exhibits columnar growth. Each column is polycrystalline in nature and constituted by elongated crystallites. It was shown that when carbon concentration is low, the coating shows a columnar morphology [17–19]. If carbon concentration is increased, the columns are replaced by a more dense structure consisting of broad pillars. These pillars are nanostructured and consist of small TiC crystallites surrounded by an amorphous carbon phase. When a high amount of a-C is introduced, the columnar structure is transformed into a "glassy" structure. Such a behavior was observed while applying substrate bias during sputter deposition of films [18].

3.2. Rutherford backscattering

RBS is an appropriate nuclear analytical technique to analyze the elemental composition in thin films. Error value was negligible when fitting is performed for RBS data. In the present study, the variation of the carbon to metal ratio is observed with the change in deposition power. The spectra show a Ti/C ratio of 2.66 in the 25 W deposited film [Fig. 2(a)] in the TiC layer. This also indicates the deposition of hypo-stoichiometric TiC_{1-x} at this particular deposition power. From this spectrum, it is clearly noticed that C is present mostly on the surface of the film in the 25 W deposited film. However, there is no carbon diffusion into the adjacent Cr interface layer. A fairly large amount (~40 at.%) of oxygen is present in the entire depth of the film. This

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