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Full Length Article

Tribological properties of TiC/a-C:H nanocomposite coatings prepared via HiPIMS

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ABSTRACT

High power impulse magnetron sputtering (HiPIMS) technology has been employed to prepare TiC/a-C:H nanocomposite coatings from a titanium target in acetylene (C_2H_2) reactive atmospheres. Gas fluxes were varied from 1.3 to 4.4 sccm to obtain C/Ti ratios from 2 to 15 as measured by electron probe microanalysis (EPMA). X-ray diffraction and transmission electron microscopy demonstrate the presence of TiC nanocrystals embedded in an amorphous carbon-based matrix. The hardness properties decrease from 17 to 10 GPa as the carbon content increases. The tribological properties were measured using a pin-on-disk tribometer in ambient air (RH = 30–40%) at 10 cm/s with 5 N of applied load against 6-mm 100Cr6 balls. The friction coefficient and the film wear rates are gradually improved from 0.3 and 7×10^{-6} mm^3/N m to 0.15 and 2×10^{-7} mm^3/N m, respectively, by increasing the C_2H_2 flux. To understand the tribological processes appearing at the interface and to elucidate the wear mechanism, microstructural and chemical investigations of the coatings were performed before and after the friction test. EPMA, X-ray photoelectron and electron energy-loss spectroscopies were employed to obtain an estimation of the fraction of the a-C:H phase, which can be correlated with the tribological behavior. Examination of the friction counterfaces (ball and track) by Raman microanalysis reveals an increased ordering of the amorphous carbon phase concomitant with friction reduction. The tribological results were compared with similar TiC/a-C(:H) composites prepared by the conventional direct current process.
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1. Introduction

Metal carbide/amorphous carbon nanocomposites have attracted much attention in the last decade as protective coatings due to their interesting combination of mechanical and tribological properties on the nanometer scale [1–10]. The combination of small crystals of a hard phase embedded in an amorphous carbon matrix has the potential to provide an enhanced tribological performance (load-bearing capability, low friction, fracture toughness and wear resistance) [11]. The magnetron sputtering technique has been primarily used as the synthesis route due to its feasibility to control the chemical composition, microstructure and functional properties in addition to easy industrial scale-up. High power impulse magnetron sputtering technology (HiPIMS) has emerged more recently as a pulsed magnetron sputtering technique in which high electron densities (up to 10^{-19} m^{-3}) and ionization degrees can be achieved. These characteristics provide additional ion bombardment and densification to the growing films and thus an improvement in the film properties. In combination with a reactive gas, additional reactivity can be obtained by means of the plasma processes induced by HiPIMS discharges. The growth of TiC nanocomposite films by reactive HiPIMS has been performed in a previous study [10]. A comparison with films prepared by conventional DC sputtering revealed higher hardness and lower resistivity values due to the high plasma density in HiPIMS processes. However, it has not yet been explored whether the tribological behavior of such carbon-based nanocomposite coatings can be enhanced by HiPIMS. In the past, we have deeply investigated the preparation, characterization and correlation of the tribological properties of metal carbide/amorphous carbon nanocomposites. The key parameter controlling the friction and wear performance was found to be the generation of a sufficient amount of amorphous free carbon phase to lubricate the contact, which is controlled by the initial film composition and stability [6,7,12]. The generation of a sp^2-hybridized C tribolayer in the contact appears to play the role of interfacial lubricant and thus lowers the friction coefficient (as low as 0.1) and wear rate (on the order of 10^{-7} mm^3/N m) depending on the testing conditions.

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The current study presents the preparation of TiC/a-C:H nanocomposite coatings by reactive HiPIMS using C_2H_2 as the carbon precursor and a titanium target. The chemical composition, crystalline phases, film microstructure and tribological properties were investigated and compared with similar TiC nanocomposite coatings prepared by conventional DC sputtering with well-known tribological behaviors.

2. Materials and methods

The TiC/a-C:H nanocomposite coatings were deposited in an industrial-scale parallelepiped-shaped one-cubic-meter large high vacuum deposition chamber fabricated by Thin Film Srl. The cryogenic pumping system allows a base pressure below 5×10^{-5} Pa to be achieved. The system is equipped with four cathodes with direct cooling (30.5 cm × 12.5 cm, AJA STLX) in a close field unbalanced magnetron sputtering (CFUBM) configuration. In this study, only one cathode was equipped with a titanium target (99.99% purity). During the deposition process, argon (99.9999% purity) and acetylene (C_2H_2, 99.5% purity) were introduced in the chamber via a gas distribution ring around the target. The fluxes were controlled by mass flow controllers. The argon flux was adjusted to obtain a pressure of 5.8×10^{-1} Pa, while the acetylene flux was varied to obtain different film compositions from 1.3 to 4.4 sccm. The substrate holder was kept parallel to the target surface at a distance of approximately 8.5 ± 0.5 cm in a fixed position and at a floating potential.

The target is powered by a Hüttinger HMP2/1_P10 HiPIMS generator set at an average fixed power of 800 W by adjusting the target voltage. The pulse repetition frequency was set to 300 Hz, and the pulse width was 60 μs, which corresponds to a peak current of approximately 1.2–1.7 A/cm^2 depending on target poisoning. The power supply conditions were chosen to avoid arcing on the target surface even with target poisoning. The process stability was monitored using an optical emission spectrometer (OES) from AvaSpec-ULS2048L with a 0.07-nm resolution connected to a quartz fiber positioned along the erosion track at 2 cm from the target surface. Fig. 1 depicts the typical voltage-current curves obtained for the 1.3 sccm C_2H_2 experiment under the selected HiPIMS conditions together with the OES analysis for 0 and 1.7 sccm. When acetylene is added to the process atmosphere, the Ti^0, Ti^+ and Ar^+ ion emission lines clearly diminish, whereas the intensity of the Hα line at ~656 nm increases as can be concluded from Fig. 1b and c.

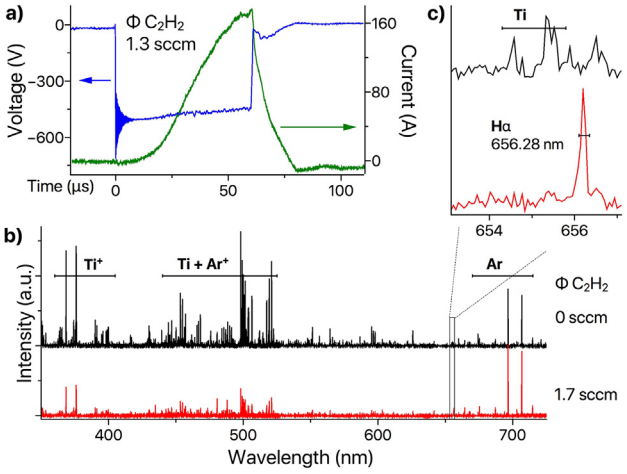

Fig. 1. Summary of the HiPIMS conditions chosen for the experiment. (a) Voltage and current curves at the target with a C_2H_2 flux of 1.3 sccm. (b) Optical emission spectra recorded with and without the C_2H_2 flux (1.7 sccm). (c) The region where the H_α emission line is enlarged shows its presence when the acetylene is introduced in the process.

The coatings were deposited on steel DIN 1.2083 disks polished with a diamond suspension of 1 μm of granulometry for the mechanical and tribological tests and on silicon wafers (1 0 0) for analytical purposes. All of the deposited samples have a thickness of approximately 2 μm as measured by a KLA Tencor profilometer (Alpha-Stepper IQ model). A titanium interlayer of approximately 200 nm was introduced to improve coating adhesion on the substrate. Before each deposition, the substrates and cathode were sputter cleaned.

The crystal structure analysis of the coatings was performed using a Philips X'Pert MRD diffractometer with Cu Kα radiation in two configurations: grazing incidence X-ray diffraction (GI-XRD) at 0.5° and θ–2θ scan repeated at different azimuthal and equatorial angles for pole figures. The data were analyzed using a simultaneous structure – microstructure texture refinement with MAUD software [14].

For transmission electron microscopy (TEM) characterization, a FEI Tecnai field emission gun scanning transmission electron microscope (STEM-FEG), mod. G2F30 with an S-Twin objective lens was used at 300 kV with a 0.2-nm point resolution. Electron energy-loss spectra (EELS) were obtained using a Gatan Imaging Filter (GIF) attached to the Tecnai microscope (QUAMTUM SE model) with an energy resolution of 0.3 eV. EELS spectra were recorded in TEM mode with a spectrometer collection angle of 2.02 mrad. Under these conditions, the energy resolution of the couple microscope/spectrometer system was ~0.8 eV. Gatan digital micrograph software was used to acquire images, EELS spectra, and perform further image and spectral processing. The amount of amorphous carbon phase ($x_{a\text{-}C:(H)}$) was evaluated by linear combinations of the C K-edge shape from TiC and a-C references as explained in [3].

XPS spectra were measured using a PHOIBOS 150 9MCD ESCA instrument equipped with aluminum $K_{\alpha 1,2}$ monochromatized radiation at the 1486.6 eV X-ray source. The measurements were performed in constant analyzer energy mode with a 20 eV pass energy for high resolution spectra. Charge referencing was performed by setting the binding energy of the sp^2 C—C(H) component of the C 1s photoelectron peak to 284.6 eV. Samples were previously cleaned using Ar^+ ion bombardment at 6.2×10^{-3} Pa; 2.9 kV; 10 mA; and 180 s. These conditions were found to be the most appropriate to preferentially remove the hydrocarbon surface contamination layer without affecting the film's elemental composition. Quantification was accomplished by determining the elemental peak areas, following a Shirley background subtraction and accounting for the relative sensitivities of the elements using Scofield cross-sections. The fitting analysis was then performed by a least squares fit of the C 1s of the films to estimate the relative amount of the different carbon bonds (carbides and amorphous carbon) in agreement with previous works [7].

Raman spectra (200–2000 cm^{-1}) were measured using a Lab-RAM Horiba Jobin Yvon spectrometer equipped with a CCD detector and a diode-pumped solid state laser (532 nm) at 5 mW. All of the samples were analyzed during 100 s of exposure time and with an aperture hole of 100 μm.

The tribological properties of the coatings were evaluated by ball-on-disk friction tests via unlubricated sliding against 6-mm 100Cr6 steel balls in ambient air at a relative humidity between 40 and 50%. The test parameters were set to 5 N for the applied load (maximum initial Hertzian contact pressure of 1.12 GPa), 10 cm/s linear speed, radius track between 6 and 10 mm and 1000 m of sliding distance. The normalized wear rates (mm^3/Nm) were evaluated from cross-sectional profiles taken across the disk-wear track using a stylus profilometer.

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