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Effect of ion bombardment on structural, mechanical, erosion and corrosion properties of Ti–Si–C–N nanocomposite coatings

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ABSTRACT

This study is one part of a series of efforts to optimize the microstructure and tribological properties of the Ti–Si–C–N coatings for a wide range of industrial applications. In this study, Ti–6Al–4V samples were coated with thick Ti–Si–C–N coatings (25–35 μm) using a plasma enhanced magnetron sputtering (PEMS) process, in which Ti was sputtered from two magnetrons at fixed power of 4 kW for each magnetron in a reactive environment of Ar, N_2 and trimethylsilane (TMS). The substrate power density (ion bombardment power density) was varied by varying the bias voltage and the ion flux, which was varied by changing the electron emission current in the PEMS process. After the depositions, scanning electron microscopy (SEM) and X-ray diffractometry (XRD) were used to study the microstructure and morphology of these coatings. Nano-indentation was performed to study the surface hardness H and modulus of elasticity E, from which the ratios of H/E^* and H^3/E^{*2} were calculated, where $E^* = E/(1-\nu^2)$ and ν is the Poisson's ratio. The solid particle erosion (SPE) resistance of the coatings was evaluated using a sand blaster with 50 μm alumina particles at two incident angles of 30° and 90°. Finally, an electrochemical test was conducted to determine the coating corrosion resistance. It was found that all coatings had a nanocomposite microstructure. But the coatings produced at the higher substrate power densities (0.13–0.20 W/cm^2) had a smaller crystallite size (5.2–5.8 nm) with a better morphological quality, i.e. free from columnar structure, defects or delamination. The substrate power density has a strong influence on the surface hardness and the ratios of H/E^* and H^3/E^{*2}. The higher the substrate power density, the higher these values. The solid particle erosion resistance and corrosion resistance of the coatings also correlated well with the substrate power density. Coatings deposited at higher power densities of ion bombardment exhibited better erosion resistance and corrosion resistance than those deposited at lower substrate power densities.

1. Introduction

Conventional coatings such as TiN and TiC have been intensively used for the past two decades due to their attractive physical, chemical and mechanical properties including high hardness, good wear resistance and thermal stability [1–3]. However, many industrial parts like dry cutting tools are increasingly exposed to elevated temperatures, around 500 °C and higher, which exceed the oxidation temperature of titanium nitride or carbide [4]. Therefore, nanocomposite coatings of Ti–Si–N, Ti–Al–Si–N and Ti–Si–C–N are being studied to replace conventional coatings for harsh industrial applications in which higher power, speed, efficiency, etc. are increasingly demanded. Nanocomposite coatings have demonstrated superior properties compared to conventional TiN and TiC coatings including the hardness, high thermal stability at elevated temperature (~1000 °C), wear resistance, and corrosion resistance [5–8]. The extraordinary mechanical and tribological properties of these materials were attributed to the nanocomposite structure mainly composed of a nanocrystalline phase or phases embedded in an amorphous matrix. Moreover, the relatively low friction coefficient (0.15–0.5) gives the Ti–Si–C–N coatings their importance in various applications [9–11].

As observed in the deposition of many other nitride or carbide coatings, the structural properties of the Ti–Si–C–N coatings depend on the plasma processing parameters such as magnetron power, gas flow rate, working gas pressure, substrate temperature and substrate power density derived from the bias voltage and the ion flux [12]. In this work, we mainly study the effects of the substrate power density on the Ti–Si–C–N coatings deposited on Ti–6Al–4V substrate using the plasma enhanced magnetron sputtering (PEMS) process [12,13]. This study is one part of a series of efforts to further optimize the microstructure, mechanical and tribological properties of the Ti–Si–C–N coatings that have been used for a wide range of industrial applications. Here we report the microstructural results and mechanical performance obtained from the studies using X-ray diffraction (XRD), scanning electron microscopy

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(SEM), nanoindentation, solid particle erosion (SPE) test and corrosion test.

2. Experimental details

Ti–6Al–4V substrates (25 × 25 × 3 mm) were used in this study. The specimens were polished using typical metallographic means. The final surface roughness Ra was measured to be ~10 nm. The specimens were then ultrasonically washed in isopropyl alcohol before they were installed in the vacuum chamber for processing. The Ti–6Al–4V substrates were mounted on an 8″ diameter drum, which was centered in the deposition chamber between the two sputter targets. High purity titanium circular targets (99.99%) with 15 cm in diameter were used to deposit the Ti–Si–C–N coatings. The target-substrate distance was approximately 10 cm. The setup and process with a schematic of PEMS have been discussed in detail previously [13]. Briefly, in the PEMS process W filaments are heated with an AC power supply to generate primary electrons, while a DC discharge power supply is applied to bias the filaments negatively with respect to the vacuum chamber to draw the electrons to the chamber walls. Due to the electron–Ar neutral impact collisions, ionization occurs and "global plasma" is generated in the entire vacuum chamber. The global plasma is independent of the magnetron plasma. It is first used for ion sputter cleaning the samples without the need of turning on the magnetrons or using high pressure glow discharge. Then during the deposition of a coating, the global plasma remains on for the enhanced ion bombardment. It is noted that at a constant discharge voltage and gas pressure, the discharge current is proportional to the plasma density, which in turn determines the ion flux to the sample surface.

After loading the samples into the PEMS chamber, the system was evacuated by a stack of mechanical pump, Roots blower and diffusion pump from atmospheric pressure to a base pressure of 7×10^{-6} mbar in about 1.5 h. Then, Ar gas (Ar flow rate = 150 sccm) is introduced into the PEMS chamber to increase the working gas pressure to about 3.42×10^{-3} mbar. Before starting the deposition process, the samples were sputter cleaned with Ar ions using a discharge current of 10 A and negative bias voltage of 120 V, corresponding to an ion current density of 5 mA/cm^2, for 90 min to remove the residual oxide. Fifty (50) minutes into the cleaning process, a low power of 500 W (490 V, 1.02 A) was applied to the magnetrons to sputter clean the Ti target surfaces with the shutter being closed so that no Ti could be deposited on the samples. Two magnetrons facing each other at 180° were used in this study. Once the samples and the targets were cleaned, while the global plasma remained, the power to the magnetrons was increased to 4 kW and the shutters were opened for the deposition of a bond layer of Ti for 10 min. Then N_2 and trimethylsilane ($[CH_3]_3SiH_4$, TMS) gas were gradually introduced to the vacuum chamber to reach the set point for the deposition of the Ti–Si–C–N coating. The total working gas pressure $p_T = p_{Ar} + p_{N_2} + p_{TMS}$ in magnetron sputter deposition of coatings was 3.85 × 10 − 3 mbar.

It is understood that the ion energy per arriving atom is a very important parameter that determines the microstructure of a coating and the internal stress [14–16]. It is proportional to $U_s i_s/\alpha_D$, where U_s is the bias voltage on the substrate, i_s is the ion current density to the substrate and α_D is the number of Ti atoms and particles deposited on the substrate. In this study, the magnetron power was not varied and the reactive gas flow rates varied little. Therefore, the rate α_D at which the Ti atoms and particles sputtered from the target arrived at the substrate surface was nearly constant. The substrate power density (the ion bombardment power density to the substrate), P_s, defined as the substrate bias voltage U_s times the ion current density i_s, was varied to study its effect on the coating microstructural and mechanical properties. The bias voltage U_s was varied from −20 to −80 V. Since the samples rotated (double rotation set-up) between the magnetrons, the ion current density i_s was obtained in a separate experiment prior to this study, in which a Faraday cage was mounted on the sample holder which was not rotated. While the discharge voltage was maintained at 120 V, by varying the W filament current, the discharge current I_D was varied and hence the ion current density i_s to the Faraday cage was obtained. Thus, in this study assuming the rotation would not change the ion current density, the ion current density i_s was calculated from the discharge current I_D. In addition, the reactive gas flow rates of N_2 and TMS, selected based on previous studies [12,13], were varied slightly to seek further improvement in mechanical properties and corrosion performance. Shown in Table 1 are the deposition parameters in this study. The substrate power density P_s is listed in column 4 of Table 1.

After the depositions, the specimens were examined using various techniques. X-ray diffraction (XRD) using Cu-Kα radiation was used to identify the crystal structure and crystallite size in the coating. The full-width at half maxima (FWHM) was analyzed by Scherrer's formula to determine average particle size. The Scherrer's equation is given by

$$D = 0.9\lambda/(\beta \cos\theta)$$

where D is the mean crystallite size, λ is the X-ray wavelength, β is the peak width at half the maximum intensity (FWHM), and theta (θ) is the Bragg's angle.

The thickness, the surface morphology and cross-sectional microstructure of the coatings were examined by scanning electron microscopy (SEM). The influence of PEMS deposition conditions on the adhesion strength of the coatings was evaluated by the Rockwell hardness indentation method. A conical diamond indenter penetrates into the surface at a standard testing load of 150 kg. Then the surface fractures were examined by scanning electron microscopy (SEM) at a magnification of 100×. The mechanical properties of the uncoated and coated specimens were measured using a PICODENTOR HM500 (Fisher Corp., max. test force 0.5 N) nanoindentation tester with a displacement resolution of 0.01 nm and a loading resolution of 50 nN. With the load/indentation depth method according to DIN EN ISO 14577 [17], the Vickers indenter is pressed with continuously increasing test load into the sample surface and then reduced in the same manner while simultaneously measuring the respective indentation depths. The indentation hardness (H) was measured under a maximum indentation load of 300 mN, while the indentation elastic modulus (E_{IT}) is determined when the test load is reduced. The effective Young's modulus was calculated from the equation of $E^* = E_{IT}/(1-\nu^2)$, where ν is the Poisson's ratio of the sample. The theory of this method (Oliver Pharr method) for the determination of E_{IT} is described in [18]. However, the elastic recovery (We) was evaluated using the indentation displacements only. The average values of the mechanical parameters were performed for each specimen from 10 single readings. The values of H/E^* (the "plasticity index", related to the elastic strain to failure) and H^3/E^{*2} (related to the resistance to plastic deformation) were then calculated. It is well known that for most indentation test instruments, reaction forces can cause the load frame to be elastically deflected; this results in an experimental error in the reported penetration depths and consequently in the mechanical measurements. Further, surface roughness and defects can results in a tip slipping on the sample surface at shallow depths. Therefore, a relatively high load of 300 mN was used in the present tests to reduce tip slipping on surface. Moreover, error bars indicating the standard deviation were calculated and combined to the hardness and elastic modulus data.

The solid particle erosion (SPE) tests were performed at room temperature according to the ASTM standard G76-04 [19], using a sand erosion tester at two incident angles of 30° and 90°. Al_2O_3 powder with an average particle size of 50 μm was used as the erosion media. The backpressure of the nozzle was 20 psi, resulting in the particle speed of 14 m/s and the flow rate of the Al_2O_3 powder of 5.19 g/min. The distance between the nozzle and the sample was set at 1 cm. To minimize the pressure drop errors during the test, a pulsed blast was used. In each test, the pulse was on for 20 s; then off for 5 s. This comprised a single spray cycle. The cumulative erosion test for each sample was conducted in six cycles, a total of 2 min of sand blasting with the total Al_2O_3 powder