EFFECT OF SUBSTRATE BIAS ON ELECTROCHEMICAL CORROSION OF AMORPHOUS CARBON NITRIDE THIN FILMS

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1. Introduction

Diamond-like carbon (DLC) and carbon nitride (CN) thin films are promising candidates for coating of standard medical metal alloys (Ti6Al4V, CoCrMo). Due to their excellent wear resistance, coefficient of friction, hardness, chemical inertness and biocompatible nature they can meet the requirements of suppressing the harmful release of ions, wear debris formation, and undesirable biological reactions with the surrounding tissue [1-4]. The properties that directly influence the corrosion behavior of DLC films are sp³/sp² ratio, film structure, porosity, adhesion to substrate, surface roughness and electrical conductivity. The sp³/sp² ratio is affected by the deposition conditions and varied also with used deposition method [5, 6]. The application of substrate bias is frequently used to control the energy around 100 eV allowing the formation of the highest number of sp³ bonds in the film [7, 8]. In this study, the influence of substrate bias on the electrochemical corrosion behavior and hardness was investigated.

2. Experimental

The a-C:N thin films were deposited on cylindrical CoCrMo samples in a vacuum system UVNIPA-1-001 described previously [9]. Mirror polished silicon substrates and cylindrical CoCrMo samples were used for deposition of the coatings. The substrates were cleaned for 10 min. with Ar ions prior to the deposition cycle. The sputtering frequency of the arc source pulses was 3 Hz and the total number of sputtering pulses 1.5k for Si and 3k for

CoCrMo samples. Background pressure was 10^{-4} Pa and working pressure was maintained at around 1 Pa according to gas flow. Argon to nitrogen (Ar:N) gas flow ratio was set up to 40:40 sccm. The temperature was kept below 150 °C. Negative substrate bias from 0 to - 2.5 kV was applied during deposition process to change the incident ions energy. Potentiodynamic polarization tests were employed to assess the corrosion performances of the films using Autolab Potenciostat Galvanostat at room temperature in 0.89 wt. % NaCl solution with Ag/AgCl reference electrode (RE). The samples were tested immediately after immersion with scan rate 80 mV/s. Hardness measurements were performed using Fisher Picodentor HM500. The structural properties of a-C:N films were studied by Raman spectroscopy with 632.8 nm radiation from a He–Ne laser. The acquired Raman spectra were fitted with a Gaussian line to illustrate the D and G peak positions, G peak full width at half maximum (FWHM) and I_D/I_G ratio.

3. Results and discussion

A remarkable change in I_D/I_G ratio, G peak FWHM and position with varying substrate bias can be observed in Fig. 1a) and 3b). As the incident carbon ion energy due to changing substrate bias increases, the I_D/I_G ratio decreases from 0 V and has a minimum value around -2 kV, whereas the G peak FWHM decreases nearly linear. The I_D/I_G falls as the number of rings per cluster falls and the fraction of chain groups (disorder) rises. The I_D/I_G is also in direct proportion to in-plane correlation length L_a or domain size [8]. The G peak position decreases from 1537 cm⁻¹ to 1525 cm⁻¹ with increasing substrate bias from 0 to -2.5 kV. It is generally accepted that increase of the I_D/I_G ratio and shifting of the G-peak toward higher wavenumber are caused by the increase of the graphite-like component in the CN films and the sp²-bonded carbon clusters size [10].



Fig.1: *a)* Dependence of Raman G peak position and I_D/I_G ratio of a-C:N deposited with different substrate bias, b) polarization curves of uncoated and a-C:N coated CoCrMo deposited with different substrate bias



Fig.2: a) G peak position and E_{corr} vs RE (Reference Electrode) dependence on substrate bias for a-C:N deposited on Si, b) E_{corr} vs RE and G peak FWHM dependence on Raman spectra G peak position for a-C:N deposited on Si

Fig. 1b) shows the polarization curves of uncoated and a-C:N coated CoCrMo substrates deposited with different substrate biases. The potential region of the a-C:N coated samples ($E_{corr} = -47.2 \text{ mV}$) was shifted towards more positive values compared to uncoated samples ($E_{corr} = -392.4 \text{ mV}$), i.e., showed more noble corrosion potentials (a shift of approximately 350 mV). Besides, it can be seen from the figures that the range of current density for protecting film formation is smaller for coated substrates than for uncoated. The samples in the corrosion behavior with lower current density and higher potential indicate better corrosion resistance evidenced by a shift of the whole polarization curve towards the region of lower current density and higher potential [11]. Fig. 2a) shows the dependence of E_{corr} on substrate bias applied during deposition. It can be seen that the line is almost similar to the G peak position dependence. The highest value of E_{corr} can be observed for the sample deposited with negative bias -0.6 kV and with further increasing of U_s the corrosion potential shifts to lower values. We can see that (Fig. 1a and 2), the highest value of E_{corr} occurs within the higher G peak position, FWHM and I_D/I_G ratio region, where the lower sp³/sp² ratio, higher number of graphitic rings per cluster and higher domain size can be expected.

In the Fig. 3a) we can see the SEM image of a-C:N layer deposited on CoCrMo after potentiodynamic polarization tests. After corrosion tests, all of the coatings seemed to have less or more noticeable amount of surface pits. The micrograph in Fig. 3 a) shows shallow wide pits with vertical grain attack. It is known that the pits initiate at defects, surface compositional heterogeneities and porosities because these imperfections degrade the cross-linking structure of the film. The increased surface roughness of CoCrMo substrates can

contribute to degradation of corrosion resistance of the protection films because of a larger exposed surface area to the electrolyte during the corrosion testing. Fig. 3b) shows also the dependence of hardness on negative bias for a-C:N on CoCrMo. We can see that the hardness has its maximum between 1 kV and 2 kV. High hardness can be reached using the optimum ion energy for the formation of high concentration of sp³ C-C and C-N bonds in the a-C:N film.



Fig.3: *a)* SEM image of corroded areas on a-C:N layer deposited on CoCrMo, shallow wide pits with vertical grain attack, b) dependence of hardness and G peak FWHM of a-C:N deposited with different substrate bias

4. Conclusions

Diamond like carbon thin films were deposited on medical grade CoCrMo alloys by glow discharge sputtering method with different substrate biasing and gas flow. The corrosion potential of the a-C:N coated samples was shifted towards more positive values and the range of current density was smaller compared to uncoated samples. This indicates that the tendency towards corrosion for coated samples has become weaker. The highest value off E_{corr} for CoCrMo substrate was measured on the coating deposited with substrate bias around -0.6 kV. The shift of E_{corr} to more positive values was approximately 350 mV. All of the coatings after polarization tests seemed to have less or more noticeable surface degradation. SEM micrographs showed a small amount of surface localized shallow wide pits with vertical grain attack and surface solid products which usually agglomerate around the defects or pores. Hardness of the coated samples was dependent on the value of connected negative substrate bias. The highest hardness on CoCrMo substrates was measured for negative bias between 1 kV and 2 kV, where the Raman spectroscopy showed the lowest I_D/I_G ratio and G peak position.

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