Recent advances in diamond-like carbon-based nanocomposites

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Abstract

Diamond-like Carbon (DLC) films have been the focus of extensive research in recent years due to its potential application as surface coatings. Crystalline diamond (NCD) and titanium dioxide (TiO_2) in the form or nanoparticles were incorporated in DLC films for different applications. The films were growth on 316L stainless steel substrates from a dispersion of these nanoparticles in hexane using plasma enhanced chemical vapor deposition. NCD particles reduced the steel pitting corrosion, improving DLC and stainless steel electrochemical corrosion resistance and preventing aggressive ions from attacking metallic surfaces. The presence of TiO_2 nanoparticles increased DLC bactericidal activity. In addition, TiO_2–DLC films increase the chemical interaction between bacteria and the films, which is an additional factor for the increasing bactericidal activity. From these results, nanoparticle-incorporated DLC films increase the range of applications of these coatings, adding them new properties.

Introduction

Diamond-like carbon (DLC) films have been actively studied over the last decades in the field of material engineering [1-2]. In our laboratory, it was developed a new technique that permits the deposit of DLC films from liquid hexane [3]. With this technique, it is possible to deposit films from a dispersion of different kind of nanoparticles in hexane in order to create different kind of DLC films for different applications. In this report, we show the main results obtained in our laboratories from the production and characterization of nanoparticle-incorporated DLC films.

The films were grown over 316L stainless steel using plasma enhanced chemical vapor deposition. Details concerning the sample preparation and deposition technique can be found in our previous publications [3-4]. To produce the nanoparticle-incorporated DLC films, crystalline diamond (NCD) and titanium dioxide (TiO_2) nanoparticles were dispersed in hexane at different proportions. These dispersions replaced the pure hexane during the DLC deposition.

Nanocrystalline diamond (NCD) particles with ~250 nm of average particle size were incorporated into DLC films in order to investigate NCD-DLC electrochemical corrosion resistance. Electrochemical tests were performed using a conventional three-electrode electrochemical cell [5]. In this cell, the reference electrode was a saturated Ag/AgCl electrode, the counter electrode was a platinum wire and the working electrodes were the stainless steel, DLC and NCD-DLC films. The electrolyte solution was a 0.5 mol/L sodium chloride (NaCl) aqueous solution, pH 5.8, which was not stirred and was naturally aerated. Potentiodynamic tests were carried out by polarization of samples in the anodic direction, from -2.0 to +2.0 V, just after exposition to the electrolyte solution. The potential sweep rate was 1 mV/s. The impedance measurements were also carried out in 0.5 mol/L NaCl aqueous solution, pH 5.8. The electrochemical impedance spectra (EIS) were obtained over the frequency range 100 kHz–10 mHz, at open circuit potential, with an AC excitation of 10 mV. All experiments were performed at room temperature.

The electrochemical stability of the systems in the test solution was investigated by the open-circuit potentials (OCP). The greatest E_{corr} value of -0.321 mV was observed for NCD-DLC films. The negative OCP values for the samples may be caused by the penetration of the test solution [6-7]. The electrochemical parameters obtained from the potentiodynamic polarization curves (Fig. 1a) are given in Tab. 1. The corrosion current density (i_{corr}) of NCD-DLC films reduced by more than 5 times with comparison to the stainless steel. The protective efficiency [7] calculated from corrosion current density also indicates NCD-DLC films offer the best protection among the uncoated samples up to 81.3%. In general, samples in the corrosion behavior with lower current density and higher potential indicate better corrosion resistance [8]. An improvement in the NCD-DLC corrosion resistance is evidenced by a shift of the polarization curve towards the region of lower current density and higher potential. Even DLC films presented the best protective effect at high anodic potentials, with a greater tendency to passivate, the presence of nanoporous on its surface increase its corrosion current density.

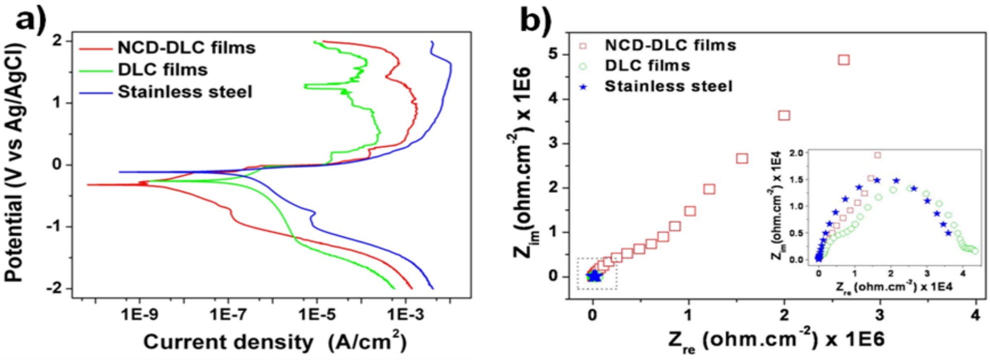

Figure 1. a) Potentiodynamic polarization curves of stainless steel, DLC and NCD-DLC films in NaCl at room temperature. b) Nyquist plot of stainless steel, DLC and NCD-DLC films, with an enlargement of the region within the rectangular box.

Table 1. Electrochemical parameters obtained from potentiodynamic polarization curves in NaCl at room temperature.

Samples	E_{corr} (mV)	i_{corr} (nA/cm^2)	Protective efficiency (%)
Stainless steel	-0.117	0.359	-
DLC films	-0.241	1.740	-748.8
NCD-DLC films	-0.321	0.067	81.3

The Nyquist plots determined by electrochemical impedance spectroscopy (EIS) in Fig. 1b show the different corrosion behavior of the samples after immersion in NaCl. NCD-DLC films present superior impedance in comparison to the pure DLC and the stainless steel. The enhancement in corrosion resistance of the NCD-DLC samples can be attributed to the reduced electrical conductivity caused by the intrinsic chemical inertness of the NCD-DLC films in comparison to the uncoated samples [8]. In addition, NCD-DLC films can act as a passive film to prevent aggressive ions from attacking the substrate and thereby improve the corrosion resistance of 316L stainless steel (Fig. 2). The chloride (Cl^-) ions of the NaCl solution attack the protective oxide layer on 316 stainless steel surface, penetrating to the austenite matrix and resulting in pitting corrosion [9]. The NCD-DLC samples show very little pitting corrosion. NCD particles may occupy the nanoporous in DLC films, preventing the attacking of the Cl^- ions. The SEM images of NCD-DLC film after the electrochemical corrosion test (Fig. 2b) shows minor NCD particles that did not belong to the film surface (Fig. 2a). These NCD particles probably block the attacking of Cl^- ions, forming a barrier against the corrosion. From the results here presented, it is possible to see NCD-DLC films improving DLC and stainless steel electrochemical corrosion resistance, becoming a potential candidate for an anti-corrosion material in industrial applications.

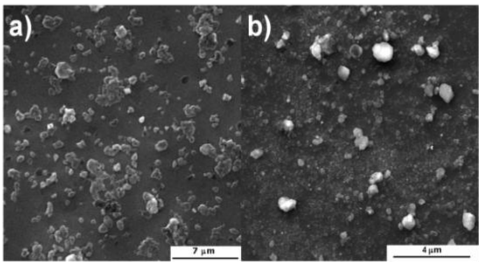

Figure 2. SEM images of NCD-DLC films (a) before and (b) after the electrochemical corrosion tests.

Concerning space application, some studies is in progress in order to get higher hardness and low friction coefficient when diamond nanoparticles under 10 nm is incorporated in DLC films.

On the other hand, due to TiO_2 photo-semiconductor properties, it may find an application as antibacterial agent for the decomposition of organisms [10-11]. TiO_2 in the anatase crystalline form is a strong bactericidal agent when exposed to near UV-light [12]. TiO_2 nanoparticles with average particle size of 21 nm, in anatase crystalline form were dispersed in hexane at 0.1, 0.5 and 1.0 g/L. These dispersions replaced the pure hexane during the DLC deposition. The antibacterial activity of the TiO_2-DLC films was determined using *Escherichia coli* ATCC 25922. More details about the antibacterial test methodology can be found in our previous publication [13].

Figure 3a shows the antibacterial activity of the stainless steel coated and non-coated with DLC and TiO_2-DLC films in different TiO_2 concentrations. The pure DLC films killed at about 32.5% of the total bacteria content. However, the bactericidal effect of TiO_2-DLC films was increasing with the increasing of TiO_2 content. The exact killing mechanism(s) underlying the TiO_2 photocatalytic reaction is not yet well understood. Huang et al. [10] proposed a detailed mechanism for the bactericidal effect of TiO_2 photocatalytic reaction. They pointed out the initial oxidative damage takes place on the cell wall, where the TiO_2 photocatalytic surface makes first contact with intact cells. Cells with damaged cell wall are still viable.

After eliminating the protection of the cell wall, the oxidative damage takes place on the underlying cytoplasmic membrane. Photocatalytic action progressively increases the cell permeability, and subsequently allows the free efflux of intracellular contents that eventually leads to cell death.

From a physicochemical point of view, the adhesion of bacteria cells to a surface is determined by the interplay of electrostatic and hydrophobic/hydrophilic interactions. The interfacial free energy of adhesion (ΔF_{Adh}) for bacteria to attach the coatings was calculate according to Schneider [14]. The as-deposited DLC films presented ΔF_{Adh} = +17.6 mJ/m^2. According to the thermodynamic theory, the bacterial adhesion is unfavorable if the work of adhesion is positive. The TiO_2-DLC films produced from 1.0 g/L TiO_2 in hexane presented ΔF_{Adh} = -5.2 mJ/m^2. In this case, the bacterial adhesion is favourable. Figure 3b compared the theoretical values of work of adhesion with the practical results of antibacterial activity. The good correlation coefficient ($R^2 = 0.9999$) shows that the bactericidal mechanism suffers influences not only from the presence of TiO_2 nanoparticles on the DLC surface, but also from the interaction between the nanoparticles and the DLC film, changing its proper characteristics. These results suggest that as the TiO_2 content in DLC films increased, they become thermodynamically favorable to bacterial adhesion, increasing the direct contact between bacteria and more TiO_2 nanoparticles, promoting the increase in the bactericidal activity.

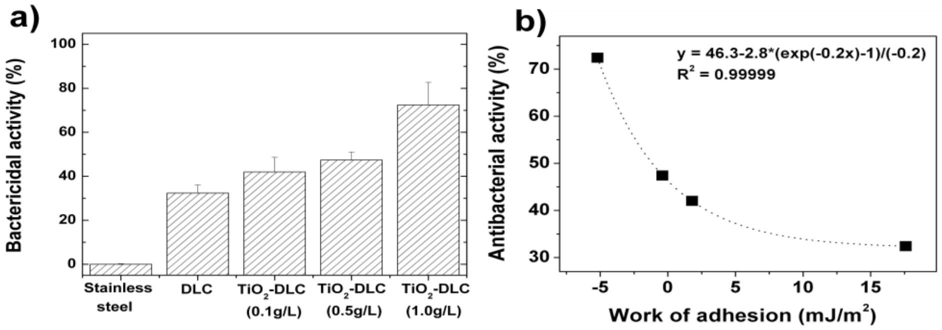

Figure 3. a) Antibacterial activity of the stainless steel coated and non-coated with DLC and TiO_2-DLC films in different TiO_2 concentrations. b) Antibacterial activity vs. work of adhesion.

In this manuscript, it was reported the main results obtained in our laboratories from the production and characterization of nanoparticle-incorporated DLC films. NCD particles improve DLC and stainless steel electrochemical corrosion resistance, reducing the pitting corrosion. NCD-DLC films prevented aggressive ions from attacking metallic surfaces, becoming a potential candidate for an anti-corrosion material in industrial applications. In addition, TiO_2 nanoparticles increased DLC antibacterial activity against *E. coli.* Thermodynamic approaches confirm these results due to the increasing of interaction between bacteria and the studied films. In general, DLC films have a huge range of applications. As it was demonstrated in this manuscript, the nanoparticle-incorporated DLC films can modified the DLC structure increasing the range of applications with new scientific and technological applications.

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