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Short Communication

Improvement of diamond-like carbon electrochemical corrosion resistance by addition of nanocrystalline diamond

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ABSTRACT

Nanocrystalline diamond (NCD) particles were incorporated into diamond-like carbon (DLC) films in order to investigate NCD–DLC electrochemical corrosion resistance. The films were grown over 304 stainless steel using plasma-enhanced chemical vapor deposition. NCD particles were incorporated into DLC during the deposition process. The investigation of NCD–DLC electrochemical corrosion behavior was performed using potentiodynamic polarization against NaCl. NCD–DLC films presented more negative corrosion potential and lower anodic and cathodic current densities. The electrochemical analysis indicated that NCD–DLC films present superior impedance and polarization resistance compared to the pure DLC, which indicate that they are promising corrosion protective coatings in aggressive solutions.

Diamond-like carbon (DLC) is a metastable form of amorphous carbon containing a significant fraction of sp^3 bonds [1]. It is known that DLC electrochemical corrosion behavior is heavily dependent on the film composition and structure, which are in turn dependent on the deposition technique and precursor gas [2]. In this paper, we show for the first time the incorporation of nanocrystalline diamond (NCD) particles into DLC films in order to investigate NCD–DLC electrochemical corrosion resistance.

The films were grown over 304 stainless steel using plasma-enhanced chemical vapor deposition. Details concerning the sample preparation and deposition technique can be found in our previous publication [3]. Ten layers containing NCD particles (0–250 nm, De Beers) were incorporated into DLC in order to form NCD–DLC films.

Electrochemical tests were performed using a conventional three-electrode electrochemical cell [4]. In this cell, the reference electrode was a saturated Ag/AgCl electrode, the counterelectrode 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 100–10 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 [5,6]. The electrochemical parameters obtained from the potentiodynamic polarization curves (Fig. 1) are given in Table 1. The corrosion current density (i_{corr}) of NCD–DLC films was reduced by more than five times compared to the stainless steel. The protective efficiency [6] calculated from corrosion current density also indicates that 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 [7]. An improvement in the NCD–DLC corrosion resistance is evidenced by a shift of the polarization curve toward 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 nanopores on its surface increases its corrosion current density.

Nyquist plots determined by electrochemical impedance spectroscopy (EIS) in Fig. 2 shows the different corrosion behaviors of the samples after immersion in NaCl. NCD–DLC films present superior impedance in comparison with 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

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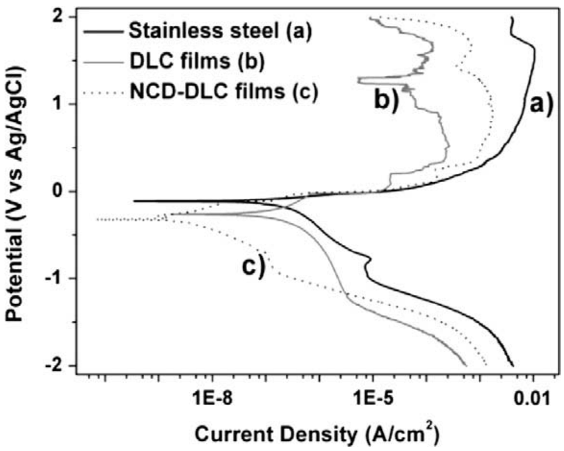

Fig. 1. Potentiodynamic polarization curves of stainless steel, DLC, and NCD–DLC films in NaCl at room temperature.

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

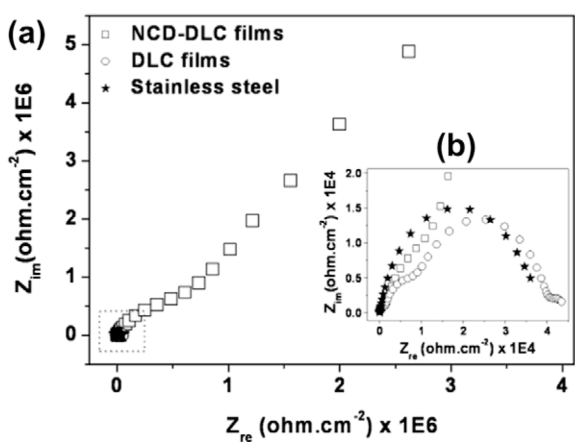

Fig. 2. (a) Nyquist plot of stainless steel, DLC, and NCD–DLC films. (b) Enlargement of the region within the rectangular box in (a).

caused by the intrinsic chemical inertness of the NCD–DLC films in comparison to the uncoated samples [7]. 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. 3). The chloride (Cl^-) ions of the NaCl solution attack the protective oxide layer on the 304 stainless steel surface, penetrating the austenite matrix and resulting in pitting corrosion [8]. The NCD–DLC samples show very little pitting corrosion. NCD particles may occupy the nanopores in DLC films, preventing attacking of the Cl^- ions.

Scanning electron microscopy (SEM) of NCD–DLC film after the electrochemical corrosion test (Fig. 3b) shows minor NCD particles

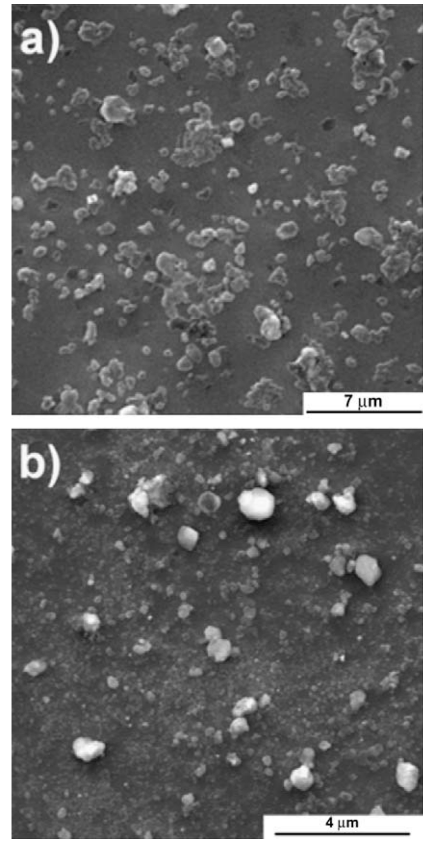

Fig. 3. SEM images of NCD–DLC films (a) before and (b) after electrochemical corrosion tests.

that did not belong to the film surface (Fig. 3a). These NCD particles probably block the attacking of Cl^- ions, forming a barrier against the corrosion.

From the results presented in this paper, it is possible to see for the first time that NCD–DLC films improve DLC and stainless steel electrochemical corrosion resistance. NCD–DLC prevented aggressive ions from attacking metallic surfaces, becoming a potential candidate for an anticorrosion material in industrial applications, such as pipelines in the petroleum industry.

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