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Evaluation of corrosion resistance of diamond-like carbon films deposited onto AISI 4340 steel

R. P. O. S. Nery · R. S. Bonelli · S. S. Camargo Jr.

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Abstract The corrosion resistance of amorphous diamond-like carbon (DLC) coatings deposited by radio frequency plasma enhanced chemical vapor deposition (rf-PECVD) technique on AISI 4340 steel substrates was evaluated under saline (5% NaCl) and acid (1700 ppm H_2SO_4) atmospheres. The corrosion process was investigated by surface characterization and electrochemical methods, such as potentiostatic polarization and electrochemical impedance spectroscopy (EIS). DLC coatings effectively protected the substrate after 48 h in a salt fog chamber and after the first Kesternich cycle. For comparison, under the same conditions, titanium nitride (TiN) coatings did not protect the substrate even for 2 h of saline exposure and even for the first Kesternich cycle. Although the DLC coatings resisted well to the corrosive action of the aggressive media, nucleation and growth of homogenous and micro-sized pinholes uniformly distributed on DLC coatings were observed as a result of the corrosion processes. The observed results suggest that the development of techniques which would reduce the porosity of the DLC films could promote further improvement on their corrosion protection ability.

Introduction

Amorphous diamond-like carbon (DLC) coatings have attracted intensive research in various fields of engineering due to their versatility and outstanding properties. High modulus of elasticity and hardness, wear resistance, biocompatibility, and chemical stability are some examples [1]. Applications range from coatings for magnetic and optical disks, video recorder drums, magnetic tapes, mechanical tools, engine parts, razor blades, optical devices, bar-code scanners, sunglasses, biomedical devices (implants and stents), polyethylene terephthalate bottles, microelectromechanical systems and others [2–9]. Most of these applications take advantage of the outstanding mechanical properties of these materials in order to provide wear and scratch protection to the substrates. However, as new and more demanding applications are being developed, other qualities of these films start to require a deeper investigation.

Studies about DLC corrosion resistance started to gain interest as it became clear that the outstanding properties of this material need to be associated with resistance to corrosion in order to allow some of the technological applications that have been proposed. At room temperature, DLC films are chemically inert to almost any solvents and are not attacked by acids or bases. Even in quite aggressive environments DLC are inert [10]. Corrosion of DLC-coated metallic substrates are thought to occur at flaws or pores of the films, followed by reaction of aggressive agents with the substrate, leading to a worsening of interface adhesion, spalling of coatings, and the exposure of substrates to the environment [11–14].

The purpose of this work is to investigate the corrosion resistance of DLC coatings deposited by radio frequency plasma enhanced chemical vapor deposition (rf-PECVD)

R. P. O. S. Nery (✉) · S. S. Camargo Jr.
Metallurgy and Materials Engineering, Federal University of Rio de Janeiro, P.O. Box 68505, Rio de Janeiro, RJ 21945-970, Brazil
e-mail: rnery@metalmat.ufrj.br

R. S. Bonelli
Corrosion Laboratory, National Institute of Technology, Rio de Janeiro, Brazil

on AISI 4340 steel substrates under saline (5% NaCl) and acid (1700 ppm H_2SO_4) atmospheres. For this purpose, samples were exposed to accelerated corrosion testing and the corrosion process was analyzed in terms of surface and electrochemical characterization. The performance of DLC-coated samples was evaluated in comparison to uncoated and TiN-coated ones.

Experimental

Substrates preparation and coatings deposition

AISI 4340 steel substrates were chosen as they are widely used for manufacturing of structural and mechanical parts. DLC films were deposited by rf-PECVD from pure methane gas (99.999% purity) at −800 V self-bias voltage. Before deposition, the substrates were mechanically polished down to 1 μm diamond paste, cleaned in an ultrasonic bath, and submitted to an in situ argon plasma cleaning for 15 min. A thin amorphous silicon layer (~30 nm) was deposited at −500 V bias voltage in order to obtain an adhesive layer. The key parameters used to produce DLC films are shown in Table 1. A total coating thickness of about 2–3 μm was achieved. Films deposited under the same conditions on crystalline silicon substrates present hardness values of 20–22 GPa and internal stress of about 1.5 GPa.

TiN coatings were deposited by BodyCote Brasimet (São Paulo, Brazil) by cathodic arc deposition using a HTC 1200 PVD unit (Hauzer Techno Coating) under deposition conditions usually employed for coating of tools, as summarized in Table 2. The coatings thickness was around 4 μm.

Table 1 Treatment key parameters used to produce DLC films by rf-PECVD technique

Step	1st	2nd	3rd
Treatment	Ar sputtering	Amorphous Si	DLC
Gas	Ar	SiH_4	CH_4
Self-bias (V)	−800	−500	−800
Pressure (Torr)	0.015	0.015	0.015
Time (min)	15	3	120

Microscopic and surface analysis

To evaluate the quality of DLC coatings, surface roughness was analyzed before and after deposition by a contact profilometer (Sloan Dektak IIA). A scanning electron microscope (Zeiss DSM 940) was also used at 20 keV to evaluate the existence of surface defects, such as pores and delaminated regions.

After performing corrosion tests, the surface of the samples was evaluated by an optical microscope (Alicona Infinite Focus). Digital multifocus technique was used for three-dimensional surface scanning so as to obtain information on surface topography and dimensions of surface defects in order to aid the corrosion analysis.

Accelerated corrosion testing

All samples were submitted to a simulated marine corrosive atmosphere by ASTM B117 salt fog test, while a different specimen of each type was submitted to a simulated industrial corrosive atmosphere by ASTM G87 Kesternich test. These tests were chosen because in general the salt fog test does not result in the formation of a passive layer on carbon steels, while the Kesternich test does. In this way, the results of these tests are expected to be in some way complementary. In the case of the salt fog test, the samples were exposed for up to 168 h, interrupted at certain times for visual inspection, and photographic recording, while in the case of Kesternich test, the samples were exposed for two cycles, interrupted for visual inspection, microscopy investigation and electrochemical analysis.

Electrochemical measurement

Potentiostatic polarization and electrochemical impedance spectroscopy (EIS) were employed to evaluate the corrosion resistance during the Kesternich tests. Both electrochemical methods were carried out with a potentiostat/galvanostat

Table 2 Treatment key parameters used to produce TiN films by cathodic arc

Steps	Steps conditions	Pressure	Temperature
Pump down and heating	–	5×10^{-5} mbar	450 °C
Metal ion etch	Substrate voltage 900–1200 V Arc current 140 A	5 min	450 °C
Reactive deposition (cathodic arc)	Substrate voltage 80 V Arc current 140 A	3×10^{-3} mbar—N_2	450 °C
Cool down	–	5×10^{2} mbar—N_2	<200 °C

(Princeton Applied Research, Parstat 2263). The polarization and EIS parameters used are shown in Tables 3 and 4.

Electrochemical experiments were performed in a three-electrode cell with a platinum counter electrode, saturated calomel 3 M KCl reference electrode and working electrode (sample) with 9.07 cm^2 exposure area. The electrolyte solution was prepared in the Kesternich chamber without samples inside. The H_2SO_4 concentration inside the chamber was estimated as 1700 ppm.

The corrosion resistance was measured in terms of polarization resistance (R_p) in the usual manner and the values of impedance were used in order to confirm the corrosion behavior.

Results and discussion

Microscopic characterization

Figure 1 shows the results of the microscopic characterization of as deposited samples. TiN coatings were observed as having a large number of micropores and surface defects, while the DLC films were smooth and presented no significant amount of microporosity. Moreover, the topography of DLC films followed closely the substrate surface topography with average surface roughness (R_a) of about 80 nm, confirming the good surface quality of these coatings.

Table 3 Key parameters used in potentiostatic polarization

Software PowerSuite (PowerSine)	
Multi-sine technique	
Frequency range	3 MHz–7.23 kHz
Points/decade	6
AC amplitude	10 mV (rms) (at open circuit potential)

Table 4 Key parameters used in EIS

Software PowerSuite (PowerCorr)	
Potential range	±250 mV (at open circuit potential)
Step height	1 mV
Scan rate	1 mV/s
Step time	1 s
Polarization way	Cathodic to anodic

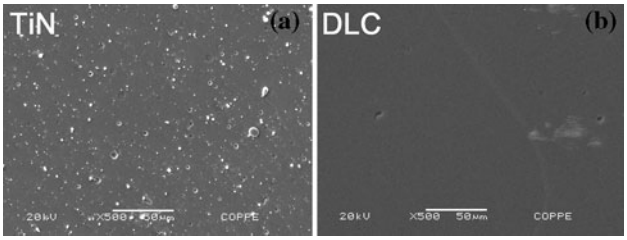

Fig. 1 SEM characterization of the surface of TiN (**a**) and DLC (**b**) samples

Salt spray tests

The uncoated substrate showed no protection to the saline aggressive atmosphere, presenting huge corrosion action even for less than 2 h of exposure, as expected. In addition, no effective passivation layer was created.

In case of TiN coatings, corrosion was less intense, but the coatings did not efficiently protect the substrate even for 2 h of exposure. The surface and cross section microscopic inspection revealed that TiN coatings suffered a widespread cracking and spalling (Fig. 2).

Diamond-like carbon (DLC) samples presented a good corrosion resistance (much better than TiN films) for all test times. For up to 48 h of exposure to salt fog atmosphere, DLC coatings completely protected the substrate showing no signs of corrosion. However, after that a few points revealing steel corrosion products could be observed. Nevertheless, even after 168 h of exposure no degradation of the DLC coating itself was observed, which remained intact presenting only small pits uniformly distributed over the surface. As shown in Fig. 3, these pits observed on DLC surface seem to be deeper than the coating thickness and therefore are the spots where corrosion takes place. However, the presence of corrosion pits could not be associated with pre-existing pinholes or defects since none were observed by microscopic inspection before the corrosion tests.

Kesternich, polarization, and EIS tests

The good results obtained for DLC in salt fog tests encouraged us to perform the Kesternich tests. Before placing the samples in the Kesternich chamber (no cycle performed) polarization and impedance measurements

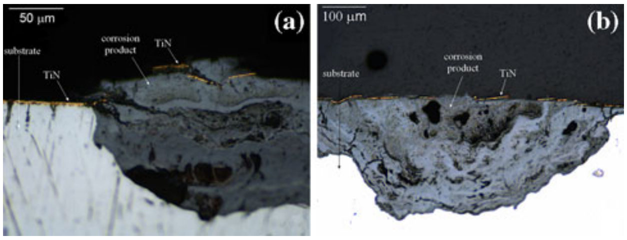

Fig. 2 Optical micrographs of cross sections of TiN samples after 168 h in saline environment, showing the cracking and spalling of the coating and the formation of corrosion products

were done. DLC samples presented the highest polarization resistance (4257 Ω) followed by TiN sample (473 Ω) and the uncoated substrate sample (50 Ω).

After the first Kesternich cycle, both DLC- and TiN-coated samples presented a decrease of about one order of magnitude on the R_p values to 578 Ω and 72 Ω for DLC and TiN samples, respectively. It is clear from the microscopic analysis that both samples suffered from a similar pit corrosion processes: nucleation and growth of micrometer-sized pinholes (Fig. 4). DLC-coated samples presented fewer and smaller pinholes than TiN ones in accordance with the polarization results. In addition, TiN coatings even started to spall-off due to the corrosion and as a consequence it was possible to observe corrosion products on the sample surface, thus indicating that TiN was not very effective as a corrosion protective coating.

After the second Kesternich cycle, both DLC- and TiN-coated samples presented an additional decrease of R_p values to 204 Ω and 40 Ω for the DLC and the TiN samples, respectively. This indicates that the protective ability of DLC coating is continuously reducing, as a result of an increase in the number and size of DLC pinholes but still is much superior to TiN samples. Lifting and cracking of the DLC coating at the corrosion spots was observed as a result of the increased corrosion process (Fig. 5).

The electrochemical evolution of DLC samples during the Kesternich test can be observed through the Tafel diagrams shown in Fig. 6. Polarization curves show an increase in current density together with a decrease of corrosion potential to less noble or more anodic potentials, as the environment exposure time (number of Kesternich cycles) increases. The decrease of corrosion potential is

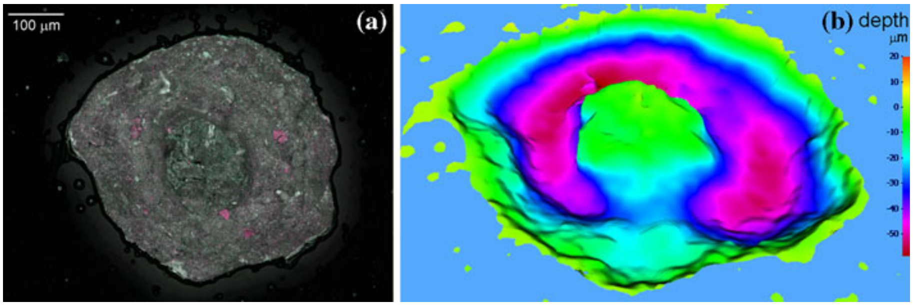

Fig. 3 Optical micrograph of the largest pinhole found on the surface DLC samples after 168 h of saline corrosion (**a**) and three-dimensional digital reconstruction of (**a**) obtained by confocal microcopy so as to obtain the pinhole dimensions (**b**). A projected area of 0.16 mm^2 and a volume of 0.0046 mm^3 were determined

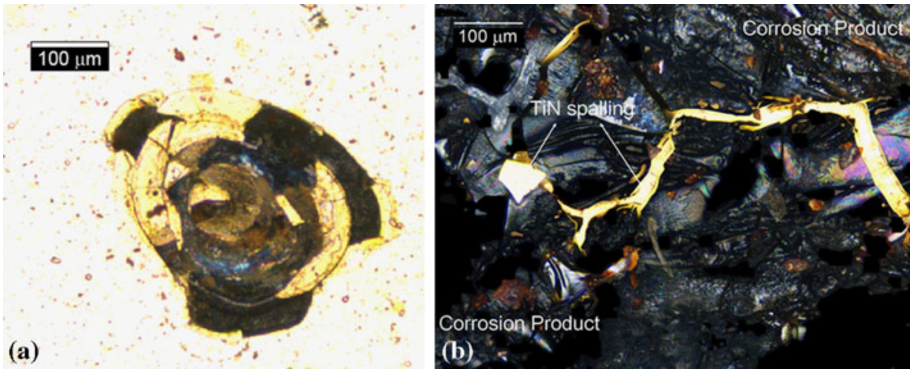

Fig. 4 Optical micrograph of a pinhole on the surface of TiN samples after 1st Kesternich test (**a**) and a detail of (**a**) showing the corrosion products and spalling of the coating (**b**)

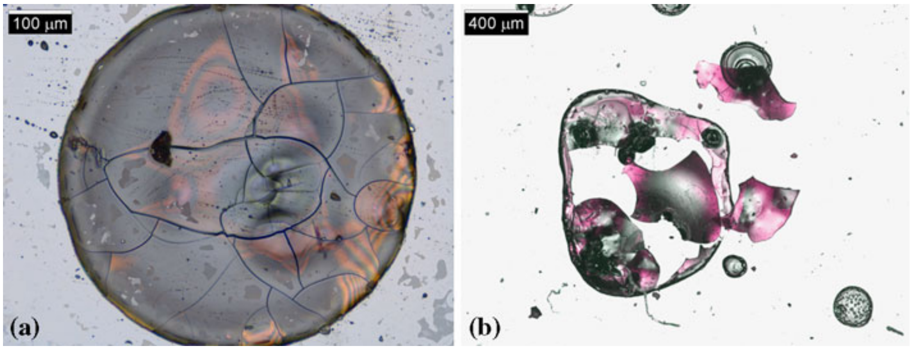

Fig. 5 Optical micrograph of a pinhole on the surface of DLC coating after 2nd cycle of Kesternich test, showing cracking (**a**) and spalling (**b**)

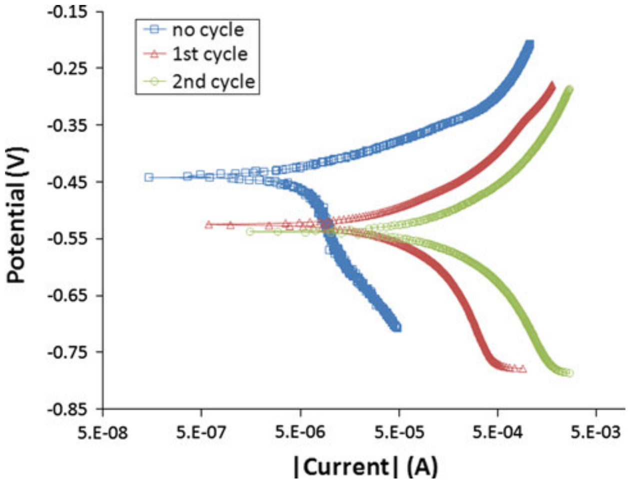

Fig. 6 Tafel diagrams showing the evolution of DLC sample during Kesternich tests

indicative of an increase of the sample pit corrosion rate and is in agreement with the continuous reduction of coating protective ability, as mentioned above.

Figure 7 shows the corresponding Nyquist plots obtained for the DLC coatings, which presented the best performance. In case of a perfect barrier coating, without pores or cracks, the Nyquist plots should present a linear behavior parallel to the imaginary axis which is equivalent to an ideal capacitor. Unfortunately, this is not the case of DLC coatings. The Nyquist plot obtained for the DLC sample before performing the Kesternich test shows a RC behavior (one main capacitive loop) with *R* approximately equal to 5.5 kΩ (the complete loop is not shown in Fig. 7 since the horizontal scale is enlarged), which may be considered as a moderate corrosion protection. This resistance decreases considerably after the first and second Kesternich cycles down to *R* ∼680 Ω and R ∼200 Ω, respectively, indicating an increasing corrosion process. This is in close qualitative agreement with the results of polarization curves and microscopic examination presented above. However, a more detailed investigation of the corrosion process is still necessary and will be object of a future publication.

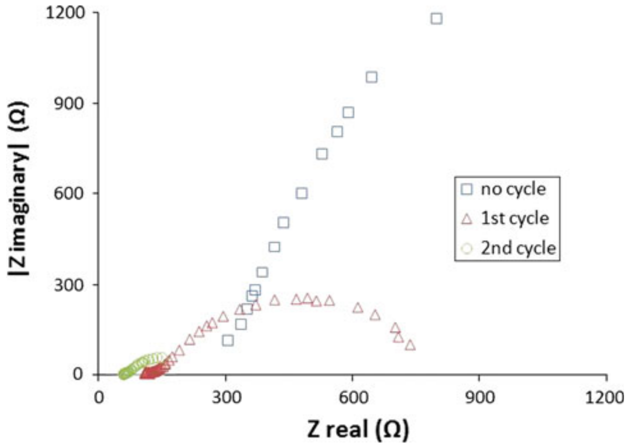

Fig. 7 Nyquist plots showing the evolution of DLC sample during Kesternich tests

The present results are in general agreement with previous studies of the corrosion behavior of DLC coatings [10–14] although a quantitative comparison cannot be done due to the different experimental conditions, coatings, and samples characteristics. In the present case, very aggressive conditions were employed in comparison to most results found in the literature. In spite of that, the coatings seemed to resist well to the corrosion media and the corrosion processes occurred only at micro-sized spots leading to spalling and the exposure of the substrates to the environment, in accordance to other works [10, 12]. It is tempting to associate the observed corrosion pits to pre-existing pinholes or defects on the sample surface but unfortunately such defects could not observed by microscopic inspection before the corrosion tests.

Conclusions

DLC coatings deposited on AISI4340 steel by rf-PECVD deposition technique produced homogeneous coatings with no significant micro-pores. The obtained coatings showed effective protection of the substrate against corrosion after 48 h in salt fog chamber and after the first Kesternich cycle. As a comparison, under the same conditions, TiN coatings did not protect the substrate even for 2 h of saline exposure and even for one Kesternich cycle. Although the DLC coatings resisted well to the corrosive action of the aggressive media, nucleation and growth of homogenous and micro-sized pinholes uniformly distributed on DLC coatings were observed as a result of the corrosion processes. The observed results suggest that the development of techniques which would reduce the porosity of the DLC films could promote further improvement on their corrosion protection ability.

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