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Electrochemical performances of diamond-like carbon coatings on carbon steel, stainless steel, and brass

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ABSTRACT

Diamond-like carbon (DLC) coatings have been deposited onto stainless steel, carbon steel and brass by plasma-enhanced chemical vapor deposition, respectively. Atomic arrangement, chemical structure, surface morphology and cross-section microstructure of the DLC coatings were examined by X-ray diffraction, Raman scattering spectroscopy and scanning electron microscopy. The electrochemical behaviors of the DLC coatings in 3.5 wt.% NaCl solution were investigated by performing an open circuit potential (OCP) measurement and a potentiodynamic polarization test. The experimental results showed that properly deposited DLC coatings could cause an increase of OCP by hundreds of millivolts and a reduction of anodic current density by several orders of magnitude as compared to that of the substrate. The results also demonstrated that electrochemical techniques could be used as tools to detect the soundness of the DLC coating by examining OCP and polarization curve, which varied with the form of defect and depended on the type of substrate.

1. Introduction

Diamond-like carbon (DLC) films exhibiting high hardness [1,2], low friction coefficient [3,4] and high corrosion resistance [5–10] have found wide applications and have become important materials for surface modification. Owing to their chemical inertness and high electrical resistivity, DLC coating makes itself as a potential candidate of corrosion barrier for metals [11]. However, the corrosion performance of DLC coating is closely related to its microstructure and/or the existence of defects within it. The properties of DLC coating in turn depend on the deposition methods and conditions employed [12–14]. The effect of deposition condition on the corrosion behavior of DLC coating has been of interest and explored by several researchers [15–24]. Since DLC has extremely high resistivity, the electrochemical parameters generated in some of these investigations were not properly explained. For those coatings with extremely low “corrosion current densities (i_{corr})”, the method for i_{corr} determination always was not properly described. The low anodic current density, in the order below nA cm^{-2}, was neither associated with the dissolution of the substrate nor with the DLC coating itself. Some of the explanations of the improve corrosion resistance with DLC coating was misleading. In fact, the role of defect within a coating or that at the interface between the substrate and the coating is the most important factor in determining the electrochemical characteristics of DLC coated material. In this study, thus, the electrochemical behavior of DLC-coated stainless steel (SS), carbon steel and brass in NaCl solution is investigated, in an attempt to justify the use of electrochemical technique as a tool for coating defect detection.

2. Experimental details

2.1. Sample preparation

The as-received 304 SS, 316 SS, carbon steel (0.05 wt.%C) and brass plates were cut into the dimension of 10 mm × 15 mm × 2 mm, which were successively ground with SiC papers and polished in a slurry containing Al_2O_3 powders with an average particle size of 0.05 μm. These specimens were ultrasonically cleaned in deionized water and dried in air. Then, the DLC films were deposited by plasma-enhanced chemical vapor deposition that used acetylene and hydrogen as the reaction gases (~1000 sccm, $C_2H_2/H_2 = 1/1$) in a pressure of 0.75 to 3.75 Pa. A radio frequency power of 220 W was used for the plasma, a direct current bias of −400 V was applied to the substrate relative to the ground, and the substrate was heated to 250 °C. The deposition rate of DLC was about 34 nm min^{-1}. All the DLC coated specimens were then subjected to material characterization and electrochemical polarization measurement.

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2.2. Material characterization of DLC films

The surface morphology and cross-section microstructure of the DLC coatings, before and after electrochemical measurement, were examined using a scanning electron microscope (SEM, Hitachi SUI500) with 15 kV acceleration voltages. Chemical compositions were determined by an attached energy dispersive spectroscopy (Horiba 8091-H). The crystal structure or atomic arrangement of the DLC coatings was analyzed by X-ray diffraction (Reguku MiniFlex II) using monochromatic CuKα radiation ($\lambda = 1.5406$ Å) at 30 kV and 15 mA with step scan mode at intervals of 0.05° in 2θ.

The chemical structure of DLC film was also characterized using a Raman Spectrometer (Renishaw 1000 system). An Ar^+ laser with a wavelength of 514 nm and 2 mW power was used as an excitation source. All Raman data acquisitions were obtained at room temperature.

2.3. Electrochemical measurements

Electrochemical tests were conducted in 3.5 wt.% NaCl solution at 25 °C (pH = 6.5). The bare substrates (304 SS, 316 SS, carbon steel, and brass) and those coated with DLC were used as the working electrodes. The counter electrode and reference electrode were a platinum sheet and a saturated calomel electrode (SCE), respectively. The open circuit potential (OCP), potentiodynamic polarization curves were measured and compared. In potentiodynamic polarization curve measurement, a three-electrode electrochemical cell controlled by an EG&G 263 potentiostat was employed. The potential sweep rate of 1 mV sec^{-1} from cathodic toward anodic direction was applied.

3. Results and discussion

3.1. Materials properties of DLC films

Fig. 1 shows the cross-section microstructure of the DLC coatings on 316 SS. The result revealed good adhesion between the DLC coating and 316 SS substrate. Similar results were observed for 304 SS. The thickness of DLC coating was about 1.5 μm.

The X-ray diffraction patterns of various DLC-coated materials are shown in Fig. 2(a)–(d). All diffraction peaks corresponded to the substrates without revealing the characteristic peaks of carbon substance. These results indicated that the DLC coatings formed on all substrates exhibited amorphous structure.

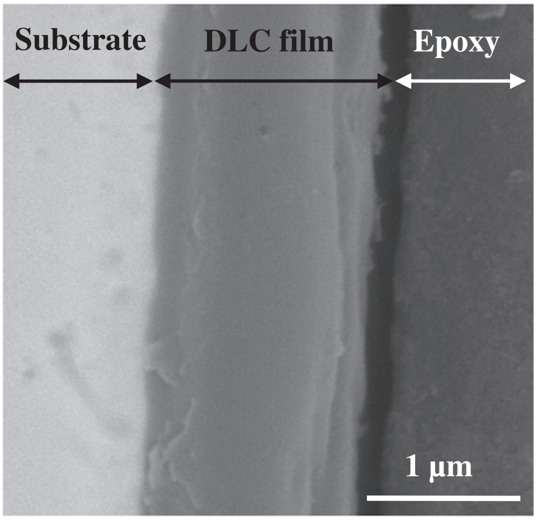

Fig. 1. SEM micrograph showing the cross-section image of the coating deposited onto 316 SS.

The chemical structure of the DLC coating formed on each substrate was evaluated by Raman scattering spectroscopy. Fig. 3 shows the spectrum of the film deposited on 304 SS. The spectrum was deconvoluted into D and G bands, each centered at 1282 cm^{-1} and 1485 cm^{-1}, respectively. The higher intensity of G band indicated that the structure of DLC coating examined was more graphite-like. Similar results were found for those deposited on 316 SS, carbon steel and brass substrates. These results were basically in agreement with those found in the literature [20,22,23].

3.2. Electrochemical behavior

The OCP values of the bare substrates measured in 3.5 wt.% NaCl solution at 25 °C are shown in Fig. 4(a). Carbon steel was most active and exhibited the lowest value of OCP in 3.5 wt.% NaCl solution, while 304 SS and 316 SS had almost the same values of OCP about −200 mV more noble than carbon steel. The OCP of brass fell in the region between carbon steel and the two austenitic stainless steels. When DLC was coated onto 304 SS or 316 SS substrate, a significant increase in OCP (about 300 mV higher) was found for each specimen, as shown in Fig. 4(b). The results suggested that perfect DLC coating could be applied on the surface of 304 SS and 316 SS. However, the OCPs of DLC-coated carbon steel and brass were nearly the same as their bare substrates, indicating the imperfect DLC coatings formed on these two metals.

Potentiodynamic polarization curves of the bare and the DLC-coated specimens, in 3.5 wt.% NaCl aqueous solution, are demonstrated in Fig. 5(a) and (b). The lower corrosion potential and the higher anodic current density of the bare carbon steel, as compared with those of 304 SS, 316 SS and brass (Fig. 5(a)), manifested its lower corrosion resistance in 3.5 wt.% NaCl solution. As shown in Fig. 5(b), a significant change in the polarization curve was found for either 304 SS or 316 SS, each coated with DLC. A wide “passive” region with a plateau current density as low as 2×10^{-8} A cm^{-2} was observed. The low anodic “passive” current density, exhibiting the extreme high resistivity characteristics of the DLC, indicated this coating was perfectly deposited on the stainless steel surface. More precisely, the low current density measured was attributed to the flow of ions under applied potential condition, not resulting from the anodic dissolution (oxidation) of DLC coating. In contrast, the polarization curves of DLC-coated carbon steel and brass had the same feature as their bare substrates. The results again implied that the DLC was not properly coated on the surfaces of these two materials. The polarization curves actually revealed the electrochemical nature of the substrates. Anodic dissolution of the substrate in the area where through-thickness defect existing in the coating gave rise to the higher anodic current density observed. The effectiveness of DLC coating on the respective substrate might be realized by comparing the polarization curves of each substrate with and without DLC coating, as demonstrated in Fig. 6(a)–(d). Again, the similar shapes of polarization curves were only found for carbon steel and brass, not for 304 SS and 316 SS. Though the shapes of the polarization curves shown in Fig. 6(c) and (d) were similar, the current densities (both cathodic and anodic) were several orders of magnitudes lower for the DLC-coated specimens. The ratio of the anodic current densities between the bare and the DLC-coated carbon steel or brass might represent the ratio of surface area where DLC was not perfectly deposited.

Fig. 7(a) and (b) compare the cross-section SEM images of the as-coated 316 SS and carbon steel, respectively. Good DLC coating was found on 316 SS, while a void with a size as large as 1 μm was seen in the DLC coating deposited on carbon steel. It was noted that the DLC films used in this study contained about 40 at.% hydrogen. The role of hydrogen in pore formation might not be excluded. A counter-pin sliding wear test was performed to evaluate the adhesion behavior of the DLC coating. Under an applied load of 4 or 8 N, the DLC coating formed on 304 SS or 316 SS remained intact without detaching from the substrate surface though cracks were seen in the