Graphene–polypyrrole thin hybrid corrosion resistant coatings for copper

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ABSTRACT

New corrosion-resistant hybrid coatings based on graphene and polypyrrole were prepared and studied. A two-step process was used to fabricate the coatings. First, graphene was grown on a commercial copper foil by chemical vapor deposition (CVD) method. As the coating consisting only from graphene was imperfect, the defects were sealed with polypyrrole using electrodeposition. Corrosion resistance of copper, copper with CVD-graphene coating, and copper with CVD-graphene/polypyrrole hybrid coating were tested by immersion in salt water and also studied by open circuit potential measurements of the samples under ultraviolet radiation exposure, linear sweep voltammetry and cyclic voltammetry. The surfaces of the samples were also characterized by different microscopy and Raman spectroscopy methods. Although CVD graphene protected copper against corrosion in a certain extent, immersion tests revealed that the metal corrosion is mainly due to the graphene defects. The hybrid coatings showed much better anticorrosion performance.

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1. Introduction

The present challenge in corrosion prevention is to find the most effective method for different materials favored in certain applications due to their other good properties [1]. In addition, for modern technology it is often demanded that a coating is a multifunctional material, in some cases fully carbon-based materials are preferred [2]. Copper and its alloys are industrial materials that have found different applications, including, for instance, tubes, taps, heat exchangers, containers for different liquids and gases. Unfortunately, these materials tend to be vulnerable to different forms of corrosion [1–5]. For example, pitting corrosion of copper in chloride-containing water is well known [5]. It has also been reported that ultraviolet (UV) radiation (300–450 nm) has an accelerating effect on copper corrosion in dilute chloride aqueous solutions [6]. Traditional wear- and corrosion-resistant coatings are thick, with thicknesses of several to tens of micrometers, but these coatings are not usable in all applications. On metal details with small sizes and/or enhanced

precision of dimensions the coating thickness is often strictly limited. Such coatings can be prepared by different physical or chemical vapor deposition methods (PVD, CVD) and they could give a good corrosion resistance on flat and homogeneous surfaces. However, in a number of cases, e.g., for heat exchanger walls thick coatings with heat conductivity much less than copper are unwanted, as well as for the details with sophisticated three-dimensional shapes or for the details with very high precision of dimensions, thick coatings and methods listed above are not efficient enough. In these cases, atomic layer deposition (ALD) method [7–12] might be a promising technology but several important materials, e.g. carbon-based materials, cannot be prepared with this technique.

Graphene (G) is a novel two-dimensional material where carbon atoms form a honeycomb structure. Its possible applications have been intensively studied over the last few years [13–17]. Graphene as many other carbon materials is chemically inert. An ideal graphene sheet is composed of only one atomic layer being, thus, the thinnest material ever produced and studied. At the same time graphene has been proven to be a good diffusion barrier and can be considered as a good ultrathin anticorrosion coating [18]. The corrosion resistance of CVD graphene has been described already [19–22]. On larger areas, however, it is hard to avoid defects in graphene, which often occur on boundaries between different

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graphene domains [21]. Each defect in a coating creates a galvanic couple between the anodic substrate and cathodic graphene, causing localized corrosion. Therefore, these defects must be repaired e.g., with a thin carbon-based layer, giving possibility to obtain a continuous defect-free electrochemically homogeneous carbon coating. One method that could be used for repairing the defects in graphene coating is electrochemical deposition of a thin electroactive polymer layer to the sample surface, which mends the defective sites. The polymers can be deposited with different physico-chemical characteristics that depend on the deposition process parameters and substrates used [23].

Electroactive polymers, such as polypyrrole (PPy) and polyaniline (PA), have been mainly studied as corrosion-resistant coatings for different metal substrates, including steel, aluminum and copper [24–28]. There are several positive examples of suppressing the corrosion processes on metals by using conductive polymer coatings but a comprehensive explanation of the electrochemical mechanisms leading to the reduced corrosion rate of metals is still missing [25]. It is known that PPy films can be electrodeposited from aqueous solutions but PA layers from organic electrolytes, and thus the production of PA films is more complicated and expensive [23]. Our recent investigations of electrodeposited PPy films showed that it is possible to reduce dopant mobility in the films substantially using bigger (aromatic) organic anions instead of traditional inorganic anionic dopands, e.g., Cl^-, NO_3^-, etc., and applying synthesis parameters that lead to denser packing of the polymer matrix during electrodeposition [29]. On the other hand, only the use of organic dopands does not guarantee the penetration of smaller inorganic anions into the polymer during longer time, it only lowers their diffusion rate in the polymer that was shown by redoping studies of the polymer [30]. Of course, the existence of oxidizing agents at the polymer–metal interface will cause corrosion of a metal substrate. Therefore, the electroactivity of the polymeric film must be suppressed already in deposition process, which can be done for example by growing ultrathin PPy films from an electrolyte with low concentration of pyrrole [31].

In this work the possibility for improving the corrosion resistance of CVD graphene coating on copper with sealing its defects with electrochemically deposited polypyrrole ultrathin films was studied and demonstrated. The corrosion resistance of the hybrid coatings was tested by immersion in salt solution, linear sweep voltammetry, cyclic voltammetry and open circuit potential measurement of the samples with and without ultraviolet radiation exposure. The coatings were characterized before and after the tests by optical microscopy (OM), scanning electron microscopy (SEM), atomic force microscopy (AFM) and micro-Raman spectroscopy (μRS) methods.

2. Experimental

Graphene was grown on 25 μm thick polycrystalline Cu foils (99.8%, Alfa Aesar) in a laboratory-assembled flow-type CVD reactor [32]. Prior to graphene deposition the foils were treated in 10% acetic acid for 1 h in order to remove the oxide layer and then rinsed in deionized water, acetone (99.5%, Carl Roth GmbH + CO) and isopropyl alcohol (Alfa Aesar). Further pretreatment of the Cu foils was carried out in the CVD reactor. First, the foils were annealed for 30 min at 950–1000 °C in a mixture of H_2 and Ar gases (both 99.999%; Linde AGA). The flows of H_2 and Ar were set at 130 and 100 sccm, respectively. Immediately after annealing graphene was grown at the same temperature in a gas mixture of 10% CH_4 in Ar (99.999%, Linde AGA) supplied at a flow of 40 sccm. The duration of deposition was 20 min. Then the samples were cooled down with a rate of 20 °C/min in Ar environment and used as soon as possible for further experiments.

Pyrrole (Fluka), used for the synthesis of PPy films, was purified by distillation over calcium hydride under vacuum and stored in the dark under Ar atmosphere at low temperature. Polypyrrole was deposited onto graphene in a three-electrode cell having a saturated calomel electrode (SCE) and Pt wire as a reference and a counter electrode, respectively, and a copper foil with or without a graphene coating as a working electrode. The depositions were performed using a potentiostat–galvanostat Reference 600 (Gamry). All potentials were measured versus SCE reference electrode. The area of the working electrode was 1 cm² in all electrochemical measurements.

The graphene sheets with low defect concentrations were coated with polypyrrole for the defect sealing purpose using a pulsed potentiodynamical deposition method that was based on potential cycling between −400 and 800 mV with an extra-high scanning rate of 10 V/s. Altogether 5000 deposition cycles were applied. All PPy depositions were carried out in 0.1 M oxalic acid aqueous solution with 0.1 M pyrrole addition.

Corrosion tests of a copper foil, the foils with CVD-graphene and with CVD-graphene/polypyrrole hybrid coating were performed in the same three-electrode cell, employing the same potentiostat, and using immersion, corrosion potential measurement, cyclic voltammetry and open circuit potential measurement under UV radiation exposure in naturally aerated 0.5 M NaCl aqueous solution. Before linear sweep and cyclic voltammetry experiments the open circuit potential (OCP) was measured during a stabilization period of 30 min. Immersion tests lasted for 65 h. For cyclic voltammetry experiments, initial potential of −1.1 V, turning potential of 0.5 V, end potential of −1.1 V and potential scan rate of 10 mV/s were used. For linear sweep voltammetry experiments, the initial and end potentials measured versus open circuit potential were −250 mV and 250 mV, respectively, while the potential scan rate was 1 mV/s. In the irradiation experiment the open circuit potential was measured with a frequency of 500 Hz for 5 min. From second to third minute the samples were illuminated with a 405(±10) nm wavelength photodiode through an optical cable, which was transparent for this radiation wavelength. The distance between the opening of the optical cable and tested substrates was 5 mm, resulting an irradiance of 20 μW/cm². To get reliable results in electrochemical tests a new sample was prepared for each test.

Optical microscopy studies were performed with a metallographic optical microscope Eclipse LV150D (Nikon) having Nomarski contrast option as well. High-resolution scanning electron microscopy (HR–SEM) analyses were done by using a dual-beam system Helios NanoLab 600 (FEI), equipped with both electron probe and focused ion beam (FIB), and with energy dispersive X-ray spectrometer (EDX) analyzer INCA Energy 350 having SSD-type X-Max 50 detector (Oxford Instruments). The Slice and View technique was applied by making cross-sections with FIB followed by imaging with HR–SEM. Raman studies with lateral resolution of 2 μm were made with an inVia Raman microscope-spectrometer (Renishaw).

3. Results and discussion

3.1. Corrosion behavior of copper and copper with CVD-graphene

Raman spectrometry (Fig. 1) and scanning electron microscopy (Fig. 2) studies of CVD graphene coatings on copper and transferred graphene on Si/SiO₂ substrates, showed that graphene covered the substrates continuously. The graphene coating consisted mainly from a monolayer but some regions had also two or more graphene layers, and it had, especially on copper, only a small number through-coating defects. This conclusion was made on the basis of the measured Raman spectra and mapping data analysis: in most