Corrosion Science xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Comprehensive electrochemical study on corrosion performance of graphene coatings deposited by chemical vapour deposition at atmospheric pressure on platinum-coated molybdenum foil

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ARTICLE INFO

Keywords:
B. Raman spectroscopy
B. XPS
B. EIS
B. Cyclic voltammetry
B. Polarization

ABSTRACT

In this work, we present the results of electrochemical, Raman, FE-SEM/EDS, and XPS studies of graphene coatings deposited by chemical vapour deposition at atmospheric pressure on Mo foil and Pt-coated Mo foil as catalysts. The results showed that the graphene coating synthesized on Pt-coated molybdenum foil was bi-layer and had fewer defects, while the graphene coating on Mo foil was few-layer with more defects. The corrosion studies indicated that both graphene coatings on bare Mo and Pt-coated Mo exhibited good protective properties and can act as a barrier against corrosion in 0.1 M NaCl.

1. Introduction

Corrosion and corrosion protection are serious concerns for many industries. Mo is a transition metal with versatile applications as it is increasingly used in the electrical industry; for example, in supercapacitors and electronic and photonic devices [1–4] and as back contacts for solar cells and catalysts [5,6]. Although Mo generally has good corrosion resistance in mild environments, there is a need for development of thin-layer coatings for protection of Mo in order to increase and prolong its stability when exposed to corrosive media. Several studies were devoted to the investigation of the Mo corrosion mechanism [7,8]. Generally, Mo is less susceptible to corrosion in acidic environments than in neutral or alkaline conditions owing to the existence of passivation regions in acidic media [7,9,10]. On the contrary, there was no observation of passive film formation in alkaline electrolytes [7,11]. The mechanism of anodic oxidation of Mo is complicated due to the formation of several different species at anodic overpotentials depending on the electrolyte pH. The surface of Mo is always more or less covered by a layer of mixed oxide, consisting mainly of Mo (III) and Mo(IV) species, that even forms spontaneously at open circuit potentials [12,13] and undergoes changes in several charge transfer steps after polarization in solutions of different pH [8]. In acidic environments, a MoO_2 oxide layer is formed first and then is converted through a series of electron transfer steps to MoO_3, which is believed to be the main cause of passivation of Mo (with the mixed oxide-hydroxide also containing MoO_2 and $MoO(OH)_2$), observed as a passive region in anodic polarization curves [14]. According to the Pourbaix diagram of Mo [15], MoO_2 is quite unstable at higher anodic overpotentials in neutral and alkaline solutions and is subjected to dissolution through the formation of intermediate Mo(III) and Mo(V) species, with the final soluble products being Mo(VI) species such as $HMoO_4^-$ and MoO_4^{2-} [7,16,17].

Many different methods of corrosion prevention have been developed, but researchers are currently paying attention to the new and robust coatings that improve electrical and thermal properties and appearance of the protected metals [18]. The introduction of the versatile material graphene has prompted many changes in diverse applications [19]. Since the discovery of graphene in 2004, this monolayer of carbon atoms, arranged in a honeycomb lattice, has emerged as a material that exhibits unparalleled electrical, thermal, and mechanical properties [20]. The vast application of graphene relies on the attractive properties of this two-dimensional material such as high carrier mobility, large theoretical specific area, good electrical and thermal conductivity, high Young's modulus, great optical transmittance, and chemically inert nature [19,21–23]. The ability of graphene to prevent ionic transport has rendered graphene a prospective protection barrier for metallic substrates against corrosion [24,25]. In recent years, there have been an increasing number of studies on graphene as thin-layer anti-corrosion coatings on various metal substrates, such as Cu, Co, Ni, and Fe [26–28], as well as filler for enhanced protective properties of

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http://dx.doi.org/10.1016/j.corsci.2017.10.021
Received 5 June 2017; Received in revised form 23 October 2017; Accepted 25 October 2017

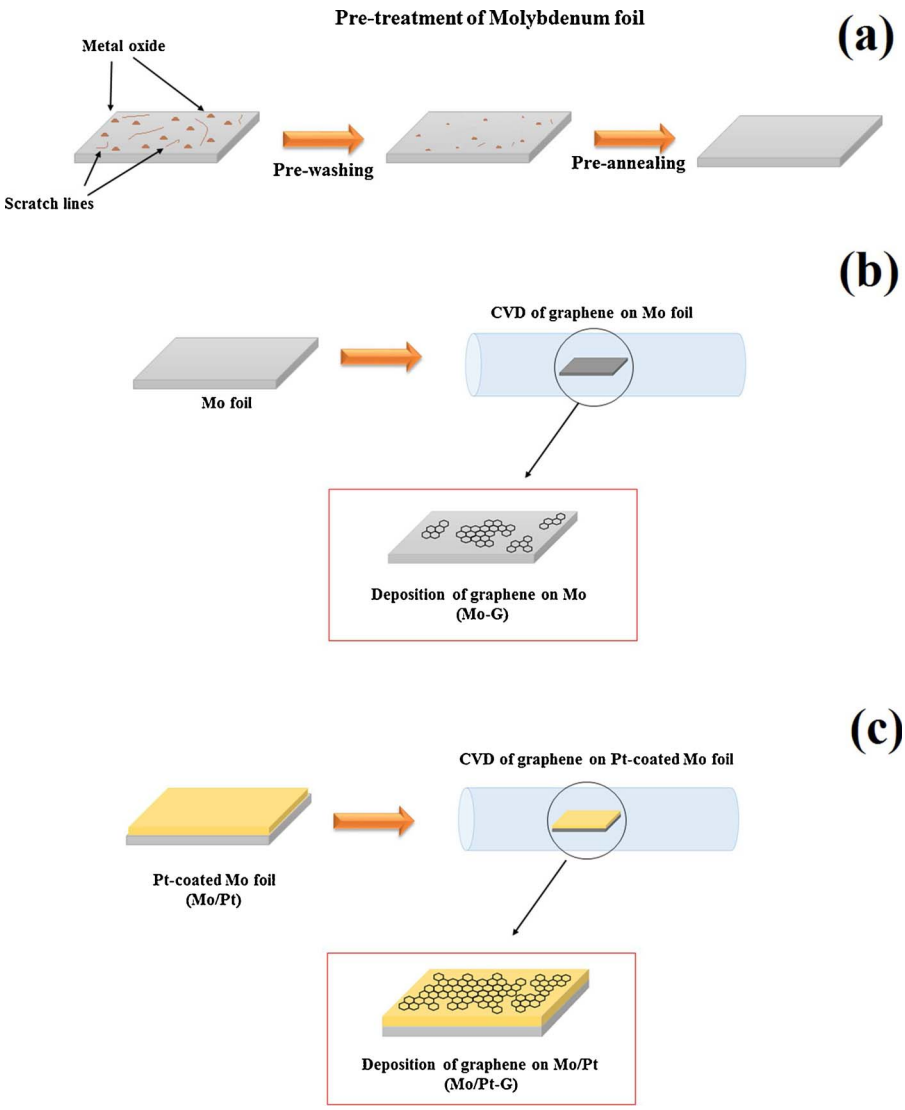

Fig. 1. (a) Pre-treatment of Mo foil, (b) CVD of graphene on Mo (Mo-G), and (c) CVD of graphene on Pt-coated Mo (Mo/Pt-G).

polymer coatings [29–31]. Many fabrication techniques including mechanical exfoliation of graphite, epitaxial growth on SiC, reduction of graphene oxide, unzipping of carbon nanotubes (CNTs), and chemical vapour deposition (CVD) have been investigated to produce high-quality graphene with good uniformity and size. Among these methods, thermal CVD, as the most scalable and inexpensive deposition technique, has emerged as a common approach for single and few-layer graphene synthesis on metal substrates [32,33]. However, CVD-grown graphene coatings can have many defects and small domain sizes, which can lead to enhanced corrosion of the metal due to intercalation of electrolyte along the grain boundary [34,35]. For this reason, various types of metal catalysts have been carefully chosen to mediate the mechanism of graphene growth [36], which is directly dependent on the distinctive solubility of carbon in different catalysts [37]. Pt is one of the known catalysts that, unlike the widely used catalysts (Cu and Ni), is more resistant to oxidation due to its inertness [38] and has better catalytic ability for decomposition of hydrocarbons and subsequent graphitization than Cu [39]. Unlike Cu, which requires a low-pressure environment to grow graphene, Pt can induce growth of large-grain graphene at ambient pressure [40], while the weak interaction of Pt substrate with graphene helps reduce the negative effect of the substrate on the quality of graphene [41,42]. Yong et al. reported the growth of uniform bi-layer graphene with giant grain size on Pt thin film [38]. They showed that the sizes of graphene grains were dependent on the Pt grain size, which was changed by pre-annealing the catalyst. Sun et al. demonstrated the dependence of high-quality multilayer graphene synthesis on proper control over the growth kinetics when using Pt as catalyst [39].

In our previous research, we successfully synthesised CVD-grown graphene coatings with good barrier properties on Cu and Al [28] and, most recently, on Mo [24]. In this work, we present graphene coatings deposited by chemical vapour deposition at atmospheric pressure on Pt-coated Mo foils. Building on our previous work, we compare the catalytic properties of bare Mo and Mo with Pt coating for the growth of uniform graphene layers and investigate the effect of Pt thin film on Mo surface on the quality of graphene and its corrosion protection properties.

2. Materials

The reaction gases of hydrogen (H_2, 99.999%), argon (Ar, 99.999%), and methane (CH_4, with 99.995% purity) were purchased from A-Rang Gas, Korea. A 0.25-mm-thick, annealed, uncoated 99.95% pure Mo foil was purchased from Alfa Aeser, USA. Automated thermal CVD equipment, from Scientific Engineers (S. Korea), was utilized to deposit graphene on the Mo foils. NaCl (Sigma Aldrich, USA) and deionised water from the Milli-Q system (Millipore, USA) were used in all electrochemical experiments.