



# Facile fabrication and corrosion behavior of iron and iron-reduced graphene oxide composite coatings by electroless plating from baths containing no reducing agent



Xingkai Zhang, Yan Zhou<sup>\*</sup>, Aimin Liang, Bin Zhang, Junyan Zhang<sup>\*</sup>

State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

## ARTICLE INFO

### Article history:

Received 21 June 2016

Revised 22 July 2016

Accepted in revised form 23 July 2016

Available online 25 July 2016

### Keywords:

Iron coating  
Graphene oxide  
Electroless deposition  
Electrochemistry  
Corrosion

## ABSTRACT

Inspired by its role in inducing electroless iron plating, aluminum was used to prepare iron coatings on copper substrates from the simple plating bath containing no reducing agents. The electrochemical investigation indicated that the coupled aluminum could shift the potential of copper substrates to an enough negative value to initiate iron plating in the alkaline plating bath and serve as the electron source for continuous deposition of iron. To improve the corrosion resistance of the iron coatings, graphene oxide (GO) was added in the former plating bath and the iron-reduced graphene oxide (Fe-rGO) composite coatings could be successfully obtained. Compared with the iron coatings, the Fe-rGO coatings exhibited smaller nodule size and denser structure as revealed by scanning electron microscope and X-ray diffraction results. Hence, Fe-rGO coatings demonstrated significant improvement in the corrosion resistance with increasing in open circuit potential (OCP) and reducing in corrosion current density.

© 2016 Published by Elsevier B.V.

## 1. Introduction

Iron coatings or films have been extensively studied because of their excellent magnetic property [1,2], catalytic performance [3,4], biocompatibility [5,6] and corrosion resistance [7,8]. A variety of methods such as sputtering [9], pulsed laser deposition [10], atomic layer deposition [11] and electroplating [12] have been used to prepare iron coatings or films. However, besides the need of complicated and costly equipments, these methods become inconvenient to deposit uniform iron coatings or films on the substrates with complex shapes. As a convenient way to prepare metals and their alloy coatings or films, electroless plating was supposed to be an important method for preparing iron coatings or films. However, because iron has a low autocatalytic deposition activity, electroless iron plating has been rarely studied despite it was successfully achieved in 1971 by coupling the substrates with the aluminum foils [13]. Multicomponent iron alloys coatings were also prepared from the plating baths using borohydride [14,15], sodium hypophosphite [16,17] and hydrazine hydrate [18] as the reducing agents by adopting the same technique. The inducing effect of coupled aluminum has been reported in a few research works [17,19], and it was found the coupled aluminum could initiate the deposition of iron by shifting the potential of substrates negatively. Because of the stronger reducing power of borohydride, FeB films were obtained by

electroless plating without the need of coupled aluminum foil [20,21]. However, a complicated substrate activation process was essential for achieving electroless FeB plating. The need for substrate activation could lead to the increasing of the overall cost and complexity of the electroless FeB plating process. It was not until 2014, direct electroless FeB plating without the using of substrate activation and coupled aluminum foil was reported by Rohan Akolkar [22], but the obtained FeB films were found to be less attractive because of their thin thickness.

The electroless iron plating baths used in the above researches were complex and generally contained ferrous salts, complexing agents, reducing agents, pH regulators, buffering agents and other additives. To simplify the complicated plating baths and replace the using of hazardous reducing agents is an area of high interest in the research of electroless plating. Based on the previous researches, especially the role of coupled aluminum in inducing iron deposition, a facile electroless plating method was developed to prepare iron coatings on the copper substrates from simple plating bath containing no reducing agents by one-step procedure. It was just needed to immersing the copper substrates coupled with aluminum foils into the plating bath comprising an aqueous solution containing  $\text{KNaC}_4\text{H}_4\text{O}_6$ ,  $\text{FeSO}_4$  and  $\text{NaOH}$ . The iron plating mechanism was studied by electrochemical method, and the surface morphology and corrosion resistance property of the resultant iron coatings were characterized.

Although iron coatings with fine structure and certain thickness could be obtained by the facile electroless plating method from reducing agent-free bath, the iron coatings had poor corrosion resistance.

<sup>\*</sup> Corresponding authors.

E-mail addresses: [zhouyan@licp.cas.cn](mailto:zhouyan@licp.cas.cn) (Y. Zhou), [zhangjunyan@licp.cas.cn](mailto:zhangjunyan@licp.cas.cn) (J. Zhang).

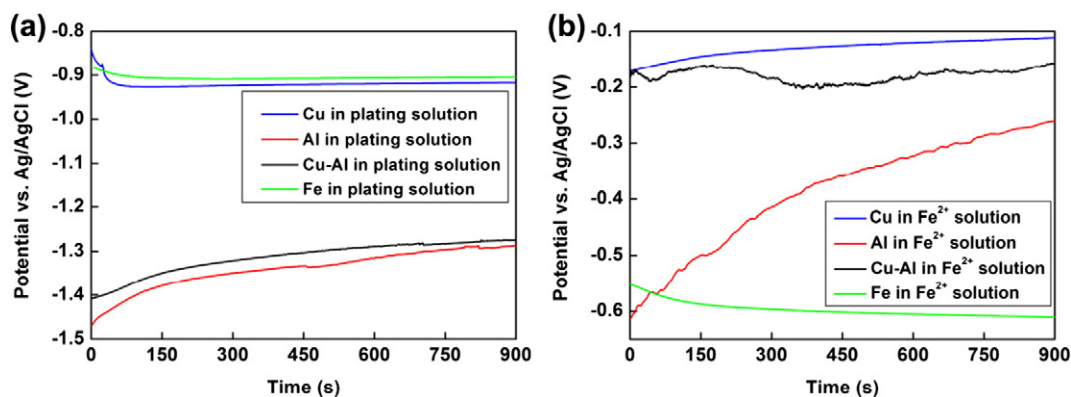


Fig. 1. OCP of copper, aluminum, iron and copper coupled with aluminum in (a) the Fe plating bath and (b) the Fe<sup>2+</sup> solution.

Recently, graphene and reduced graphene oxide (rGO) are considered to be ideal candidates for corrosion protection coatings because of their chemical inertia, impermeability and environmental friendliness [23]. It has been demonstrated that graphene or reduced graphene oxide (rGO) coatings could inhibit the corrosion of copper [24], nickel [25], iron [26], aluminum [27] and so on. Using graphene or rGO as a second phase material to generate Ni-graphene [28,29], Co-graphene [30], Zn-graphene [31] and Sn-graphene [32] composite coatings with enhanced corrosion resistance also has been demonstrated. Therefore GO was added into the reducing agent-free iron plating bath. The GO might be reduced by Fe<sup>2+</sup> [33] and the nascent hydrogen generated by the reaction of aluminum and hydroxyl [34] and incorporated into the iron coatings. The experimental results showed that Fe-rGO composite coatings were successfully obtained on the copper substrates coupled with aluminum, which could be confirmed by Raman spectrum. It was also found that the Fe-rGO coatings had finer and denser structure, and therefore higher corrosion resistance.

## 2. Experimental

The commercial pure copper foils were used as the substrates for electroless Fe and Fe-rGO plating. The electroless plating process included the following steps. Firstly, the substrates were degreased by acetone, etched in 5 wt.% HCl solution for 1 min, and then rinsed with deionized water and ethanol. The electroless plating bath was prepared by dissolving analytical grade reagents purchased from Sinopharm Chemical Reagent Co. Ltd. (China) into ultrapure water. Graphene oxide (GO) was obtained from Nanjing Xianfeng nano Co. (Nanjing, China). The composition of electroless Fe and Fe-rGO plating baths was as follows: (a) Fe plating bath containing: potassium sodium tartrate (KNaC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>·4H<sub>2</sub>O) 30 g·L<sup>-1</sup>, ferrous sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O) 12.5 g·L<sup>-1</sup>, sodium hydroxide (NaOH) 20 g·L<sup>-1</sup>; (b) Fe-rGO plating

bath containing: KNaC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>·4H<sub>2</sub>O 30 g·L<sup>-1</sup>, FeSO<sub>4</sub>·7H<sub>2</sub>O 12.5 g·L<sup>-1</sup>, NaOH 20 g·L<sup>-1</sup>, GO 2 g·L<sup>-1</sup>. For preparing Fe-rGO plating bath, GO was firstly dispersed in ultrapure water by stirring for 1 h and subsequently ultrasonically for 2 h to form stable GO suspension with the concentration of 4 mg·ml<sup>-1</sup>. 3 g KNaC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>·4H<sub>2</sub>O, 1.25 g FeSO<sub>4</sub>·7H<sub>2</sub>O and 2 g NaOH were dissolved in 50 ml ultrapure water, and 50 ml GO suspension (4 mg·ml<sup>-1</sup>) was slowly added into the former solution under fast stirring to get the homogeneous Fe-rGO plating bath. The final concentration of GO in Fe-rGO plating bath was 2 g·L<sup>-1</sup>, which was a relatively high value while ensuring the stability of plating bath. During the electroless plating process, the copper substrates were connected with aluminum foils, which were necessary to form Fe and Fe-rGO coatings. The plating process was carried out at 40 °C for 60 min. After plating, the samples were rinsed with ultrapure water and alcohol successively, and then dried in nitrogen stream.

The surface and cross-sectional morphology of Fe and Fe-rGO coatings were observed with JEOL-7001F field-emission scanning electron microscope (FESEM) and JEOL-5600LV SEM equipped with Oxford energy dispersive X-ray spectroscopy (EDX) for qualitative elemental chemical analysis. The X-ray diffraction (XRD) and Raman spectra profiles were obtained by using a X'Pert PRO X-ray diffractometer and JY-HR800 Raman spectroscopy. The effect of plating time on the thickness of Fe coatings was studied. The samples plated in Fe plating bath for 5 min, 15 min, 30 min, 60 min and 120 min were weighed by Mettler electronic microbalance (precision, 0.1 mg) respectively, and the weight was compared with initial weight of copper substrates to determine the weight of the Fe coatings. The coating thickness was calculated by dividing the coating weight by the surface area of substrates and coating density (assuming a density of 7.8 g·cm<sup>-3</sup>). Three samples were measured and calculated, and the average results were used for each plating time.

All electrochemical tests were performed with a traditional three-electrode cell with specimen as working electrode, Ag/AgCl electrode

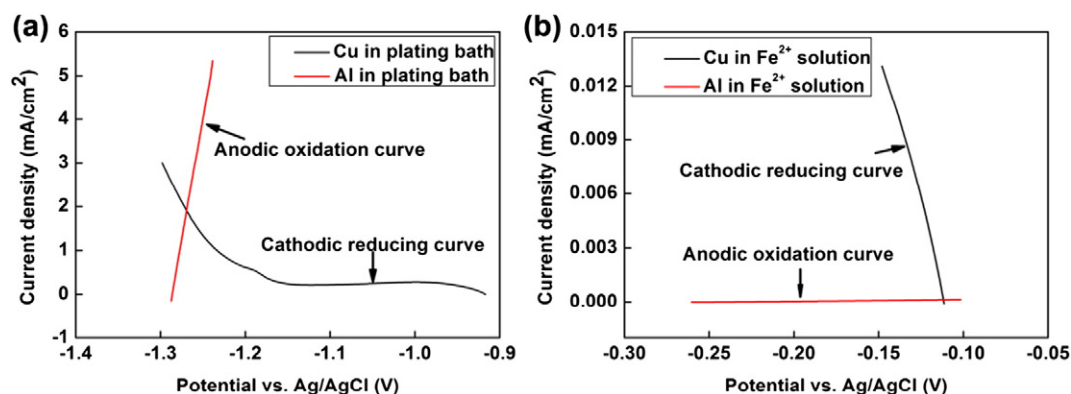


Fig. 2. The cathodic reducing and anodic oxidation curves in (a) the Fe plating bath and (b) the Fe<sup>2+</sup> solution.

Download English Version:

<https://daneshyari.com/en/article/8025076>

Download Persian Version:

<https://daneshyari.com/article/8025076>

[Daneshyari.com](https://daneshyari.com)