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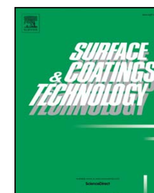

One-step immersion plating method to deposit anticorrosion nickel-sulfur coatings on copper

Xingkai Zhang, Kaixiong Gao, Fuguo Wang, Yan Zhou, Junyan Zhang*

R&D Center of Lubricating and Protecting Materials, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

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A B S T R A C T

Although nickel has a lower standard electrode potential than copper, nickel-sulfur coatings were successfully deposited on copper through one-step immersion plating method, which was carried out in the aqueous solution consisting of $NiSO_4{\cdot}6H_2O$ and $Na_2S_2O_3{\cdot}5H_2O$ at room temperature. The open circuit potential tests demonstrated that copper had a more negative potential than nickel in $Na_2S_2O_3{\cdot}5H_2O$ solutions, which made the deposition of nickel on copper through immersion plating feasible. Because of the decomposition of sodium thiosulfate, sulfur could be codeposited with nickel and the nickel-sulfur coatings were finally obtained. The surface morphology and composition of the coatings were characterized with SEM, EDS, XPS and XRD analyses, and the results indicated the coatings were mainly composed of metallic nickel and Ni_3S_2. The deposition process of the nickel-sulfur coatings was investigated by analyzing the morphology evolution of copper substrates. The as-prepared nickel-sulfur coatings possessed good anticorrosion ability for its compact structure and could lower the corrosion current density of copper in 3.5 wt% NaCl solution to its 1/20.

1. Introduction

Printed circuit board (PCB) is an important component for electronic products, and copper is commonly adopted as the conductor in PCBs for its good electrical conductivity [1,2]. However, copper is prone to be oxidized or corroded, and therefore the reliability of the PCBs will be seriously affected [3,4]. Hence, surface treatments are required to prevent the copper circuits in PCBs from oxidization and corrosion [5]. Because of their excellent anticorrosion ability, nickel-phosphorus coatings prepared by the electroless plating method have been extensively employed to protect the copper circuits [6,7]. While, as copper cannot catalyze the hypophosphite oxidation, palladium activation steps are generally required to induce the electroless nickel-phosphorus plating on copper circuits [8,9], which can obviously increase the cost and complexity of the nickel-plating process. Therefore, it is urgent to find a Pd-free method to prepare nickel-based coatings on copper. One of the effective methods is using nickel to induce the electroless nickel-phosphorus plating on copper owing to the autocatalytic behavior of electroless nickel plating. To realize the Ni-activation method, Tian et al. [10,11] reported the deposition of Ni-S films on copper substrates in high concentrated thiourea solutions, and Yagi et al. [12] reported the use of Ti^{3+} as the reducing agent to deposit nickel layers on copper substrates. Although electroless nickel-phosphorus plating could be carried out on copper after adopting the above Pd-free Ni-activation method, the inevitable activation steps were also complicated or expensive. To avoid adopting activation step, hydrazine or dimethylamine borane was used as the second reducing agent in the electroless plating bath to realize the direct electroless nickel-phosphorus plating on copper [13,14]. However, an alkaline environment was essential for hydrazine and DMAB to provide the reducibility, but was bad for the stability of the plating solution.

For its simplicity to operate and control, one-step immersion plating can be a potential surface treatment strategy to deposit nickel-based coatings on copper. However, because nickel has a lower standard electrode potential ($E_{Ni2+/Ni} = -0.23$ V) than copper ($E_{Cu2+/Cu} = 0.34$ V) [15], it is impossible to deposit nickel-based coatings on copper through immersion plating in simple nickel salts aqueous solutions. Therefore, it needs to reverse the electrode potential difference between nickel and copper by adjusting the plating bath composition or decreasing the size of substrates [16]. Yang et al. [17] found the redox potential for Cu^+/Cu^0 was more negative than that of Ni^{2+}/Ni^0 in ethaline, and therefore porous nickel nanostructures could be successfully fabricated on copper through immersion plating.

In this work, compact nickel-sulfur coatings were directly fabricated on copper substrates through immersion plating carried out in the aqueous solution consisting of $NiSO_4{\cdot}6H_2O$ and $Na_2S_2O_3{\cdot}5H_2O$ at room temperature. The mechanism of depositing nickel on copper was investigated by electrochemical method. Because of the decomposition of

* Corresponding author.
E-mail address: zhangjunyan@licp.cas.cn (J. Zhang).

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sodium thiosulfate, sulfur existed in the coatings and nickel-sulfur coatings were finally obtained. The deposition process of the nickel-sulfur coatings was investigated by analyzing the morphology evolution of copper substrates. The as-prepared nickel-sulfur coatings possessed good corrosion resistance for their compact structures. This one-step immersion nickel-sulfur plating method will provide a potential surface treatment strategy for the denser and finer copper circuits in PCBs.

2. Experimental procedure

2.1. Preparation and characterization of the nickel-sulfur coatings on copper

The copper substrates (with the purity of 99.9%) were first pickled in 5 wt% HCl solution for 1 min to remove the surface oxides and contaminants, and then rinsed with deionized water and ethanol successively before dried by a hairdryer. As the common used sulfur source, sodium thiosulfate had been used to synthesize Ni_3S_2 nanostructures or CoS_2 material through its reaction with nickel foam or cobalt acetate using hydrothermal method, respectively [18,19]. Although Ni-S films had been prepared with the $Na_2S_2O_3{\cdot}5H_2O$ as the sulfur source by electrodeposition process [20], a one-step immersion plating method was developed to obtain nickel-sulfur coatings on copper substrates in this work. The facile immersion plating process for preparing nickel-sulfur coatings on copper was carried out in the solution consisting of $NiSO_4{\cdot}6H_2O$ (50 g·L^{-1}) and $Na_2S_2O_3{\cdot}5H_2O$ (160 g·L^{-1}) at room temperature for 10 min at room temperature. The obtained samples were rinsed with deionized water and ethanol, and then dried by a hairdryer. The as-prepared samples were characterized by scanning electron microscopy (SEM, JSM-6701F, JEOL), energy-dispersive X-ray spectrometer (EDS, Oxford), X-ray photoelectron spectroscopy (XPS, ESCALAB-250Xi, Thermo Scientific) and glancing angle X-ray diffraction (XRD, Empyrean, Panalytical). To investigate the deposition process of the nickel-sulfur coatings, the samples deposited for 20 s, 1 min and 5 min were also taken for digital image, SEM and EDS characterization.

2.2. Electrochemical measurements

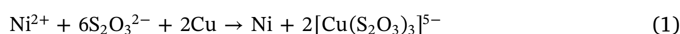
All electrochemical experiments were performed on an electrochemical workstation (μAutolab III, Metrohm) with the Ag/AgCl electrode (in saturated KCl solution) as reference electrode and platinum wire as counter electrode. The open circuit potential (OCP) of pure copper and nickel were measured in 50 g·L^{-1} $NiSO_4{\cdot}6H_2O$ solution, 160 g·L^{-1} $Na_2S_2O_3{\cdot}5H_2O$ solution and the immersion plating solution, respectively. OCP-t measurements were also used to investigate the nickel deposition mechanism. To evaluate the corrosion resistance of the as-prepared nickel-sulfur coatings, potentiodynamic polarization tests were performed in 3.5 wt% NaCl solution with a scan rate of 5 mV·s^{-1} after the OCP measurements for 30 min. The values of corrosion potentials and corrosion current densities were extracted from the polarization curves by making the tangent of the anodic polarization and cathodic polarization curves, and then the crossing points of the tangent lines were corresponding to the corrosion potentials and corrosion current densities.

3. Results and discussion

3.1. Thermodynamic possibility of the immersion nickel plating on copper

To explore the possibility of depositing nickel on copper through immersion plating process, the OCPs of pure copper and nickel in different solutions were characterized firstly. As shown in Fig. 1a, the OCP of copper (− 0.011 V) was higher than the OCP of nickel (− 0.314 V) in 50 g·L^{-1} $NiSO_4{\cdot}6H_2O$ solution, and therefore nickel could not be deposited on copper in $NiSO_4{\cdot}6H_2O$ solution through immersion plating. However, the OCPs of copper were decreased to − 0.619 V and − 0.438 V in 160 g·L^{-1} $Na_2S_2O_3{\cdot}5H_2O$ solution and the immersion plating solution, which were 449 mV and 56 mV lower than those of nickel (− 0.170 V and − 0.382 V), respectively (shown in Fig. 1b and c). It indicated the deposition of nickel on copper through immersion plating was thermodynamics feasibility in the immersion plating solution.

To further understand the mechanism of immersion nickel plating on copper, the OCP-t technique was used. OCP transients are largely dependent on the composition of the electrolyte, which have been widely used to interpret electroless metal deposition processes [21]. As shown in Fig. 2, adding $Na_2S_2O_3{\cdot}5H_2O$ solution into the $NiSO_4{\cdot}6H_2O$ solution caused a steep shift in the OCP of copper toward a more negative value, − 0.462 V from − 0.011 V. It also demonstrated that $Na_2S_2O_3{\cdot}5H_2O$ could lead to the obvious decline in the potential of copper and make the deposition of nickel on copper through immersion plating possible. The reason for lowering the potential of copper might be attributed to the strong copper-complexing action of $Na_2S_2O_3{\cdot}5H_2O$ [22], and the deposition of nickel on copper was supposed to carry out through the following equation:



$$Ni^{2+} + 6S_2O_3^{2-} + 2Cu \rightarrow Ni + 2[Cu(S_2O_3)_3]^{5-} \quad (1)$$

3.2. Preparation and characterization of the nickel-sulfur coatings

To verify the feasibility of depositing nickel on copper through immersion plating, copper foils were immersed in the plating solution at room temperature. After 10 min, a silvery metallic-like deposit had been obtained on copper (top-right inset image in Fig. 3a). The SEM analysis showed that the obtained coating was mainly constituted of nano-nodules with the diameters of about 70 nm and the nano-nodules were tightly packed to form a compact structure. While, from the EDS result (bottom-right inset image in Fig. 3a), it was found that the obtained coatings contained sulfur except nickel. The detailed surface chemical states of the coating were surveyed by XPS. As shown in Fig. 3b, the peaks corresponding to Cu, Ni, O, C, and S could be seen in the full XPS spectrum. The detection of O and C might be attributed to the oxidation and organic contamination of the freshly deposited coating. The atomic ratio of Ni to S was about 1:1 according to the XPS results.

The high-resolution spectrum of Ni2p signals and the corresponding fitting curves were shown in Fig. 4a. The peaks located at 852.6 eV and 869.9 eV could be attributed to metallic nickel. The Ni2p3/2 and Ni2p1/2 peaks at 855.8 eV and 873.6 eV corresponded to Ni^{2+} species such as NiO [23]. Because of the multi-electron excitation, two intense satellite peaks were observed at 861.3 eV and 879.8 eV, which also belonged to Ni^{2+} species. The S2p signal (Fig. 4b) showed two broad peaks centered at 162.2 eV and 163.4 eV, which corresponded to the S2p3/2 and S2p1/2 contributions [24]. The existence of sulfur in the coatings might be attributed to the decomposition of sodium thiosulfate and the codeposition of sulfur together with nickel [25].

To confirm the structure and phase of nickel-sulfur coatings, XRD measurements were carried out. As shown in Fig. 5a, except the three strong diffraction peaks attributed to the copper substrates, some weak diffraction peaks could be found and they were clearly shown in Fig. 5b. It can be seen that the characteristic peak of nickel (111) crystal face at about 44.5° could be observed in the pattern. The other peaks located at about 21.8°, 31.1°, 37.8° and 55.2° could correspond to (101), (110), (003), and (122) planes of the Ni_3S_2 crystal, respectively [26,27]. The atomic ratio of Ni to S was larger than the obtained result from XPS results, and it was mainly because the XPS analysis mainly detected the composition in the outermost surface layer of the coatings. Based on the above EDS, XPS and XRD results, it was indicated that the obtained nickel-sulfur coatings were mainly consisted of Ni and Ni_3S_2.

It was possible that the formation of Ni_3S_2 was preceded according to the following reaction mechanism. As sodium thiosulfate possessed

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