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Preparation of Cu–Ni–Fe alloy coating and its evaluation on corrosion behavior in 3.5% NaCl solution

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ABSTRACT

In this paper, an attempt had been made to prepare a Cu–Ni–Fe alloy coating for improving the corrosion resistance of the low-carbon steel. The surface heat treatment of coated low-carbon steel was performed at 1000 °C for 3 h under hydrogen atmosphere. The structure and microstructure of coatings was separately analyzed by X-ray diffraction (XRD) and scanning electron microscope (SEM). The corrosion resistance of the samples was evaluated by potentiodynamic polarization (Tafel) and electrochemical impedance spectroscopy (EIS). Results indicated that a compact alloy coating was formed on the surface of low-carbon steel and the Ni content had a prodigious impact to the microstructure, composition and structure of Cu–Ni–Fe alloy coating. Apart from that, significant improvements in corrosion resistance were achieved by using the Cu–Ni–Fe alloy coating, which constituting of homogeneous γ-phases.

1. Introduction

Given the well-documented global corrosion challenge, the development of universal coating systems for metals that provide both passive and active protection is desirable [1,2]. To meet the demands of specific properties where they are most needed, there has been an extensive research on the possibilities for coating material design and their protection mechanisms. Recently, Cu–Ni alloy coatings and Fe–Ni alloy has been widely used due to their exciting mechanical, corrosion properties and reasonable price [3–10]. At the same time, the literatures concerning the ternary and quaternary alloy coatings are very numerous because of their more preeminent properties. As previous literatures indicated, the protective action of Cu–Ni–Fe alloy seems to be dependent on a good adherence to the metal and high resistivity towards electronic and ionic conductance [11–14]. Iron can provide added resistance to corrosion in Cu–Ni based alloys, nickel can enter the defective structure of Cu_2O, decreasing its conductivity. Hence, the corrosion resistance can be improved with increasing iron or nickel content as long as it remains in solid solution [15]. Generally, the addition of iron to Cu–Ni improves the corrosion resistance in a sea water and polluted water environment. Cu–Ni–Fe alloys also show good resistance to stress corrosion and high-temperature corrosion. Because of these interesting properties, Cu–Ni–Fe alloys are widely used in industrial applications such as inert anodes in aluminium electrolysis, heat exchange equipment, hydraulic pipelines, oil rigs and platforms [11,15–17].

However, the iron (Fe)–copper (Cu) system does not form intermetallic compounds and has negligible mutual solid solubility. Cu–Ni–Fe alloys present a two-phased microstructure (Cu-rich and Fe–Ni-rich phases) due to their spinodal decomposition [16–18]. This chemical inhomogeneity may have a negative influence on the corrosion resistance of the material [19]. Therefore, conventional surface alloying processes such as salt bath treatment or electrodeposition technique are unsuitable for preparation of homogeneous Cu–Ni–Fe alloy coating.

Recently, many new modified treatment processes are applied for preparation of homogeneous ternary Cu–Ni–Fe alloy. Baricco et al. declare that rapid solidification is a viable process and the addition of Ni to binary Fe–Cu alloys promotes the solubility of Fe in the fcc phase [20]. Mondal et al. [21] and Helle et al. [6,19] both have demonstrated the high efficiency of the ball milling technique for producing monophased Cu–Ni–Fe alloys over a large stoichiometric range. Consequently, design of monophased Cu–Ni–Fe alloy coatings for improving corrosion behavior is considerable. With the above aspects as the backdrop, an attempt is made to develop a more economical and simple possibilities process for improving the corrosion resistance of low-carbon steel. We adopted the nano-hybrid particles (nano-sized CuO–NiO) and applied the surface treatment of low-carbon steel to develop the homogeneous Cu–Ni–Fe alloy coatings. The corrosion behaviors of Cu–Ni–Fe alloy coatings were investigated by using the potentiodynamic polarization curve and electrochemical impedance spectroscopy in conjunction with impedance fitting.

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2. Experimental process

2.1. Preparation of nano-sized particles and samples

For the preparation of the coating, nanoCuO was used as the copper source and nanoNiO as the nickel source. CuO and NiO were placed in an agate jar with absolute ethanol used as the dispersing agent and then ball-milled for 24 h. Molar ratio of CuO:NiO was 1:x (x = 1, 2, 4) and liquid: solid ratio was 80:15. All the sizes of CuO–NiO particles were controlled at 100 nm_{max}.

The low-carbon steel ($10 \times 10 \times 1.2\ \text{mm}^3$) was used as substrate, which was mechanically polished using 240–1200 grit papers in sequence. Then the samples were rinsed in acetone, ethanol and distilled water for 5 min respectively by an ultrasonic cleaner in order to degrease and clean the surfaces to improve the adhesion of the coating. After the cleaning process, the low-carbon steel was placed horizontally. The coating solution was vertically sprayed onto the substrates from a distance of approximately 15 cm using a detail spray gun (IT-powered Manufacturing, HD-470). The spray-dry cycle consisting of spraying for 15 s followed by air-drying the sample for 45 s was repeatedly applied up to 20 times to achieve the desired coating uniformity and thickness. It is noteworthy to underline that the weight of nano-hybrid particles layer should be controlled at $62 \pm 0.50\ \text{g/dm}^2$. Then the heat treatment was carried out at temperatures of 1000 °C for 3 h under hydrogen atmosphere with the heating rate of 10 °C/min. At the last step, a mass of hydrogen was continually used on the sample surface to accelerate cooling rate for prevention of the spinodal phase separation. Three samples were prepared by different particles in this paper and they are denoted by Cu–Ni–Fe I, Cu–Ni–Fe II, Cu–Ni–Fe III (as shown in Table 1).

2.2. Characterization of the Cu–Ni–Fe alloy coatings

After the heat treatment, the structural characters of the coatings were investigated by X-ray diffraction (XRD) with a diffractometer D/max-2200 V and Cu Kα radiation. The surface morphology and cross-section of Cu–Ni–Fe alloy coatings was evaluated by scanning electron microscope (SEM) using the JEOL JSM-6700F microscope, at the same time, the chemical composition of the coatings was determined by an energy dispersive spectroscopy (EDS).

The corrosion behavior of the coating was studied using polarization techniques (Tafel) and electrochemical impedance spectroscopy (EIS) with an electrochemistry station (CHI660C). Tafel and EIS experiments for the substrate and the coatings were performed in 3.5 wt.% NaCl solution with a conventional three-electrode cell. A saturated calomel reference electrode (SCE) and a platinum wire as counter-electrode were used in the tests. The surface area of the test coupons (as the working electrode) exposed to the electrolyte was $1\ \text{cm}^2$. The impedance data were obtained at the open circuit potential, when the corrosion potential remained stable, a sinusoidal AC signal of 5 mV amplitude at the open circuit potential (OCP) was applied to the electrode over the frequency which ranged from 100 kHz to 0.01 Hz. Each type of electrochemical measurement was repeated at least 3 times until good reproducibility of the data was obtained, and the average results were presented here.

3. Results

3.1. EDS analysis

Compositions of different Cu–Ni–Fe alloy coatings were analyzed by use of EDS analysis and the results are shown in Table 1. It reveals that all coatings are composed of Cu, Ni and Fe. Although presence of little oxygen at surface of the coating layer is quite probable, however EDS analysis is not accurate enough in detection of such microscale elements. The appearance of Fe in the coatings is caused by the solid diffusion of new generated metal atoms or fusion of nanoparticles with the low-carbon steel surfaces in the coating process. The elements composition of the Cu–Ni–Fe alloy coatings varies with the composite particles. The Cu content decreases and Ni content increases on the surface coating. Moreover, the ratio of Cu/Ni in the coating is much higher than that in particles, suggesting that the Ni is diffused more easily than Cu.

3.2. Morphological analysis

The SEM micrographs of Cu–Ni–Fe coatings are shown in Fig. 1. In all cases, the coatings are uniform and crack-free. However, the surface morphology of the coatings is strongly influenced by the Cu content and Ni content in the coating. As shown in Fig. 1a, the small dendrite phase exists in the sample Cu–Ni–Fe I, and the coating surface becomes generally smoother as the Cu content decreases and Ni relatively increases (Fig. 1b and c). It shows that the increase of Ni content in the coating has a significant impact to produce a uniform and homogenous Cu–Ni–Fe alloy coating. The cross-section morphology of the sample Cu–Ni–Fe III is displayed in Fig. 1d. As shown, a compact and homogenous alloy layer is formed on the surface. The average thickness of the coating is about 30 μm and satisfactory adhesion between coating and substrate is observed. In addition, a transition zone which contained two phase, is clearly observed between the alloy coating and the substrate.

3.3. XRD analysis

Fig. 2 shows the XRD patterns of the three coatings. As shown in Fig. 2, Cu–Ni–Fe I coating exhibits diffraction peaks of both α-phases and γ-phases, while there is an obvious increase in the intensity of γ-phases together with a sharp decrease in that of α-phases, of which Cu–Ni–Fe II coating was nearly disappeared. Moreover, diffraction peaks of α-phases disappear completely for Cu–Ni–Fe III.

3.4. Potentiodynamic polarization

The corrosion behavior of coating can be studied by polarization curves in corrosive media that yield specific data on the behavior of the coating system [22]. Fig. 3 shows the polarization curves of coated low-carbon steel in 3.5 wt.% NaCl solution at ambient temperature, and the data for corrosion current density (I_{corr}) and corrosion potential (E_{corr}) obtained from the polarization curves by Tafel extrapolation method are tabulated in Table 2. The protective efficiency (P_i) of the coatings is also listed in Table 2 and it was estimated by the following equation [23]:

$$P_i(\%) = \left(1 - \frac{I_{\text{corr}}}{I^0_{\text{corr}}}\right) \times 100$$

where I^0_{corr} represents the corrosion rate of the low-carbon steel (substrate). I_{corr} represents the corrosion rate of the Cu–Ni–Fe coatings.

It is obvious from Fig. 3 that the bare low-carbon steel reacted acutely in the sodium chloride solution. In contrast with bare carbon steel, all the coated samples have more noble corrosion potential and much lower corrosion current density ranging from 15.30 to 5.20 $\mu\text{A cm}^{-2}$, indicating that the Cu–Ni–Fe alloy coating improved the corrosion resistance of carbon steel distinctly.

In comparison with the inhomogeneous coating (Cu–Ni–Fe I), the homogeneous coatings (Cu–Ni–Fe II and Cu–Ni–Fe III) show

Table 1
The composition of Cu–Ni–Fe alloy coating in this study.

Samples	Composite particles CuO/NiO (at.)	Surface composite (wt.%)			
		Cu	Ni	Fe	Cu/Ni (at.)
Cu–Ni–Fe I	1/1	46.3	22.8	30.9	1/0.53
Cu–Ni–Fe II	1/2	30.3	25.0	44.7	1/0.89
Cu–Ni–Fe III	1/4	20.6	46.1	33.4	1/2.42