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Electrochemical Studies on the Passivation Behavior of Cu-Ni-Fe Alloy Coating in Borate Buffer Solution at pH 8.4

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Abstract: Cu-Ni-Fe alloy-layer was prepared on the surface of mild steel by nano technology in this paper. Polarization techniques and Mott-Schottky analysis in conjunction with the point defect model (PDM) have been used to investigate the semiconductor properties of the passive films formed on the surface of nano Cu-Ni-Fe alloy layer in borate buffer solution at pH 8.4. The results showed that the passive film formed on the surface was more compact, highly protective with higher heating temperature. Carriers density and vacancies diffusion coefficient of the passive film formed on nano Cu-Ni-Fe alloys decreased with higher heating temperature. The vacancies diffusivity is about magnitude of 10^{-20}m^2·s^{-1} in borate buffer solution at pH 8.4.

Keywords: Passivation; Mott-Schottky analysis; Carriers diffusivity

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Introduction

The widespread use of Cu-Ni alloys depends on a combination of good corrosion resistance, excellent pyroelectricity and attreeactive mechanical properties [1]. The electrochemical behavior of Cu-Ni alloys has been extensively studied under different experimental conditions using various techniques [2-4]. Passive films act as a reacting ion barriers between metal surface and aggressive environment in corrosive solutions, and thereby protect metals from corrosion [5-6]. A lot of researches have been done on the passive films on iron, stainless steels [7-9], however, not many investigations have been reported on the passivation behavior of Cu-Ni-Fe alloys, especially of its semiconductor properties.

The present work attempt to clarify the mechanism of the passivating processes in borate buffer solution at pH 8.4. The semiconductor properties of the passive films were also studied. Different electrochemical techniques, e.g., polarization techniques and the capacitance measurements were used.

Experimental details

Substrates of mild steel (Bao Steel Ltd., Shanghai, China, 10×10×2 mm in size) were grinded with No. 400 diamond plate, and cleaned in pure acetone and distilled water. Then copper oxide- nickel oxide mixed powder was deposited on the surface of mild steel samples. The samples were heated up to various temperatures ranging from 700 to 1000℃ in an electric furnace, hydrogen gas was used to reduce metal oxides and protect the samples, kept at the desired temperature for 5 h and allowed to cool in the furnace.

The microstructure and composition of the samples were carried out by SEM (HITACHI SU-1510) and EDS (INCA) respectively. The electrochemical exper-

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iments were carried out in a classical three-electrode cell with an electrochemistry work station (CHI660C). The working electrode was the samples (10×10 mm). The counter electrode was a platinum plate and the reference electrode was a saturated calomel electrode (SCE). The experiments were carried out in borate buffer solution (0.15 mol/L $B(OH)_3$+0.075 mol/L $Na_2BO_4{\cdot}10H_2O$, PH=8.4) at ambient temperature. Prior to potentiostatic polarization experiments, the specimens were initially reduced potentiostatically at −1 V for 2 min to remove air-formed oxides. The potentiostatic polarization experiments were performed at potentials of 0.2 V, 0.3 V, 0.4 V respectively. After cathodic reduction (at −1 V for 2 min), the curves of capacitance as function of potential were measured. Prior to this, the electrodes were polarized at designated potentials for 30 min so that a stable passive film could form on the electrode surfaces. The potential was applied by successive displacements of 20 mV in the cathodic direction. The testing frequency was 1000 Hz. All the reagents used in the experiments were of analytical purity.

Results and discussion

Figure 1 shows the SEM photographs of the samples at different temperatures. It is obvious that the surface formed more compactly and the porosity of the surface decreased greatly with the increase of the temperature. The composition of elements in the samples analyzed by EDS was showed in Fig. 2. It is clear that the surfaces of the samples were Cu-Ni-Fe alloys. The content of copper and nickel increased with higher heating temperature, correspondingly the content of ferride decreased.

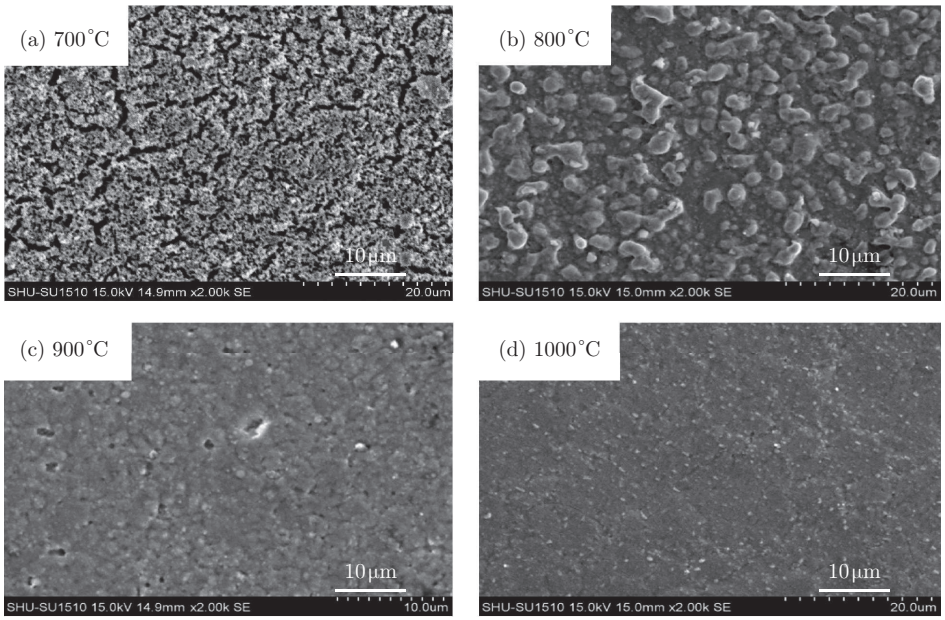

Fig. 1 SEM photographs of the surfaces of sample (A) 700℃, (B) 800℃, (C) 900℃, (D) 1000℃.

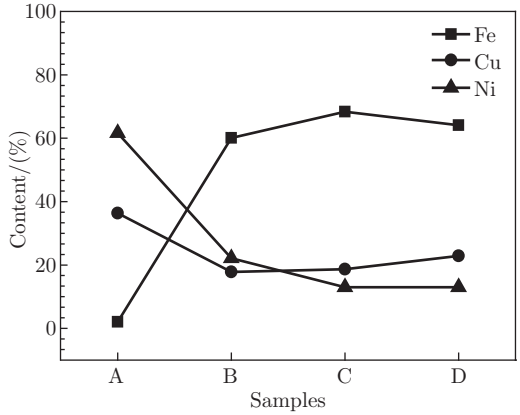

Fig. 2 The elements composition of sample (A) 700℃, (B) 800℃, (C) 900℃, (D) 1000℃.

After cathodic reduction, the work electrodes were used to measure the variation of current with time at the potentiostatic potential. The current decreased with time according to the Eq. (1).

$$I = 10^{(A+k\lg t)} \tag{1}$$

where k represents the slope of the double-log plot for potentiostatic polarization. Fig. 3 shows the double-log plots for potentiostatic polarization at a potential of 0.2 V. The value of k decreased with higher heating temperature. When the temperature was 1000℃ the value of k was −1.09. According to the literature [10-11], the result displayed in Fig. 3. indicates the formation of more compact, highly protective passive film on the electrodes surface with higher heating temper-

ature. The value of k decreased with higher heating temperature.

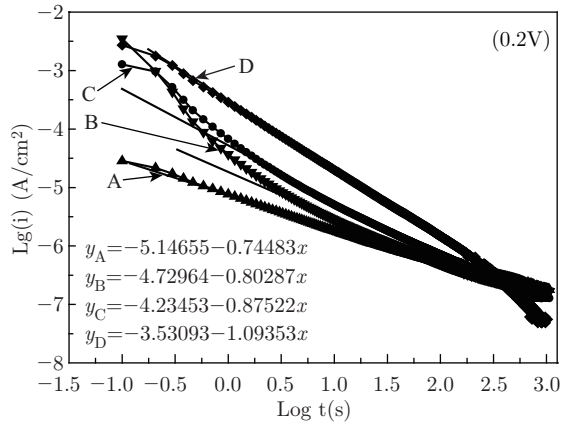

Fig. 3 Double log plots of current time for sample (A) 700℃, (B) 800℃, (C) 900℃, (D) 1000℃.

The curve in Fig. 4 clearly shows a negative slope. It indicated that the passive film formed on all samples showed p-type semiconductor behavior [12-13], The p-type semiconductor is closely related to the copper oxide and nickel oxide of the passive film. The carrier density (Na) can be estimated using the M-S relationship in Eq. (2). ε is the dielectric constant, ε_0 stands for the vacuum permittivity, e and k is respectively the electron charge and Boltzman's constant, T is the absolute temperature, and $U_{\rm fb}$ is the flat band potential. The values of Na estimated using Eq. (2). are shown in Table 1. It is clear that the carriers density decreased with higher heating temperature.

$$\frac{1}{C_{SC}^2} = -\frac{2}{\varepsilon\varepsilon_0 e N_A}\left(U - U_{fb} - \frac{kT}{e}\right) \qquad (2)$$

Table 1 The Na of the oxygen films of the sample in borate buffer solution

Samples	Temperature (℃)	0.2 V Na ($C\cdot m^{-3}$)	0.3 V Na ($C\cdot m^{-3}$)	0.4 V Na ($C\cdot m^{-3}$)
A	700	3.96×1027	3.69×1027	3.23×1027
B	800	2.01×1027	2.50×1027	1.62×1027
C	900	1.94×1027	1.75×1027	1.43×1027
D	1000	1.74×1027	1.71×1027	1.37×1027

The calculation of diffusion coefficient is according to PDM theory [14-15]. This paper is concerned only with

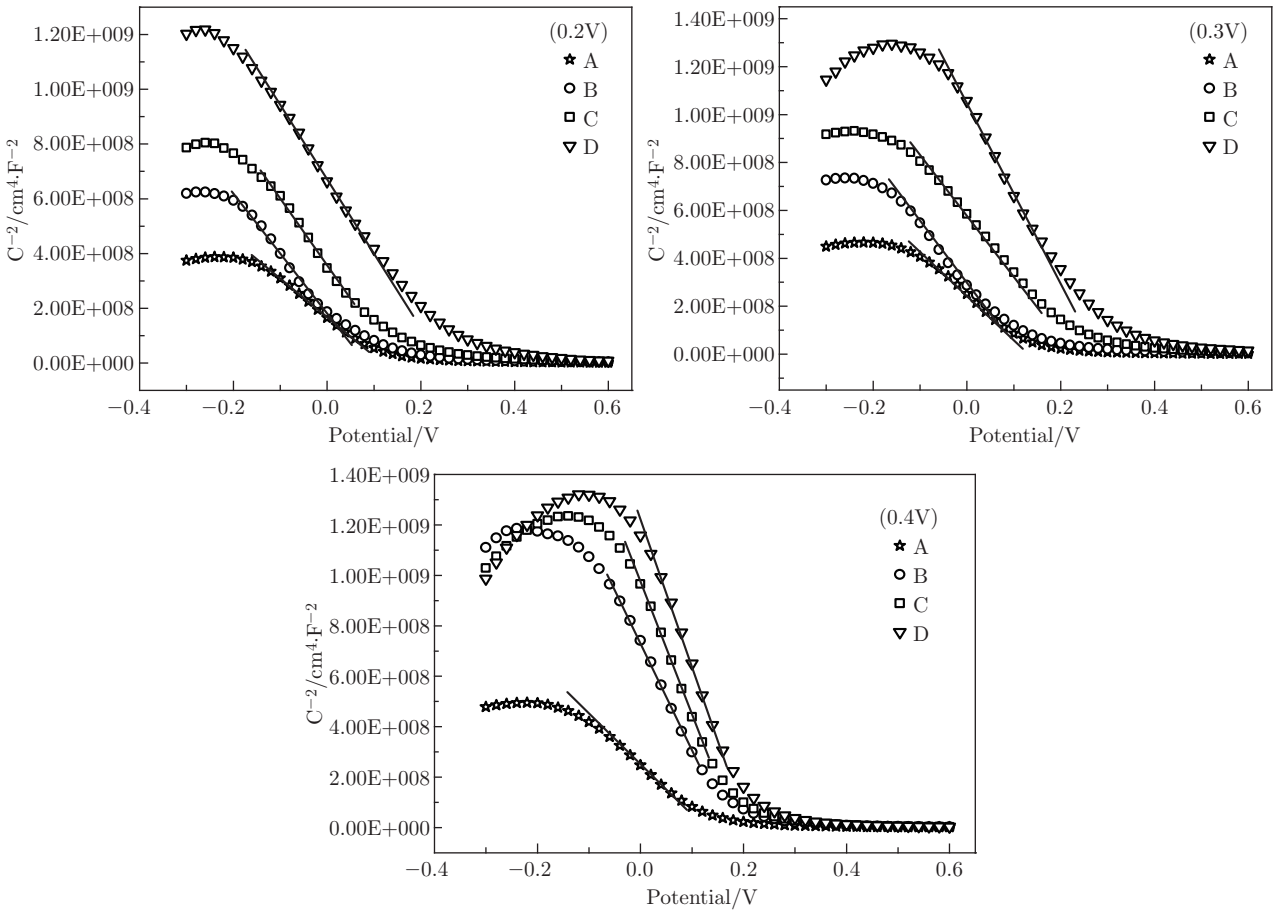

Fig. 4 The Mott-Schottky plots for different passive samples in borate buffer solution.

the N_a as a function of E started from the Nernst-Plank equation, concluding that the density of donors (N_a) is given by the following relationship Eq. (3).

$$N_{\mathrm{a}} = \omega_1 \exp(-bE) + \omega_2 \tag{3}$$

where ω_1, ω_2, and b are unknown constants that are to be determined from the experimental data. Through measuring the curve of the variation of N_a with potential (U_f) at different polarization potential, in this paper we adopted polarization potential 0.2 V, 0.3 V, 0.4 V respectively. The fitting result of ω_2 can be obtained in Eq. (3), the fitted values are as Eq. (4) to Eq. (7)

$$N_{\mathrm{a}}^{A} = -1.32 \times 10^{26} \exp(0.19E) + 3.39 \times 10^{27} \tag{4}$$

$$N_{\mathrm{a}}^{B} = -1.94 \times 10^{25} \exp(0.13E) + 3.95 \times 10^{27} \tag{5}$$

$$N_{\mathrm{a}}^{C} = -3.44 \times 10^{23} \exp(0.05E) + 4.29 \times 10^{27} \tag{6}$$

$$N_{\mathrm{a}}^{D} = -7.38 \times 10^{22} \exp(0.04E) + 4.77 \times 10^{27} \tag{7}$$

Guo et al. [16] demonstrated that ω_2 in Eq. (8) could be related to the diffusivity of the oxygen vacancies D_0 by the following equation:

$$D_0 = \frac{i_{ss} RT}{4eF\varepsilon_L \omega_2} \tag{8}$$

where F is the Faraday constant, ε_L the mean electric field strength within the passive film. ε_L is a great quantity value, the studies constantly consider it was 10^6 V cm^{-2}. R is the gas constant, T is the absolute temperature, e is the charge of an electron and i_{ss} is the steady-state passive current density, which can be determined from the polarization curves.

Table 2 The diffusion coefficients (D_0) of vacancies of the sample

samples	Temperature (℃)	D_0(10^{-20}m^2·s^{-1})
A	700	3.74707
B	800	2.49838
C	900	1.18397
D	1000	0.92263

The calculated vacancies diffusion coefficients was showed in Table 2. The magnitude was approximately of 10^{-20}m^2·s^{-1}. MacDonald [5] calculated the metal cation diffusion coefficient approximately magnitude of 10^{-19}m^2·s^{-1} respectively, which is close with this paper. Results in table 2 shows that there are obvious differences in diffusion coefficient of passive films formed on the surface of the samples. The diffusion coefficient of sample D (1000℃) is the smallest (0.92263×10^{-20}m^{2}s^{-1}). In the same environment, the smaller the diffusion coefficient the lower vacancy mobility, and result to a better protection for substrate.

Conclusions

1. Cu-Ni-Fe alloy layer were prepared on the surface of mild steel and the content of copper and nickel increased with higher heating temperature, correspondingly the content of ferride decreased.

2. The slope of the double-log plot for potentiostatic polarization decreased with higher heating temperature. When the temperature was 1000℃, the value of k was1.09, a compact, protective passive film was formed on the electrodes surface in borate buffer solution at pH 8.4.

3. The carriers density and vacancies diffusion coefficient of the passive film formed on Cu-Ni-Fe alloys decreased with higher heating temperature. The vacancies diffusivity are about magnitude of 10^{-20}m^2·s^{-1} in borate buffer solution at pH 8.4.

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