

ELECTROCHEMICAL BEHAVIOR OF ELECTRODEPOSITED NANOCRYSTALLINE COBALT-IRON ALLOY COATING IN DIFFERENT PH

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Article history

Received

15 February 2015

Received in revised form

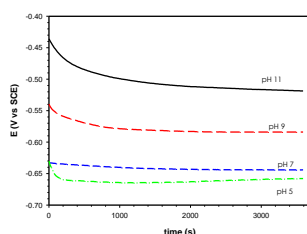
30 April 2015

Accepted

31 May 2015

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Graphical abstract



Abstract

The electrochemical behavior of a cobalt-iron (CoFe) alloy electrode in 0.1 M Na₂SO₄ (sodium sulphate) aqueous solution of different pH was investigated. The presence of a different concentration of dissolved sulphide ions with different pH on the corrosion of electrodeposited cobalt-iron was investigated using the EQCM technique. The corrosion rates of the alloys in acidic solutions are pronouncedly high, compared to those measured in neutral or basic solutions. The presence of sulphide ions accelerates markedly the anodic reaction for all deposits in the basic medium. The dissolution rate was twice two times faster when S²⁻ was added. By employing the EQCM, it was observed that the mass decrease or dissolution rate was significant with an increase in pH concentration.

Keywords: Electrochemical quartz crystal microbalance (EQCM), nanocrystalline cobalt-iron alloy, pH concentration, sulphide ion

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1.0 INTRODUCTION

It is known that the use of coating is one of the methods employed to prevent corrosion. Electrochemically-deposited nanocrystalline CoFe alloy coatings have attracted attention due to their wide applications in a variety of electronic fields such as microelectronics [1], magnetic recording [2], micro-electro-mechanical systems (MEMs) [3], and energy conversion devices [4]. This has led to extensive research in producing these alloy coatings with optimum properties to confirm their optimum performance and reliability as an integral part of the devices.

From the literature, most research work on nano CoFe alloy coatings were focused on their magnetic properties [5,6]. However, in order to further expand their future applications, the corrosion behavior of these nanocrystalline coating alloys is of great importance. To date, there have been very few studies conducted to investigate the electrochemical behavior of nanocrystalline CoFe alloy coatings. It is known that corrosion occurring on alloys in an aqueous

solution is often affected greatly by a number of factors which include pH and the presence of aggressive ions in the surrounding environment [7,8]. The corrosion of Co and its alloys are also dependent on the pH solution. Different electrochemical behaviors were observed in low and high pH solutions. Active dissolution without any passivation was observed in 0.01 M H₂SO₄ (sulphuric acid) + 0.99 M Na₂SO₄ (pH 2.55) [9] and Na₂SO₄ solutions with pH 3, 6, and 7 [10]. On the other hand, mixed observations have been reported for the passivation behavior in alkaline solution [11]. This may be due to the variety of thermodynamically-stable cobalt oxides and/or cobalt hydroxides could be formed as predicted from the E-pH diagram of cobalt-water system at 25 °C [12].

Although several investigations on the corrosion of CoFe have been performed, its corrosion behavior is still not completely understood. Obtaining more information on the electrochemical dissolution of CoFe alloys is necessary and crucial to obtain better understanding. Thus, in this paper the

electrochemical reaction of the CoFe alloy coatings in a sodium sulphate solution with different pH value was investigated using the electrochemical quartz crystal microbalance (EQCM).

2.0 EXPERIMENTAL

2.1 Electrochemical Quartz Crystal Microbalance

Electrochemical Quartz Crystal Microbalance (EQCM) measurements were performed with AT-cut, mirror-finished Ti coated on both sides of the quartz crystals. CoFe alloy was deposited from a solution containing cobalt sulphate (250 g/L^{-1}), iron sulphate (80 g/L^{-1}), boric acid (30 g/L^{-1}) and saccharin (3 g/L^{-1}). The quartz crystal microbalance QCM 922 was used in conjunction with a Princeton Applied Research Versastat 4 potentiostat. A saturated calomel electrode (SCE) and graphite was used as the reference and counter electrode, respectively.

2.2 Electrolytes

The electrolyte solutions employed for the electrochemical studies were $0.1 \text{ M Na}_2\text{SO}_4$ with a pH of 5, 7, 9, and 11. The pH of the solution was adjusted by adding H_2SO_4 or NaOH . Before each measurement, the pH of the test electrolyte was controlled by a standard pH meter. All experiments were conducted using 30 mL of solution at room temperature.

2.3 Electrochemical Measurements

Potentiodynamic polarization test was performed with Princeton Applied Research (PAR) VersaStat 4 potentiostat. The cathodic and anodic behaviors of the samples were obtained in the range of -0.25 V vs. OCP (Open Circuit Potential) to 0.8 V vs. SCE (Saturated Calomel Electrode) with a scan rate of 0.167 mV s^{-1} . All potentials are referred to the SCE electrode. In order to extract polarization resistance (R_p) linear polarization resistance (LPR) test were performed within $\pm 20 \text{ mV}$ of OCP at the standard scan rate of 0.167 mV s^{-1} . All tests were repeated at least twice to ensure reproducibility.

2.4 EIS Measurement

The interfacial processes and surface interactions of the film/liquid interface was analyzed by electrochemical impedance spectroscopy (EIS). The EIS measurements were performed at the OCP with AC disturbance signal of 10 mV , a measurement frequency range between 0.01 Hz and 20 kHz and a sampling rate of 10 points/decade. The EIS results were analyzed and fitted to equivalent circuit using ZSimpWin® v3.40.

3.0 RESULTS AND DISCUSSION

3.1 Effect of pH Solution

The free corrosion potential of CoFe alloy coatings was traced for 60 min in stagnant $0.1 \text{ M Na}_2\text{SO}_4$ aqueous solutions of different pH covering the acidic, neutral, and basic media as shown in Figure 1. It can be seen that exposure to the test solution with the pH varying from 5 to 11, caused a change in the potentials of the alloy coatings. The electrode potential in the low pH solution was found to shift towards less negative values and the steady state was reached in less than 10 min. Meanwhile, it is obvious that the potential of the electrodes took about 25 min before reaching a steady-state in the neutral and basic solution. The potential shift towards more negative values could correspond to the dissolution of native oxide layers. The steady state for the CoFe alloy in basic solutions took a bit longer to reach as compared to the electrode in the low pH solution. This process is partially dependant on the type of alloy and electrolyte composition. The time taken to reach a relatively stable value is related to the activation or the formation of an oxide film on the alloy surface [13]. This indicates that the corrosion resistance of the alloy changes with time and eventually reaches a stable value. Meanwhile, the electrode potential in neutral solutions was found to be almost constant with a potential value of $-0.63 \text{ V}_{\text{SCE}}$ for the whole hour of immersion. This shows that the electrode did not experience any significant electrochemical changes. The electrode immersed in basic solution of pH 11 was found to exhibit the noblest potential of $-0.51 \text{ V}_{\text{SCE}}$. By decreasing the pH value to 9, the electrode potential slightly shifted to a more negative value ($-0.57 \text{ V}_{\text{SCE}}$). Meanwhile, exposure to the acid solution resulted in the most negative potential of about $-0.67 \text{ V}_{\text{SCE}}$.

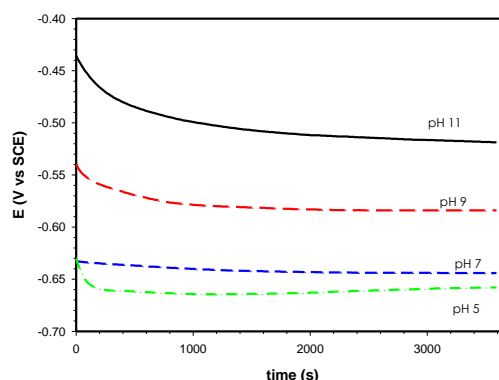


Figure 1 Potential changes of CoFe alloy coating measured in $0.1 \text{ M Na}_2\text{SO}_4$ solutions at pH of 5, 7, 9, and 11

The corrosion rates were obtained from the LPR (Linear Polarization Resistance) measurements using the following Eq. (1) and (2):

$$i_{corr} = \frac{B}{R_p} \quad (\text{Eq. 1})$$

$$B = \frac{1}{2.3 \left(\frac{1}{\beta_{ox}} + \frac{1}{\beta_{red}} \right)} \quad (\text{Eq. 2})$$

where i_{corr} stand for the corrosion current, B (V/dec) is a constant defined by Eq. (2), R_p (Ω cm) is the polarization resistance, and β_{ox} and β_{red} are the oxidation and reduction Tafel slopes, respectively. Figure 2 illustrates the LPR of the CoFe alloy coatings immersed in different pH solutions. In between the low pH solution and high pH solution, an overall increase in polarization resistance, R_p was observed. It is known that corrosion current density, i_{corr} is inversely related to R_p , implicating that corrosion activity decreases from low to high pH solution.

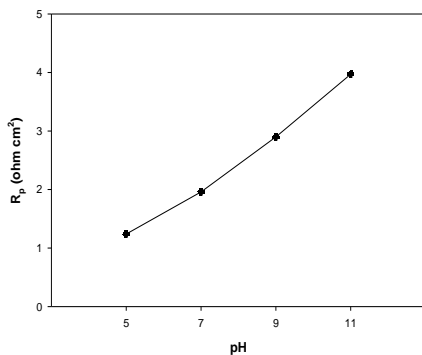


Figure 2 Polarization resistance (R_p) of CoFe alloy coating after immersion for 1 h in 0.1 M Na_2SO_4 solutions at pH of 5, 7, 9, and 11.

3.2 EQCM Measurements

Figure 3 shows the mass changes measurement of the deposited CoFe alloy coating after 1 h of immersion in different pH solutions. The immersion of the electrode in the pH 5 solution leads to an increase of measured resonant frequency which according to the Sauerbrey equation corresponds to a decrease in mass of the EQCM electrode which can be seen through the mass loss (Fig. 3).

The increase in frequency and loss in mass is due to the dissolution of the CoFe alloy coating. On the other hand, the opposite trend was observed for the electrodes in neutral and basic solutions where resonant frequency was decreased indicating a mass increase. However, a mass loss was observed for the electrode in the pH 11 solution at the beginning of the immersion before a mass increase. This mass loss could be related to the dissolution of an oxide layer formed in air prior to the immersion of the electrode in the solution while the mass increase is likely due to alloy

oxidation by water and accumulation of corrosion products (oxides/hydroxides) on the surface alloy.

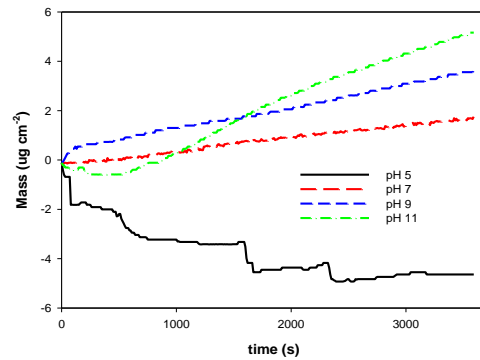


Figure 3 Mass changes of CoFe alloy coating after 1 h OCP measured by EQCM in 0.1 M Na_2SO_4 solutions at pH of 5, 7, 9, and 11.

3.3 Electrochemical Polarization Measurements

The potentiodynamic polarization of deposited CoFe alloy coatings in 0.1 M Na_2SO_4 solutions at pH of 5, 7, 9, and 11 is presented in Fig. 4. A scan rate of 0.167 mV/s was used for all measurements.

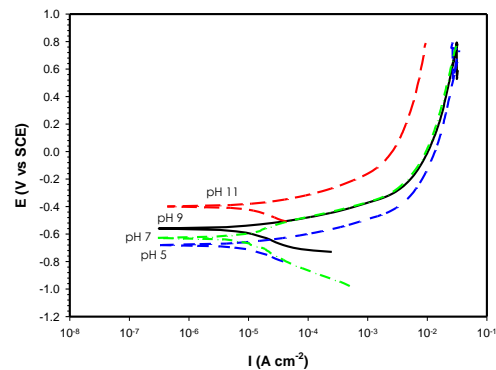


Figure 4 Potentiodynamic polarization of CoFe alloy coating in 0.1 M Na_2SO_4 solutions at pH of 5, 7, 9, and 11. Scan rate: 0.167 mV/s

Similar polarization curves were obtained for all alloy coatings in different pH solutions. An active dissolution behavior without any transition to passivation was observed for all pH values. Basically, the two reactions: $\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$ and $\text{Co} \rightarrow \text{Co}^{2+} + 2e^-$ are considered to be anodic reactions for these alloy coatings. The preferential dissolution of iron from this alloy coating is expected where similar corrosion behavior was reported [14]. It can be observed that a decrease in pH solution moves the corrosion potential in the cathodic direction by hundreds of mV. The decrease in corrosion potential with decreasing pH could be explained by oxide layer formation which are more readily formed at higher pH and thus increased the corrosion potential.

3.4 EIS

The study of corrosion by EIS has proven to be a powerful and accurate method for measuring

corrosion rates for coatings and thin films. The expression for impedance is composed of a real and imaginary part known as the Nyquist plot. Figure 5(a) demonstrates the Nyquist plot of the alloy electrode in different pH solutions. The Nyquist plot for CoFe alloy coatings immersed in different pH solutions showed that the impedance spectra increased from low to high pH solution indicating an enhanced capacitive behavior for the solid/liquid interface. The Nyquist plots showed that the diameter of the capacitive loop of CoFe alloy coatings in acidic solution was smaller than that in the neutral and basic solution. Moreover, no induction effects were observed at lower frequencies which suggest the absence of significant adsorption processes occurring outside the double layer. Bode plots are important to make an accurate interpretation as it explicitly shows frequency information. It is a useful alternative to the Nyquist plot as it can avoid possible errors in the fitting of the Nyquist semicircle and the measurement times associated with low frequency.

Figure 5(b) presents the EIS results in the form of Bode plots during immersion in the test solution for 1 h at E_{corr} . In the Bode plot, the high frequency relaxation process is related to the corrosion product formed on the metal surface and the low frequency process is attributed to the relaxation process obtained by adsorption species [15]. In the higher-frequency region, the phase-angle values were seen to move toward 0° with increasing frequency. This is a response typical of resistive behavior and corresponds to the solution resistance, R_s . In the medium-frequency range, a phase-angle maximum of less than -90° are observed for both samples, indicating that the passive films were not fully capacitive.

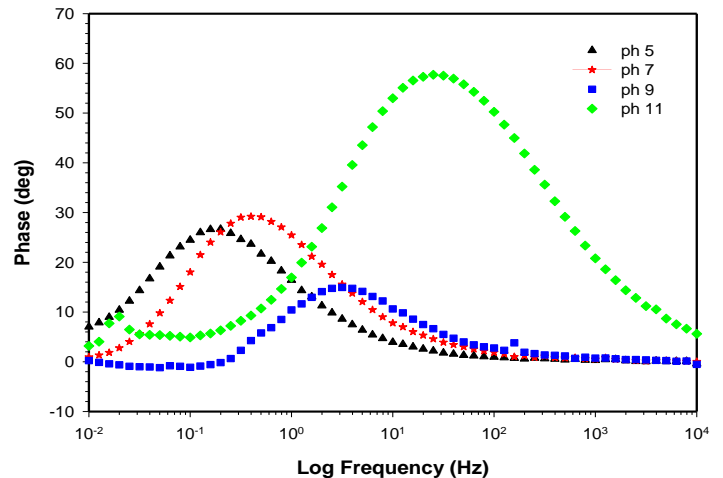


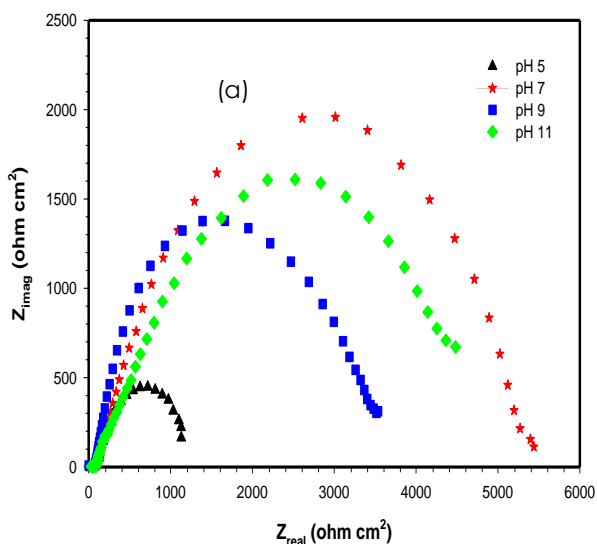
Figure 5 (a) Nyquist (b) Bode phase EIS after 1 h OCP in 0.1 M Na_2SO_4 solutions at pH of 5, 7, 9, and 11.

4.0 CONCLUSION

Based on the current electrochemical study, it was demonstrated that the deposited CoFe alloy coating exhibit only an active behavior without any passivation in 0.1 M Na_2SO_4 at pH 5, 7, 9, and 11. Increasing the solution pH shifted the entire polarization curve to a more anodic potential. Significant mass loss of the electrode was also observed through the EQCM measurement in acidic solution. Interestingly, mass increase in neutral and basic solution was obtained indicating accumulation of corrosion products or formation of a protective film on the surface electrode.

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