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The effect of pH on NiFeP Alloy Electrodeposition for Development of Steam Generator Tube Repair Technique

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Abstract

The effect of bulk pH on deposition mechanism and material properties of NiFeP ternary alloy electrodeposits from sulfamate bath was investigated to develop steam generator tube repair technique. Impedance studies on NiFeP ternary alloy electrodeposition were carried out and it was concluded that increasing bulk pH in the range from 1 to 3.8 did not vary the mechanism of NiFeP ternary alloy electrodeposition, but decreased solution resistance(Rs) and charge transfer resistance(Rct) in Nyquist plots measured under –0.85V because of decreasing hydrogen bubbles on the surface in an adsorbed state. When bulk pH in electrolytes increased during electrodeposition, residual tensile stress in deposits increased with increasing NH_4^+ ion in electrolytes, Ni content in deposits increased with decreasing polarization, and the degree of crystal irregularity in deposits decreased.

1. Introduction

During the long period of time operation of Pressurized Water Reactor(PWR) steam generators, it has been observed to result in localized corrosive attacks on the inside (primary side) or outside (secondary side) of steam generator tubing. The conventional approach to tube rehabilitation is to repair the damaged area of tubes via the insertion of tubular sleeves, which are either welded or mechanically bonded at their extremities to the host tubing [1]. Those methods have the disadvantages like as parent tube deformation, requirement for PWHT(Post Weld Heat Treatment), corrosion concerns associated with weldments, etc [2]. But, repair technique using electrodeposition provides a continuous bond of high strength micro alloyed nickel to the parent tube internal diameter, spanning the defective region. No deformation of the parent tube occurs, and stress relief is not required [3].

Important parameters in electrodepositon process are pH, temperature, current density, metal concentration, and etc. They have to be studied case by case because the effects of them on alloy deposition are very different and complex among them.

Hydrogen with related to pH affects the mechanism of electrodeposition, current efficiency, chemical composition, stress and embrittlement of deposits as the second element produced at the cathode.

NiFe and NiP binary alloy electrodeposits are particular interest in industry due to their superior material properties. However in NiFe alloy electrodeposition, control of Fe content is difficult, and in NiP alloy electrodeposition, mechanical properties decrease with rapid grain growth at the temperature of above 350°C. It was reported that presence of P ion in NiFe electrodeposition controlled Fe codeposition and presence of Fe ion in NiP electrodeposition increased the temperature which rapid grain growth occurred [4].

In this paper, the effect of hydrogen concentration on deposition mechanism and material properties of NiFeP alloy electrodeposits was investigated to develop steam generator tube repair technique.

2. Experimental

Ni sulfamate as a Ni source, Fe sulfamate as a Fe source, phosphorus acid as a P source, Pt plated Ti with a surface area of 3x16cm^2 as an anode and alloy 600 plate with a surface area of 3x10cm^2 as a cathode were used in NiFeP alloy electrodeposition, respectively. Table 1 shows bath compositions used in this study. NiFeP alloy electrodeposition was performed from sulfamate bath with the electrolysis condition as follows: temperature 60°C, current density 5A/dm^2, deposition time 180 min and agitation 0.75L/min using N_2 gas. pH was controlled and adjusted in the range from 1 to 3.8 by sulfamic acid or ammonia. The deposit could be separated easily from the substrate due to the weak adhesion between the deposit and the oxide layer already existing in the surface of substrate.

The cathodic polarization curve was measured from the open circuit potential to –1.8V under the temperature of 60 °C at the scan rate of 10mV/s using potentiostat EG&G 273A. Impedance measurements were done with a frequency response analyzer(Schlumberger SI 1260) connected to the potentiostat. Potential varied with a amplitude of 5mV around applied DC potential and the frequency varied from 100kH to 1Hz. Alloy 600 plate with surface area of 1x1cm^2 as a working electrode, Pt wire as a counter electrode and SCE(Saturated Calomel Electrode) as a reference electrode were used, respectively.

Alloy composition analysis of deposits was performed using ICP analyzer(Model JY80C(Jobin Yvon)). Stress in deposits was in-situ measured using deposit stress analyzer(683EC).

3. Results and Discussion

3-1 Cathodic Polarization Curve and Impedance Spectra

Fig. 1 shows cathodic polarization curve obtained from the sulfamate bath with bulk pH at 60°C. For pH 1, reduction of hydrogen started at potential nearly 0.35V more cathodic than the standard potential +0.19V(SCE). Polarization of Ni activation appeared between potential –0.65V and –0.71V(SCE). After polarization of Ni activation, current density with decreasing the potential rapidly increased. Polarization curve with bulk pH could be divided into two region. First region was between open circuit potential and –0.71V(SCE), and second region was more cathodic than –0.71V. Polarization curve moved left at first region but right at second region with increasing bulk pH. The reduction of hydrogen appeared to be rapidly retarded by the reduction of nickel when potential moved first to second region.

Fig. 2 shows Nyquist plots obtained from the sulfamate bath with bulk pH under the potential of -0.85V. There was no variation in the shape of impedance spectra. This indicates that bulk pH in the range from 1 to 3.8 did not vary the mechanism of NiFeP electrodeposition from the sulfamate bath. Solution resistances(Rs) and charge transfer resistance(Rct) decreased from $1.86\Omega cm^2$ to $0.93\Omega cm^2$ and from $3.19\Omega cm^2$ to $1.61\Omega cm^2$ with increasing bulk pH from 1 to 3.8, respectively. Hydrogen bubbles clung to the surface in an adsorbed state. This led to increasing Rs and Rct, and pore growth as deposit forms bubbles before they were released. The results of these impedance spectra were similar with the results by Epelboin and Wiart [5]. Metal ion species had a relationship of competitive adsorptions in NiFe alloy electrodeposition [6] and there was no variation in the shape of impedance spectra compared with the results on Ni electrodeposition from Watts and sulfamate baths by Epelboin and Wiart, and others [7], respectively. Therefore, the mechanism of NiFeP alloy electrodeposition from sulfamate bath was analogous to pure Ni electrodeposition from Watts and sulfamate baths. According to Epelboin and Wiart, the mechanism of nickel electrodepositon from Watts bath was as follows.

$$Ni^{2+} + H_2O \rightarrow (NiOH)^+ + H^+ \tag{1}$$

$$(NiOH)^+ + e \rightarrow (NiOH)_{ads} \tag{2}$$

$$(NiOH)_{ads} + (NiOH)^+ + 3e \rightarrow 2Ni + 2OH^- \tag{3}$$

High reduction rate reactions appeared at high frequencies on the impedance spectra, while adsorbed films appeared at lower frequencies. Therefore, it can be suggested that the amounts of Fe and P in NiFeP alloy electrodeposition was so small that they did not affect an electrochemical impedance spectra.

3-2 Material properties

Fig. 3 shows bulk pH variation of electrolytes with deposition time for 180min. For pH 1 and 3, we monitored the change of bulk pH in electrolytes with deposition time, so we found that bulk pH of electrolytes at the end of experimental reached at pH 0.94 and 1.5, respectively. Lower pH did not easily vary because pH is log scale of hydrogen concentration. For pH 2 and 3.5, we checked bulk pH of electrolytes every 30min and tried to maintain it constantly. This indicates that bulk pH decreased with deposition time in all experiments. But, there was a question why bulk pH decreased in spite of production of hydroxyl ions during electrodeposition as shown in equation (3). The cause was related to anodic reaction. For soluble anode bulk pH in electrolytes during electrodeposition can increase because the metal dissolution reaction occurs as well as oxygen evolution occur as equation (4) at the anode. For insoluble anode such as Pt electrode, bulk pH can decrease during electrodeposition because there was an only oxygen evolution reaction at the anode.

$$4OH^- \rightarrow O_2 + 2H_2O + 2e \quad (4)$$

Fig. 4 shows deposition rate and residual stress of deposits with bulk pH in electrolytes. Deposition rate increased with increasing bulk pH in electrolytes. It was consistent with the result of current efficiency explained in details later. Residual tensile stress in deposits increased with increasing bulk pH of electrolytes. Internal stress refers to forces created within deposits as a result of the electrocrystallization process and/or the codeposition of impurities such as hydrogen, sulfur, and other elements. Lin, et al. [8] reported that the internal stress and hardness increased with the amounts of ammonium ions(NH_4^+) and reached saturation, furthermore ammonium ions suppressed the lateral growth of Ni deposits. For pH 2 and 3.5 in this study, ammonia was added to try bulk pH in electrolytes constantly during electrodeposition, hence the results on stress in deposits were coincident with the report by Lin.

Fig. 5 shows current efficiency and chemical composition of deposits with bulk pH in electrolytes. Fe in NiFeP alloy had a good catalytic activity for hydrogen evolution reaction [9]. H^+ was reduced to H_{ads} in the presence of freshly deposited Ni, which strongly bonds to the electrode surface and inhibited reduction of metal. Decreasing bulk pH increased the diffusion gradient, enhanced hydrogen evolution and decreased the current efficiency [10]. Ni content increased with increasing bulk pH in electrolytes, which decreased polarization. Decreasing polarization led to increasing Ni content in deposits more noble than Fe [11]. In NiFe binary electrodeposition increasing bulk pH at higher than $2.5A/dm^2$ increased Fe content in deposits and in NiP binary electrodeposition there was no variation of P content in deposits with bulk pH [12].

Fig. 6 shows preferred orientation in deposits obtained from sulfamate bath with bulk pH. Decreasing bulk pH decreased the peak intensity and broadened the peak. This indicates that increasing hydrogen concentration in electrolytes decreased the degree of crystal regularity and grain size in deposits. All deposits showed (111)+(200) plane preferred orientation.

4. Conclusions

The effect of bulk pH on deposition mechanism and material properties of NiFeP ternary alloy electrodeposits was investigated to develop steam generator tube repair technique. And then it was concluded as follows.

1. There was a no variation in the mechanism of NiFeP alloy electrodeposition with bulk pH in the range from 1 to 3.8.
2. Increasing bulk pH decreased Rs and Rct in Nyquist plots measured under –0.85V due to decreasing hydrogen bubbles on the surface in an adsorbed state.
3. When bulk pH increased during electrodeposition, residual tensile stress in deposits increased with increasing NH_4^+ ion in electrolytes, Ni content increased with decreasing polarization, and the degree of crystal irregularity in deposits decreased.

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Table 1 Electrodeposition process conditions.

Sample No.	**Solution**	**Current Density (A/dm^2)**	**pH**	**Agitation (N_2 gas, L/min)**
H1	Sulfamate Bath	5	1	0.75
H2			2	
H3			3.5	
Sulfamate bath = $Ni(SO_3NH_2)_2$ 1.39M + $Fe(SO_3NH_2)_2$ 0.005M + H_3PO_3 0.007M + H_3BO_3 0.65M				

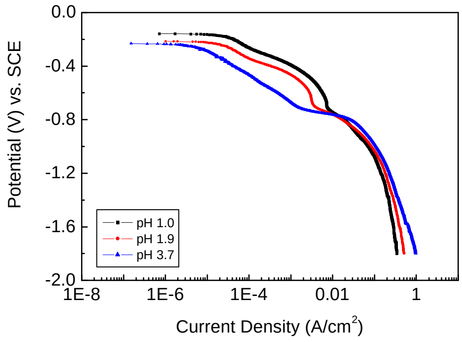

Fig. 1 Cathodic polarization curve obtained from the sulfamate bath with bulk pH at a scan rate of 10mV/s.

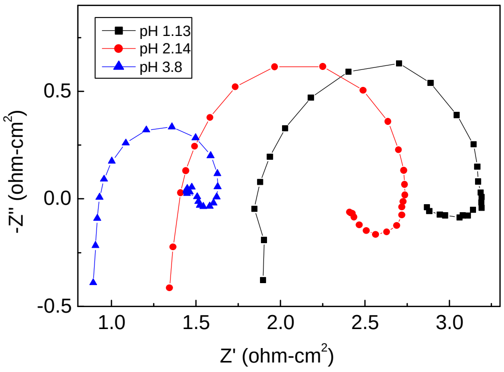

Fig. 2 Nyquist plots obtained from the sulfamate bath with bulk pH under -0.85V(SCE).

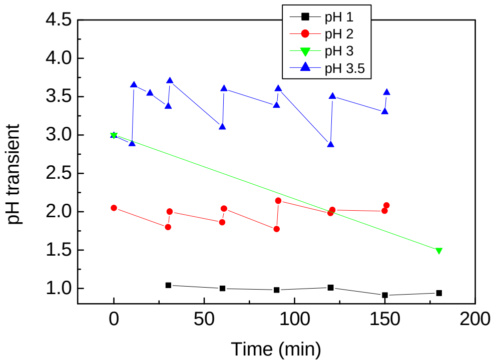

Fig. 3 pH variation of electrolytes with deposition time for 180min.

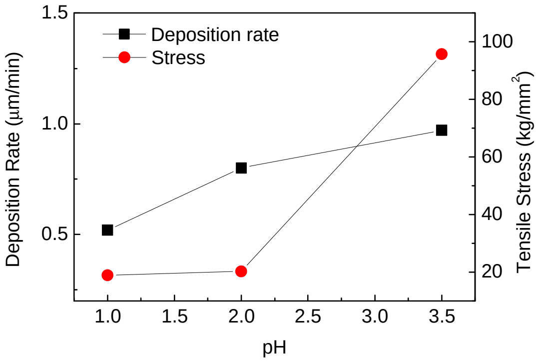

Fig. 4 Deposition rate and residual stress of deposits with bulk pH in electrolytes.

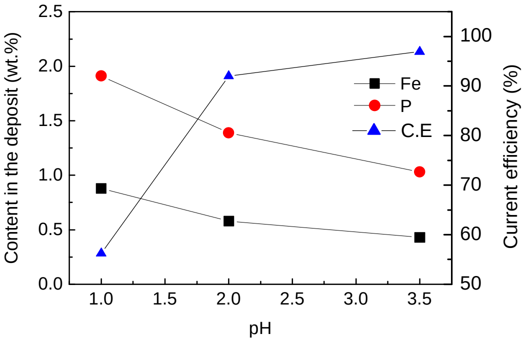

Fig. 5 Current efficiency and chemical composition of deposits with bulk pH in electrolytes.

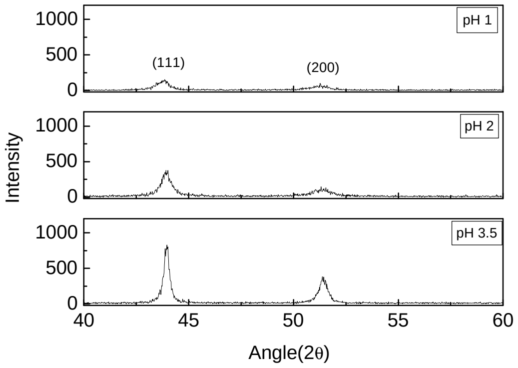

Fig. 6 Preferred orientation of deposits from the sulfamate bath with bulk pH.