

# MATERIAL RELIABILITY OF Ni ALLOY ELECTRODEPOSITION FOR STEAM GENERATOR TUBE REPAIR

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Due to the occasional occurrences of stress corrosion cracking (SCC) in steam generator tubing (Alloy 600), degraded tubes are removed from service by plugging or are repaired for re-use. Since electrodeposition inside a tube does not entail parent tube deformation, residual stress in the tube can be minimized. In this work, tube restoration via electrodeposition inside a steam generator tubing was performed after developing the following: an anode probe to be installed inside a tube, a degreasing condition to remove dirt and grease, an activation condition for surface oxide elimination, a tightly adhered strike layer forming condition between the electroforming layer and the Alloy 600 tube, and the condition for an electroforming layer. The reliability of the electrodeposited material, with a variation of material properties, was evaluated as a function of the electrodeposit position in the vertical direction of a tube using the developed anode. It has been noted that the variation of the material properties along the electrodeposit length was acceptable in a process margin. To improve the reliability of a material property, the causes of the variation occurrence were presumed, and an attempt to minimize the variation has been made. A Ni alloy electrodeposition process is suggested as a primary water stress corrosion cracking (PWSCC) mitigation method for various components, including steam generator tubes. The Ni alloy electrodeposit formed inside a tube by using the installed assembly shows proper material properties as well as an excellent SCC resistance.

**KEYWORDS :** Stress Corrosion Cracking, Steam Generator Tubing, Electrodeposition, Repair, Anode Probe, Material Reliability

## 1. INTRODUCTION

Due to occasional occurrences of a localized corrosion, such as a stress corrosion cracking (SCC) and pitting in steam generator tubing (Alloy 600), degraded tubes are removed from service by plugging or are repaired for re-use. Typical sleeving repair techniques introduce welding and mechanical expansions that lead to residual stress in the parent tube, which should be relieved to improve the in-service life [1,2]. However, electrodeposition inside a tube does not introduce parent tube deformation and, hence, entails negligible residual stress.

Particular equipment and conditions are needed to perform an electrodeposition inside a tube successfully, including the following: an anode to be installed inside a tube, a degreasing condition to remove dirt and grease, an activation condition for surface oxide elimination, a tightly adhered strike layer forming condition between the electroforming layer and the parent tube, and the condition for an electroforming layer. Through a combination of

these various process parameters, the desired material properties can be realized. For application in a plant, the material reliability of an electrodeposit with a variation of the material properties as a function of the electrodeposit position in the vertical direction of a tube is also very important.

It is logical to select a Ni alloy electrodeposition in a proper electrodeposition system, because Alloy 600 is mainly composed of nickel and because nickel electroplating has been widely studied to improve corrosion resistance as well as mechanical and magnetic properties [3,4]. Moreover, a Ni alloy electrodeposition process can be used for primary water stress corrosion cracking (PWSCC) mitigation for various components, including steam generator tubes, because Ni alloy electrodeposit shows excellent SCC resistance [5].

This work deals with the process development for tube repair and is especially focused on anode development, a strike layer forming condition, and the material properties and the reliability of the layer formed by electrodeposition.

## 2. EXPERIMENTAL PROCEDURE

For a plate specimen, a Ti plate coated with Pt and a stainless steel plate with an area of  $3 \times 10 \text{ cm}^2$  were used as an anode and a cathode, respectively. For a tube specimen, the developed anode was installed inside a tube using air pressure, and then a solution was circulated using a solution pump at a flow rate of about 100ml/min.

A strike layer was formed in an aqueous solution that included nickel chloride (1.6 mol) and boric acid (0.65 mol) with/without hydrochloric acid, while the temperature and thickness were in the range of  $40 \sim 60^\circ\text{C}$  and  $1 \sim 20 \mu\text{m}$ , respectively.

For the electrodeposition layer, Ni sulphamate, phosphorous acid, Fe sulphamate and DMAB (dimethyl amine borane) were used as a Ni source, a P source, an Fe source, and a B source, respectively. The bath was composed of Ni sulphamate of 1.39mol and boric acid of 0.65mol with/without additives. Concentrations of the P, Fe, and B sources were in the range of  $0 \sim 0.007 \text{ mol}$ . The pH was maintained at 2 by using sulphamic acid, and the temperature was maintained at  $60^\circ\text{C}$ .

During electrodeposition, the average applied current density and duty cycle were varied from 50 to  $200 \text{ mA/cm}^2$  and from 30 to 100% (DC), respectively. Duty cycle (%) is defined as the ratio of the on-time over the time of one period (on-time + off-time). One period was constant at 10msec in this study.

An alloy composition analysis of the deposit was performed using an inductively coupled plasma (ICP) analyzer (Model JY80C, Jobin Yvon).

Hardness was measured by applying a 50g load for 10sec for 10 times, and the average was determined as the hardness value.

A stress-strain curve for the specimens prepared by electro discharge machining (EDM) was obtained with a strain rate of  $1 \text{ mm/min}$  using an Instron 8872.

For the stress corrosion cracking (SCC) test, the C-ring specimens were fabricated by using the tube specimen where an electrodeposit was formed and were stressed up to 150% with reference to the yield strength of a Korea standard nuclear power plant (KSNP) steam generator tubing. An SCC test was carried out for the prepared C-ring specimens by applying 200mV above an open circuit potential in a 40wt% NaOH solution at  $315^\circ\text{C}$  for 30 days, followed by an optical microscopy examination.

Thermal stability was evaluated from the change of the hardness value induced by a heat treatment at  $343^\circ\text{C}$  for up to 2 months.

## 3. RESULTS AND DISCUSSION

Figure 1 shows the schematic design and actual parts of the anode probe. The anode can be positioned at a desired location and it is electrically insulated from the

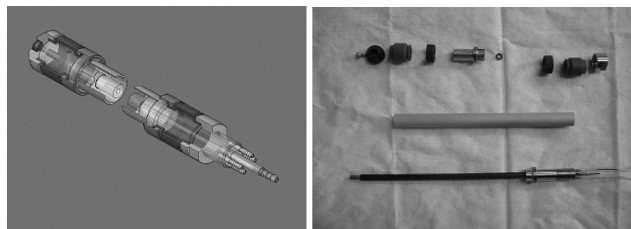


Fig. 1. Schematic Design for an Anode Probe and the Actual Parts Assembled into an Anode Probe

cathode (Alloy 600) by using two seals expanded by the air provided through the air line. Through two inlets and three outlets, the solution is refreshed continuously. A Pt coated tube inside the anode probe and an Alloy 600 tube are used as the anode and the cathode, respectively. This anode can be installed in a multiple electrodeposition system, as shown in Fig. 2. A multiple electrodeposition system was assembled to form three electrodeposits simultaneously, so that three anodes, power supplies, solution pumps, and air pressure controllers can be controlled independently. The temperature of the six baths for cleaning, degreasing, activation, strike layer, and electrodeposition can also be controlled independently.



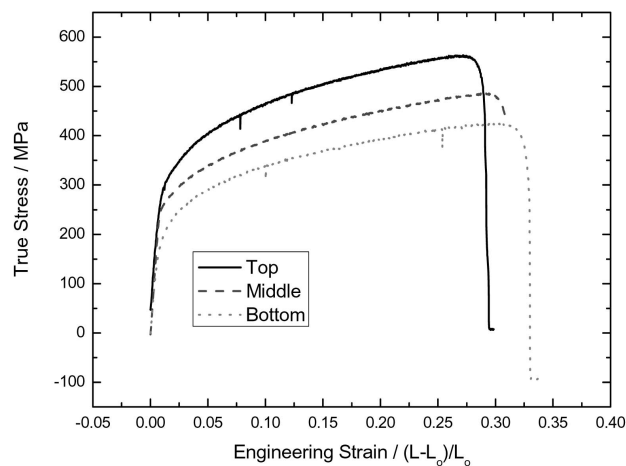
Fig. 2. Multiple Electrodeposition System

Table 1 presents the Vickers hardness values for the pure Ni, Ni-P-Fe, and Ni-P-B as a function of the electrodeposit position in the longitudinal direction. The upper parts of the electrodeposit showed higher hardness values than those for the lower parts.

Figure 3 shows the stress-strain curves for a pure Ni electrodeposit as a function of the electrodeposit position in the longitudinal direction. Similar to the hardness

**Table 1.** Vickers Hardness Values for Pure Ni, Ni-P-Fe and Ni-P-B as a Function of the Electrodeposit Position in the Longitudinal Direction

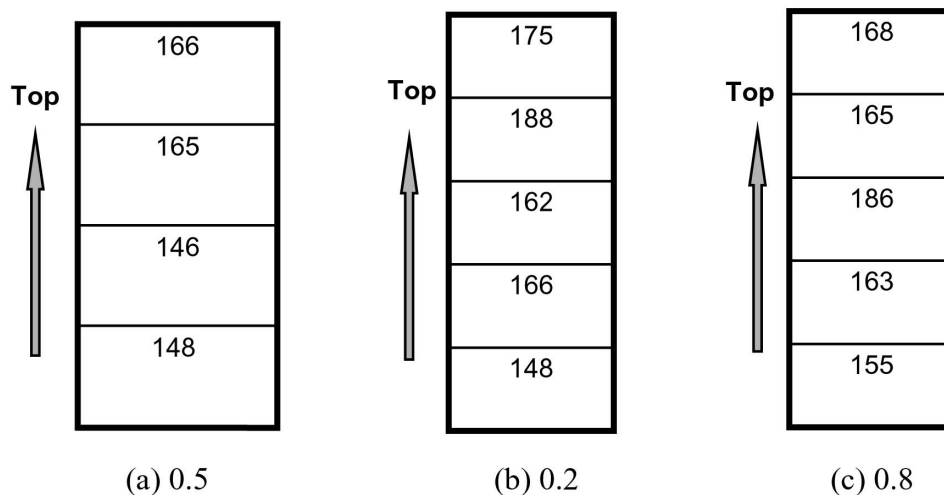
Hardness	Pure Ni	Ni-P-Fe	Ni-P-B
High	166	200	220
Middle-high	165	208	213
Middle-low	146	168	179
Low	148	167	218

**Fig. 3.** Stress-Strain Curves for a Pure Ni Electrodeposit as a Function of the Electrodeposit Position in the Longitudinal Direction

results of Table 1, the yield strength and tensile strength of the upper parts of the electrodeposit were higher than those of the lower parts. On the other hand, the elongation of the upper parts was smaller than that of the lower parts. However, a variation of the material properties along the electrodeposit length is acceptable when considering the process margins.

In spite of a relatively small variation of the material properties, it is presumed that a decrease of the variation should be attempted. This variation may be due to three main causes. Firstly, a hydrogen evolution reaction occurs on the cathode surface (Alloy 600), thus generating hydrogen gas which moves toward the upper part of the electrodeposit. This hydrogen gas can serve as a nucleation site leading to a hardness increase caused by a grain refinement. Secondly, an oxygen evolution reaction occurs on the anode surface (Pt) as an anodic reaction, thus vividly generating oxygen gas. This oxygen gas can also serve as a nucleation site at the upper part. Thirdly, a variation can occur by an intrinsic factor such as a local and micro current distribution or other unknown factors.

The fraction of hydrogen evolution reaction decreases with a duty cycle increase, leading to a current efficiency increase because a hydrogen evolution reaction is faster than a nickel electrodeposition reaction during the on-time [6]. From this, it is expected that the variation of the material properties can be improved with a duty cycle increase. Figure 4 shows the Vickers hardness values for pure Ni in the longitudinal direction as a function of the duty cycle. It was found that the Vickers hardness in the longitudinal direction was not susceptible to the duty cycle. From the result shown in

**Fig. 4.** Vickers Hardness Values for Pure Ni in the Longitudinal Direction as a Function of the Duty Cycle of (a) 0.5, (b) 0.2 and (c) 0.8

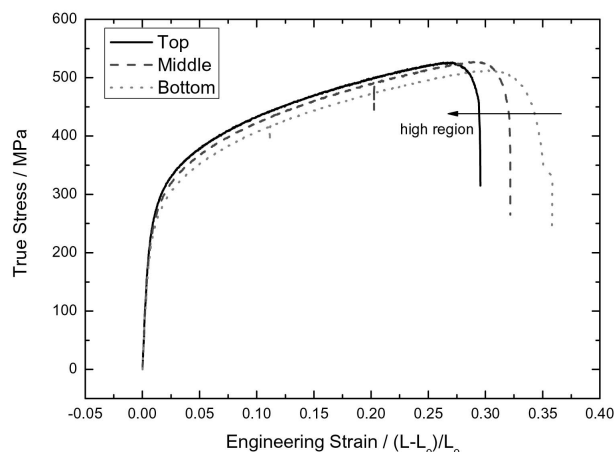


Fig. 5. Stress-Strain Curves for a Pure Ni Electrodeposit Obtained by Using a Rolled Ni Anode as a Function of the Electrodeposit Position in the Longitudinal Direction

Fig. 4, hydrogen gas generation is not a determining reaction for a variation of hardness in the longitudinal direction.

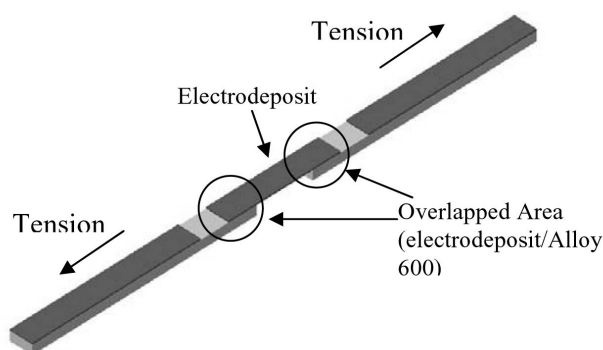
Secondly, a rolled Ni anode as a soluble one was used for an electrodeposition to reduce the oxygen gas generation on the anode surface. Figure 5 shows the stress-strain curves for a pure Ni electrodeposit as a function of the electrodeposit position in the longitudinal direction. By using an insoluble Pt anode, the tensile strength and elongation were varied from about 510 to 530 MPa and from about 0.29 to 0.34, respectively. In contrast, the tensile strength and elongation of the electrodeposit obtained by using an insoluble anode (Pt) were varied from about 420 to 560 MPa and about 0.28 to 0.33, respectively. The results in Fig. 3 show the small effect of an oxygen gas evolution on the variation of the tensile strength in the longitudinal direction. However, the use of a soluble anode is not practicable due to the frequent need to replace the anode.

In spite of the change of the duty cycle and the change from an insoluble Pt anode to a soluble Ni anode, it should be noted that there were still some variations in the electrodeposit longitudinal direction. The remaining variations may be attributed to intrinsic factors, such as local and micro current distributions or other unknown factors. Moreover, even when a soluble anode is used instead of insoluble anode, some fraction of oxygen evolution reaction still occurs at the soluble anode contributing to the variation of the material properties. The slight decrease of solution pH during the electrodeposition by using an insoluble anode should be considered.

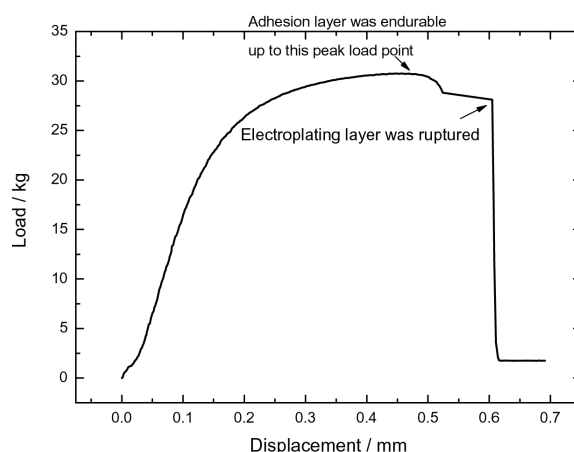
Despite some unknown variations, it should be emphasized that the variation of the material properties along the electrodeposit length is acceptable even without an attempt at any improvement.

Figure 6(a) shows a schematic drawing of the specimen for measuring adhesion strength between the electrodeposit and Alloy 600 (substrate). A strike layer, which plays a role as an adhesive layer was deposited, followed immediately by a thick electrodeposit on Alloy 600. The electrodeposit/strike layer/Alloy 600 assembly was machined as shown in Fig. 6. If the adhesive strength of the overlapped area (electrodeposit/strike layer/Alloy 600) is large enough to be detached, an electrodeposit would be ruptured at an ultimate tensile strength (UTS) during a tensile test. Otherwise, the overlapped area would be detached instead of the rupture of the electrodeposit.

A strike layer was formed in an aqueous solution that included nickel chloride and boric acid with/without hydrochloric acid, as mentioned in the experimental procedure section. Among these experimental conditions, the strike layer forming condition of 40°C, 1.6mol NiCl<sub>2</sub>



(a)



(b)

Fig. 6. (a) Schematic Drawing of the Specimen for Measuring an Adhesion Strength Between the Electrodeposit and Alloy 600 and (b) Stress-Strain Curve for a Specimen for Measuring an Adhesion Strength

+0.6mol  $\text{H}_3\text{BO}_3$ +5%  $\text{HCl}$ , and a  $5\text{ }\mu\text{m}$  thickness showed the best performance judging from the results of the surface observation and bending test. Figure 6(b) shows the stress-strain curve for a specimen with the schematic

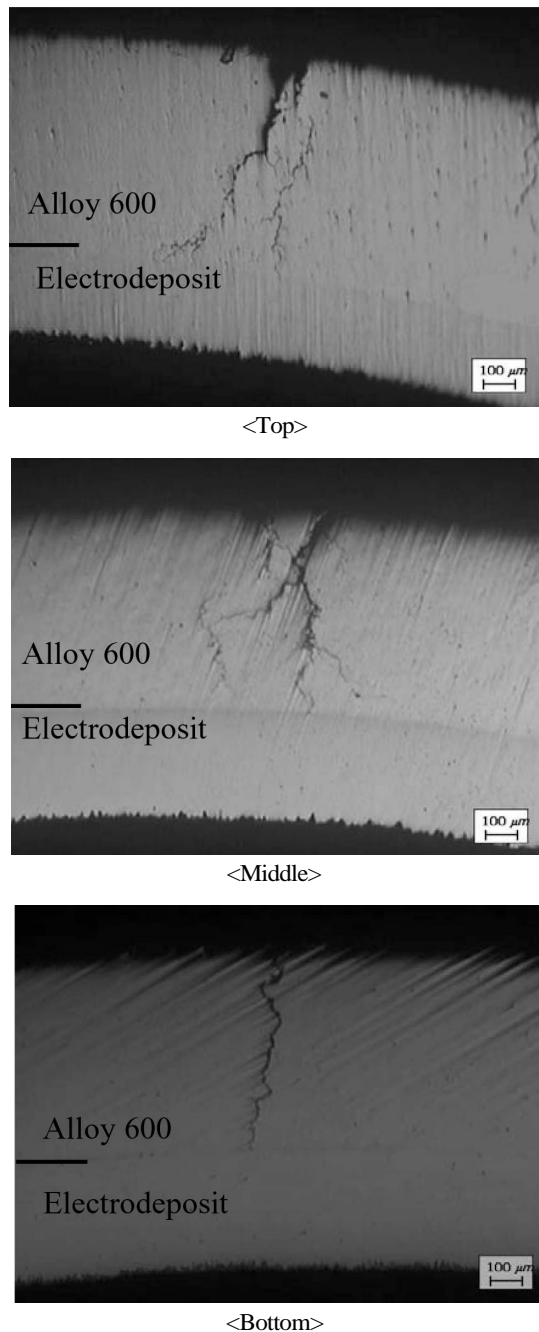


Fig. 7. Optical Micrograph Examined After the C-Ring Test for the Ni-P-Fe Electrodeposit as a Function of the Position in the Longitudinal Direction of the Electrodeposit. C-Ring Test was Carried out by Applying 200mV Above an Open Circuit Potential in a 40wt% NaOH Solution at  $315^\circ\text{C}$  for 30 Days

geometry of Fig. 6(a). For a UTS of a 30.75kg load, the electrodeposit/strike layer of an overlapped area of  $0.5\text{mm} \times 4\text{mm}$  was not detached from the Alloy 600. From this result, it was found that the adhesion strength of the strike layer was larger than  $150\text{MPa}$  ( $=30.75(\text{load}) \times 9.8$  (acceleration of gravity) / 2 (overlapped area)), which is a sufficient value for a strike layer adhesion strength.

Figure 7 presents the optical micrograph examined after the C-ring test for a Ni-P-Fe electrodeposit as a function of the position in the longitudinal direction of the electrodeposit. It was observed that a stress corrosion crack was initiated on the outer surface of the Alloy 600, which propagated through the inner surface, followed by a SCC arrest on the electrodeposit surface, irrespective of the position in the longitudinal direction of the electrodeposit, which indicates the excellent SCC resistance of the electrodeposit.

Figure 8 illustrates the hardness values obtained as a function of the heat treatment duration at  $343^\circ\text{C}$ . Nearly constant hardness values for pure Ni and Ni-P-Fe electrodeposits appeared, irrespective of the heat treatment duration at  $343^\circ\text{C}$ , while the hardness value for the Ni-P-B electrodeposit increased slightly with a heat treatment duration, which may be related to a solid solution hardening of the nickel boride. It is worthwhile to note that the deterioration of the hardness value was not observed for the Ni-P-B electrodeposit or the pure Ni and Ni-P-Fe electrodeposits, indicating the superior thermal stability

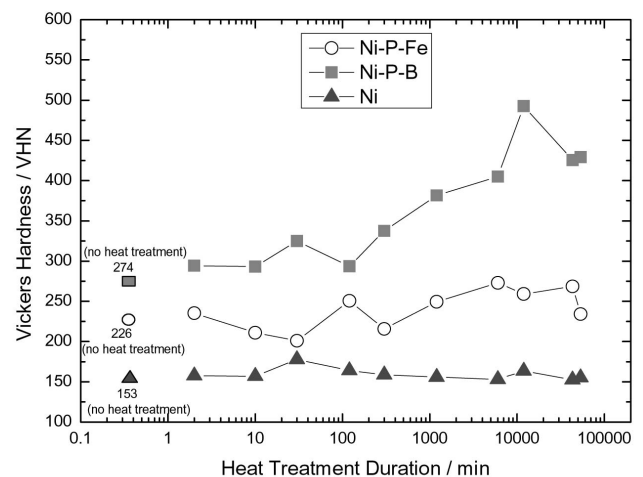


Fig. 8. Vickers Hardness Value for the Ni, Ni-P-Fe and Ni-P-B Electrodeposits as a Function of the Heat Treatment Duration at  $343^\circ\text{C}$

of these electrodeposits.

#### 4. SUMMARY

For a tube repair using an electrodeposition inside a

steam generator tubing, we have developed the following: an anode probe to be installed inside a tube, a degreasing condition to remove dirt and grease, an activation condition for surface oxide elimination, a tightly adhered strike layer forming condition between the electroforming layer and the Alloy 600 tube, and the condition for an electroforming layer. Using the developed anode, the material reliability of the electrodeposit with a variation of the material properties was evaluated as a function of the electrodeposit position in the vertical direction of a tube. A variation of the material properties along the electrodeposit length is acceptable when considering the process margins. For an improvement of the reliability of material property, the causes of the variation occurrence were presumed, and an attempt to decrease this variation was conducted. A Ni alloy electrodeposition process is suggested as a primary water stress corrosion cracking (PWSCC) mitigation method for various components, including steam generator

tubes. The Ni alloy electrodeposit formed inside a tube by using the installed assembly shows proper material properties as well as an excellent SCC resistance.

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