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Material Integrity Assessment for a Ni Electrodeposit inside a Tube

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Due to the occasional occurrence of a localizedcorrosion such as a SCC and pitting in steam generator tubing(Alloy 600), leading to a significant economical loss, an effective repair technology is needed. For a successful electrodeposition inside a tube, many processes should be developed. Among these processes, an anode to be installed inside a tube, a degreasing condition to remove any dirt and grease, an activation condition for a surface oxide elimination, a strike layer forming condition which needs to be adhered tightly between an electroforming layer and a parent tube and a condition for an electroforming layer should be established. Through a combination of these various process condition parameters, the desired material properties can be acquired. Among these process parameters, various material properties including a mechanical property and its variation along with the height of the electrodeposit inside a tube as well as its thermal stability and SCC resistance should be assessed for an application in a plant. This work deals with the material properties of the Ni electrodeposits formed inside a tube by using the anode developed in this study such as the current efficiency, hardness, tensile property, thermal stability and SCC behavior of the electrodeposit in a 40wt% NaOH solution at 315℃. It was found that a variation of the material properties within the entire length of the electrodeposit was quite acceptable and the Ni electrodeposit showed an excellent SCC resistance.

***Keywords** : SCC, Steam generator, repair technology, Ni electrodeposition, nuclear power plant*

1. Introduction

A localized corrosion such as a SCC and pitting in a steam generator tubing (Alloy 600, Ni 75wt%, Fe 10wt% and Cr 15wt%) has occurred occasionally in nuclear power plants leading to a removal from service by a plugging or a repair for re use of the degraded tube. A typically applied sleeving approach has introduced a residual stress in the parent tube, caused by welding and mechanical expansions which should be relieved to improve its in service life.[1,2]

However, an electrodeposition inside a tube does not induce a parent tube deformation and hence a negligible residual stress so that a post heat treatment for a stress relief is not required, thus avoiding the associated heat affected zone. Moreover, an electrodeposition inside a tube provides a continuous bond of a high strength micro alloyed nickel to a host tube, spanning a defective region. Contrary to these advantages, there is a limitation to the electrodeposition method that a sleeve made through an electrodeposition has quite a low sleeving rate when compared with the other repair methods. Therefore, great attention should be paid to an electrodeposition in view of a high electrodeposition rate and a low residual stress.

It is reasonable to select a Ni alloy electrodeposition as a proper electrodeposition system because Alloy 600 is mainly composed of nickel and because a nickel electroplating has been widely studied to improve a corrosion resistance, and the mechanical and magnetic properties.[3,4] Especially, it has also been reported[5,6] that Ni electrodeposits of a relatively higher deposition rate and lower internal stress are obtained in a Ni sulfamate bath rather than Ni chloride and sulfate baths. Additionally, a low sleeving rate could be improved by using a multiple electrodeposition concept of a well controlled electrodeposition process.

In order to perform an electrodeposition inside a tube successfully, many processes should be developed. Among these processes, an anode to be installed inside a tube, a degreasing condition to remove dirt and grease, an activation condition for a surface oxide elimination, a tightly adhered strike layer forming condition between an electroforming layer and a parent tube and the condition for an electroforming layer should be established. Through a

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combination of these various process parameters, the desired material properties can be accomplished. For an application in a plant, the material integrity assessment such as various material properties, a variation of the material properties as a function of the electrodeposit position in the vertical direction of a tube and SCC resistance as well as a proper anode development for electrodeposition inside a tube are needed.

Therefore, this work dealt with the tensile property of a Ni alloy electrodeposit as a function of the duty cycle and the thermal stability as a function of the heat treatment temperature. Hardness, tensile property and SCC resistance were assessed along with the position in the vertical direction of an electrodeposit formed inside a tube by using the developed anode.

2. Experimental

For a plate specimen, Ti plate coated with Pt and a stainless steel plate with an area of 3x10 cm^2 were used as an anode and a cathode, respectively. For a tube specimen, the developed anode was installed inside the tube using air pressure and then a solution was circulated using a solution pump at a flow rate of about 100 ml/min.

Strike layer was formed in an aqueous solution including nickel chloride (1.6 mol) and boric acid (0.65 mol) with hydrochloric acid. Temperature and thickness were 40 ℃ and 5㎛, respectively.

With regards to the electrodeposition layer, Ni sulphamate, phosphorus 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 1.39 mol and boric acid of 0.65 mol with/without additives. Concentrations of the P, Fe and B sources were in the range of 0~0.007 mol. The pH and temperature of the prepared bath were controlled to be 2 by using sulphamic acid and 60 ℃, respectively.

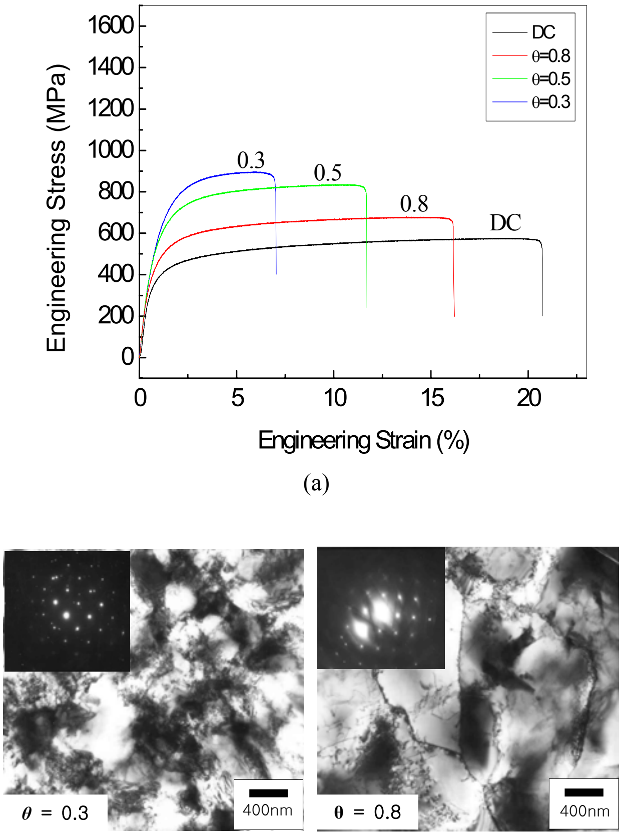
During an electrodeposition, the applied average current density and duty cycle were varied from 50 to 200 mA/cm^2 and from 30 to 100% (DC), respectively. Duty cycle (%) is defined as the ratio of the on time over the time of one period (on-time + off-time). One period is constant at 10msec in this study.

Hardness was measured by applying a 50 g load for 10sec for 10 times and the average was determined as a hardness value. Stress strain curve for the specimens prepared by EDM (electro discharge machining) was obtained with a strain rate of 1mm/min using Instron 8872.

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

3. Results and Discussion

Figs. 1(a) and (b) present the stress strain curves and the TEM micrographs for the Ni-P-B electrodeposits obtained as a function of the duty cycle at a peak current density. As the duty cycle increased, the yield strength and tensile strength decreased but the elongation increased, which is analogous with the results of a Ni-P-Fe electrodeposit.$^{7)}$ It is expected that the concentration of the reacting species at the interface of an electrodeposit/electrolyte is more depleted as the duty cycle is increased because the off time to recover a depleted ion at the interface is



(a)

(b)

Fig. 1. (a) Stress-strain curves and (b) TEM micrographs for the Ni-P-B electrodeposits obtained as a function of the duty cycle at a peak current density.

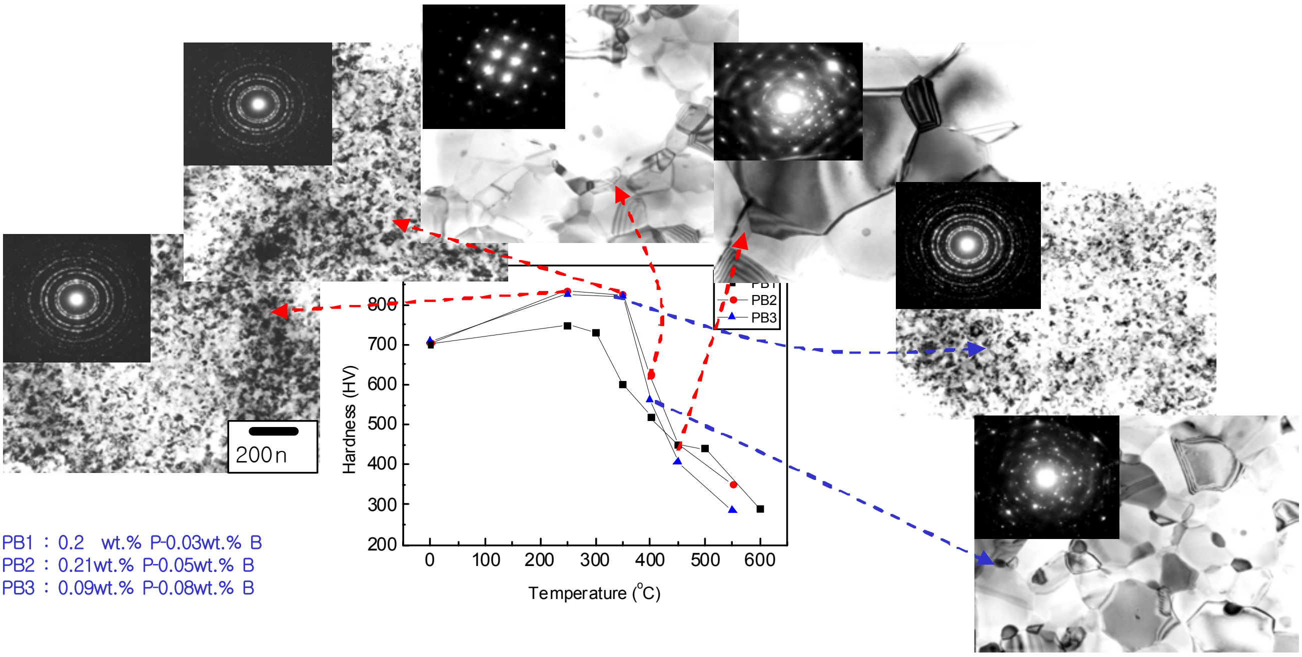


Fig. 2. Vickers hardness and microstructure of the Ni-P-B electrodeposit containing various P and B contents as a function of the heat treatment temperature.

decreased. Hence large grain sized electrodeposit was obtained as shown in Fig. 1(b), which was caused by a reduction of the nucleation rate.

Fig. 2 presents the Vickers hardness and the microstructure of the Ni-P-B electrodeposits containing various P and B contents as a function of the heat treatment temperature. Hardness reached a maximum value in the temperature range of 250 to 350 ℃ where a pressurized water reactor is operated, followed by an abrupt decrease above this temperature range. The segregated P and B and the precipitated Ni alloys(NiP_x and NiB_y) at the grain boundary effectively impeded a grain growth leading to a hardness of a high value. However, as the heat treatment temperature increased, a rapid decrease of the hardness caused by a precipitate coarsening, grain growth and recrystallization took place. It should be noted that the hardness value increased more or less as the P and B contents increased. It seems that the restraining force against a grain growth caused by an increase of the particle fraction increased as the P and B contents increased.

According to various electrodeposition variables such as the solution concentration, duty cycle, current density, temperature, pH and so on, the material properties are varied considerably. Therefore, prior to an electrodeposition inside a tube, an optimum electrodeposition condition required for a steam generator tube repair should be found. Efforts to elucidate the effects of the material property on various electrodeposition parameters can be found elsewhere.[7~9]

Fig. 3 shows a schematic design and the actual parts of the developed anode probe. The anode can be positioned at a desired location and it is electrically insulated from the 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. Pt coated tube inside the anode probe and Alloy 600 tube are used as the anode and the cathode, respectively. This anode can be installed in a multiple electrodeposition system. Multiple electrodeposition system was assembled to form three electrodeposits simultaneously, so that the three anodes, power supplies, solution pumps and air pressure controllers can be controlled independently. The temperature of the six baths for a cleaning, degreasing, activation, strike layer and electrodeposition can also be controlled independently.

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.

Fig. 4 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 results of Table 1, the yield strength and tensile strength of the

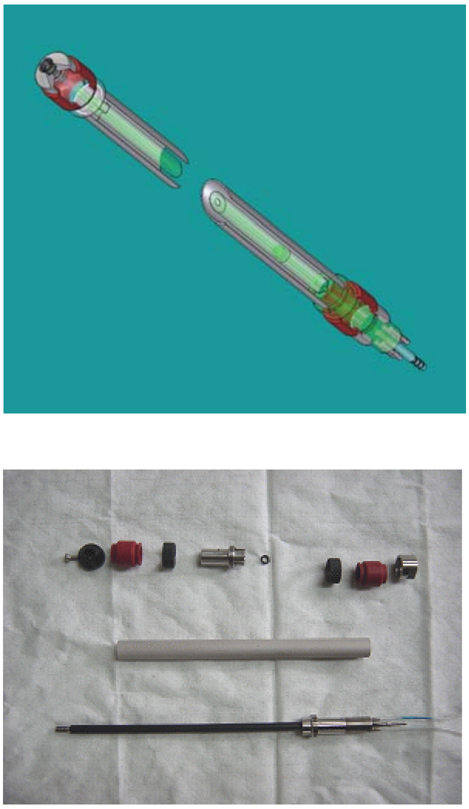


Fig. 3. Schematic design for an anode probe and the actual parts assembled into an anode probe.

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

upper parts 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.

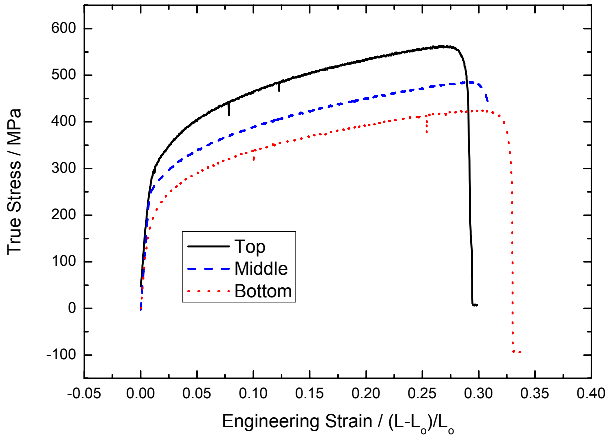
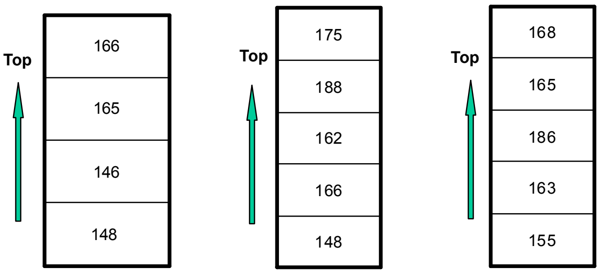


Fig. 4. Stress-strain curves for a pure Ni electrodeposit as a function of the electrodeposit position in the longitudinal direction.

In spite of a relatively small variation of the material properties, it is desirable to attempt a decrease of this variation, which 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. 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 the 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 an on time.[7] From this, it is expected that a variation of the material properties can be improved with a duty cycle increase. Fig. 5 shows the Vickers hardness values for pure Ni in the longitudinal direction as a function of the duty cycle. From this result, it was found that Vickers hardness in the longitudinal direction is not susceptible to the duty cycle indicating that hydrogen gas generation is not a determining reaction for a variation of the 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 rate on the anode surface. Fig. 6 represents 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 510 to 530 MPa and from 29 to 34%, respectively whereas the tensile strength and elongation of the electrodeposit obtained by using an insoluble anode (Pt) were varied from 420 to 560 MPa and from 28 to 33%, respectively, as shown in Fig. 4, which shows a small effect of the oxygen gas evolution on a variation of the tensile strength in the longitudinal direction. However the use of a soluble anode is not practicable due to a frequent replacement of the anode which



(a) 0.5 (b) 0.2 (c) 0.8

Fig. 5. 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.

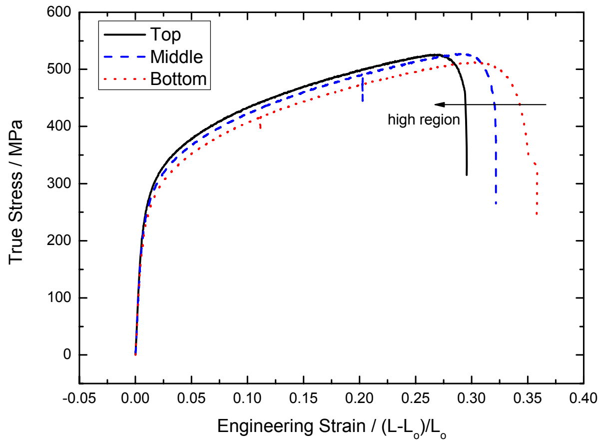


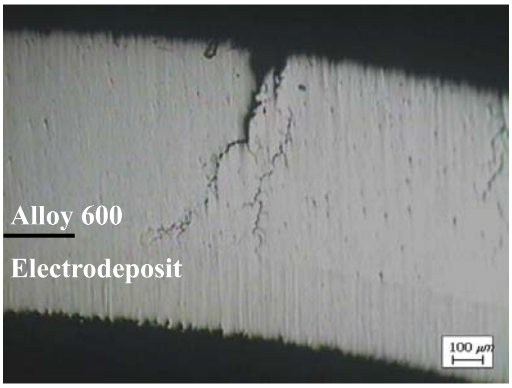
Fig. 6. Stress strain curves for a pure Ni electrodeposit obtained by using a rolled Ni anode as a function of the electrodeposit position in the longitudinal direction.

is needed for its use.

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

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

Fig. 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 and propagated through the inner surface, followed by a SCC arrest on the electrodeposit surface, irrespective of its position in the longitudinal direction of the electro-



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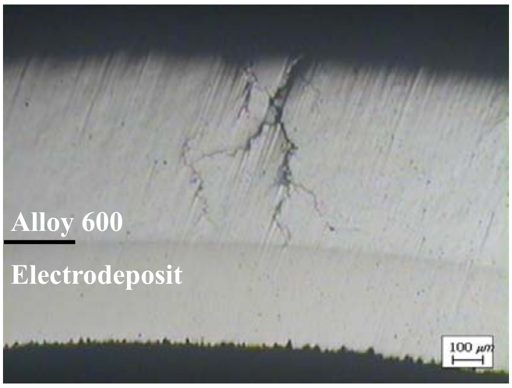

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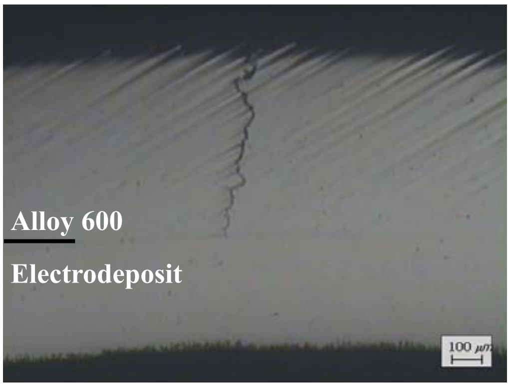

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Fig. 7. Optical micrograph after the C-ring test for the Ni-P-Fe electrodeposit as a function of the position in the longitudinal direction of the electrodeposit. C-ring test was carried out by applying 200mV above an open circuit potential in a 40wt% NaOH solution at 315℃ for 30 days.

deposit, which indicates an excellent SCC resistance of the electrodeposit.

4. Summary

For a tube repair using an electrodeposition inside a steam generator tubing, an anode probe to be installed inside a tube, a degreasing condition to remove dirt and grease, an activation condition for a surface oxide elimination, a tightly adhered strike layer forming condition between an electroforming layer and an Alloy 600 tube, and a condition for an electroforming layer were developed. Prior to an anode development, an optimum electrodeposition condition was found through an investigation of the effects of the material properties on various parameters. Using the developed anode, the material integrity of the electrodeposit with a variation of the material properties was assessed 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 the material properties, the causes of a variation's occurrence were presumed and an attempt to decrease these variations was conducted. Ni alloy electrodeposition process can be suggested as a PWSCC mitigation method for various components including steam generator tubes because 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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