# Ni Alloy Electrodeposition for Steam Generator Tube Repair

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#### 1. Introduction

Ni alloy electrodeposition has been widely studied to improve corrosion resistance, mechanical and magnetic properties[1,2]. Especially, Ni alloy electrodeposition is needed to repair the degraded nuclear steam generator tube composed of Ni base alloy.

Nuclear steam generator tubing is degraded by localized corrosion such as stress corrosion cracking and pitting leading to economic damage and system derating[3]. A common rehabilitation method has been to repair the damaged areas of the tubes by welding or mechanical bonding, which induced the crevices, the tube deformation and an introduction of stress onto the host tube. These should be relieved for improvement of in-service life. However tube repairing using electrodeposition is far from undesirable material degradation so that any post-treatment after repair is not needed[4].

Organic additive is often introduced into the electrodeposition bath to improve surface finishing and decrease internal stress of electrodeposit even though the use of additive reduces the ductility[5,6]. In order to minimize the ductility decrease, the additive should be added into the bath as small as possible. It is reported[7,8] that pulse plating can achieve the decrease of internal stress and the low hydrogen content as well as better surface finishing. Hence, material properties of electrodeposit can be enhanced by varying the pulse parameters.

This work is related to material property of Ni alloy electrodeposits(Pure Ni, Ni-P-Fe and Ni-P-B) obtained in Ni sulphamate bath as a function of pulse plating conditions. For this, chemical composition, current efficiency, potentiodynamic curve, XRD, stress-strain curve and microstructure were analyzed.

#### 2. Experimental

Ni sulphamate, phosphorus acid, Fe sulphamate and DMAB(dimethyl amine borane) are used as a Ni source, a P source, an Fe source and a B source, respectively. Boric acid of 0.65mol and the additive are added into the bath. The pH and temperature of the prepared bath were controlled to be 2 using sulphamic acid and 60°C, respectively.

Ti plate coated with Pt and stainless steel plate with a surface area of  $3x10cm^2$  were used as an anode and a cathode, respectively. Cathodic polarization curve was obtained with a scan rate of 10mV/s using SCE(standard calomel electrode) as a reference electrode.

During electrodeposition, the applied average 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 on-time to one period(on-time + off-time) and the one period is constant to be 10 msec in this study.

Alloy composition analysis of the deposit was performed using an ICP analyzer(Model JY80C(Jobin Yvon)).

Stress-strain curve for the specimens prepared by EDM(electro discharge machining) was obtained with a strain rate of 1mm/min using Instron 8872.

In order to determine the crystallinity and preferred orientation of the deposits, the X-ray diffraction pattern was obtained by the Rigaku X-ray diffractometer(Cu- $K\alpha$ ).

TEM microstructure of the specimen was investigated using a Jeol 2000FX. Thin foil was prepared by jet polishing using a 90% acetic acid + 10% perchloric acid solution at  $10^{\circ}$ C and DC 20V.

#### 3. Results and discussion

Figs. 1 (a) and (b) present stress-strain curves for the electrodeposits obtained as a function of peak current density at the same duty cycle((a) 30 and (b) 50%). As peak current density decreased, yield strength and ultimate tensile strength increased but elongation decreased, irrespective of pulse current and direct current.

Fig. 2 illustrates TEM micrographs for the electrodeposits obtained as a function of peak current density at a duty cycle 50 %. Grain size decreased as peak current density decreased from about 6 to 0.5  $\mu$ m, consistently with the results of stress-strain curves of Fig. 1.

First of all, it is needed to discuss overpotential as current density is changed. Total overpotential is composed of mainly activation controlled polarization expressing Butler-Volmer equation and concentration polarization determining limiting current density because ohmic polarization is small in aqueous system. As current density increased, concentration polarization increased due to increase of reaction rate leading to increased concentration depletion at interface of electrodeposit/electrolyte. Hence, insufficient supply of reacting species at the interface reduced nucleation rate during electrodeposition and consequently increased grain size. It was reported[9] that grain size of the electrodeposit was coarsened by concentration depletion as current density and on-time increased.

It is worthwhile to note that current efficiency increased as current density increased. This indicates that hydrogen reduction reaction, one of important side reactions decreased. As pH of the electrolyte is 2, limiting current density of hydrogen reduction reaction is about 20mA/cm<sup>2</sup>. It is possible that fraction of hydrogen reduction reaction decreases slightly as current density increased in the range of this study leading to increase of current efficiency. It is known that hydrogen can be nucleation site of electrodeposit[10]. Therefore large grain size at high current density can be caused by decrease of hydrogen reduction reaction.

It should be noted that chemical composition of electrodeposit decreased as applied current density increased. It is expected that the decrease of chemical composition at high current density reduces the minor alloying element effect on grain size refinement since alloying element acts as nucleation site to refine the grain size. It is explained that ductile and coarse grain sized electrodeposit is obtained at a relatively higher current density by combining the concentration depletion at the interface, the hydrogen reduction reaction rate and the chemical composition,.

### 4. Conclusion

Increasing peak current density or increasing duty cycle decreased yield strength and ultimate tensile strength leading to increase of ductility and increased grain size. This was described by concentration depletion at the interface of the electrodeposit/solution, fraction decrease of hydrogen reduction reaction and the decrease of chemical composition.

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(b)

Fig. 1. Stress-strain curves for the electrodeposits obtained as a function of peak current density at the same duty cycle of (a) 30 and (b) 50 %.



Fig. 2. TEM micrographs for the electrodeposits obtained as a function of peak current density at a duty cycle of 50%.