

Materials Properties of Nickel Electrodeposits as a Function of the Current Density, Duty Cycle, Temperature and pH

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Alloy 600 having a superior resistance to a corrosion is used as a steam generator tubing in nuclear power plants. In spite of its high corrosion resistance, there are many tubings which experience corrosion problems such as a SCC under the high temperature and high pressure environments of nuclear power plants. The Alloy 600 tubing can be repaired by using a Ni electroplating having an excellent SCC resistance. In order to carry out a successful Ni electrodeposition inside a steam generator tubing, the effects of various parameters on the material properties of the electrodeposit should be elucidated. Hence this work deals with the effects of an applied current density, duty cycle ($T_{on} / (T_{on} + T_{off})$) of a pulse current, bath temperature and solution pH on the material properties of Ni electrodeposit obtained from a Ni sulphamate bath by analyzing the current efficiency, potentiodynamic curve, hardness and stress-strain curve. Hardness, YS(yield strength) and TS(tensile strength) decreased whereas the elongation increased as the applied current density increased. This was thought to be by a concentration depletion at the interface of the electrodeposit/solution, and a fractional decrease of the hydrogen reduction reaction. As the duty cycle increased, the hardness, YS and TS decreased while the elongation increased. During an off time at a high duty cycle, the concentration depletion could not be recovered sufficiently enough to induce a coarse grain sized electrodeposit. With an increase of the solution temperature and pH, the YS and TS increased while the elongation decreased. The experimental results of the hardness and the stress-strain curves can be supplemented by the results of the potentiodynamic curve.

Keywords : Alloy 600, steam generator tubing, Ni electroplating, SCC, duty cycle, pulse, current efficiency, hardness, stress-strain curve

1. Introduction

Ni alloy electrodeposition has been widely studied to improve a corrosion resistance, mechanical and magnetic properties.¹⁾⁻⁴⁾ It is reported⁵⁾ that the Ni electrodeposits obtained in a Ni sulphamate bath have the advantages of a relatively higher deposition rate and lower internal stress than those obtained in Ni chloride and sulfate baths.

Nuclear steam generator tubing is degraded by a localized corrosion such as a stress corrosion cracking and pitting leading to an economical damage and a system derating.⁶⁾ A commonly applied approach for a rehabilitation has been to repair the damaged areas of the tubes via the insertion of tubular sleeves which are either welded or mechanically bonded at their extremities to the host tube. Such intrusive sleeves have weak points, such as the crevices, a tube deformation and an introduction of

a stress onto the host tube which then usually requires a stress relief to improve its in-service life. Therefore an electrodeposited sleeve needs to be developed as a repair method free from these weak points.^{7),8)}

Generally, electroplating parameters such as the current density, duty cycle ($T_{on} / (T_{on} + T_{off})$), temperature, pH and additive greatly affect the material properties of an electrodeposit, i.e. microstructure, grain size, yield strength, tensile strength, elongation, internal stress, hardness and so on. Especially according to an electroplating by using a pulse technique, it is reported⁹⁾⁻¹¹⁾ that it is possible to achieve a decrease of the internal stresses and the low hydrogen content as well as a better surface finishing by using a pulse plating, instead of adding an additive into the bath which induces a reduction of the ductility. Hence it can be expected that the material properties of an electrodeposit are considerably altered by varying the pulse parameters. Therefore in order to accomplish a successful electrodeposition, the effect of the electro-

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plating parameters on the material properties of an electrodeposit should be investigated.

This work aims at an elucidation of the effects of the applied current density, duty cycle of a pulse current, bath temperature and solution pH on the material properties of Ni electrodeposit obtained from a Ni sulphamate bath. For this, the current efficiency, potentiodynamic curve, hardness and stress-strain curve were analyzed.

2. Experimental

The electroplating bath of 3L was composed of Ni sulphamate of 1.39 mol/L and boric acid of 0.65 mol/L. The solution pH was measured to be about 3.5. Ti plate coated with Pt and Alloy 600 plate with a surface area of $3 \times 10 \text{ cm}^2$ were used as an anode and a cathode, respectively. The applied average current density, duty cycle, bath temperature and pH were varied from 20 to 350 mA/cm², from 0.3 to 1(DC), 50~70 °C and 1~5, respectively. The pH was controlled by adding sulfamic acid for a pH decrease and sodium hydroxide for a pH increase. Duty cycle was defined as the ratio of on time to one period(on time + off time) and one period was constant at 100 msec in this study.

Potentiodynamic curve was obtained by using the EG&G 273 Potentiostat at a scan rate of 10 mV/s. Hardness was measured by applying a 50 g load for 10sec. This measurement was repeated 10 times. The average was used as the hardness value. Stress-strain curve for the specimens prepared by EDM(electro discharge machining) was obtained with a strain rate of 1mm/min by using Instron 8872.

3. Results and discussion

Fig. 1 presents the potentiodynamic curve obtained in a 60 °C electroplating bath with a scan rate of 10 mV/s. As the applied potential was decreased from the open circuit potential, the cathodic curve related to a hydrogen evolution appeared to be a value of 10 mA/cm² which closely indicates the limiting current density for the hydrogen evolution reaction, followed by the cathodic curve concerned with the Ni reduction reaction. From the potentiodynamic curve, it was found that the limiting current density for the Ni reduction reaction was about 1 A/cm². The current efficiency obtained from the weight of the electrodeposit increased with the current density indicating that the fraction of the hydrogen evolution reaction was decreased with the current density.

Figs. 2 and 3 depict the microhardness and stress-strain curves for the electrodeposits obtained as a function of

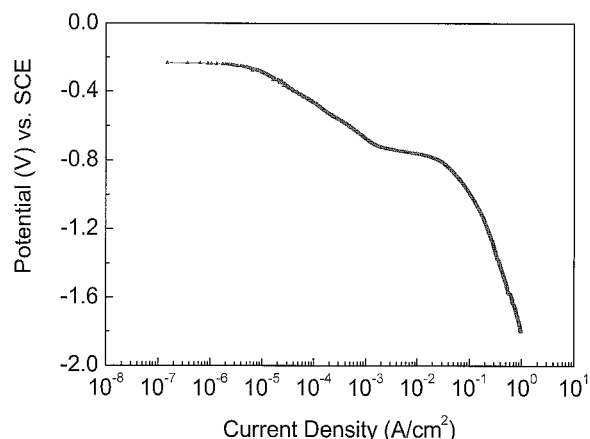


Fig. 1. Potentiodynamic curve obtained for the electroplating solution of 1.39 mol Ni sulphamate and 0.65 mol boric acid at 60 °C at a scan rate of 10 mV/s.

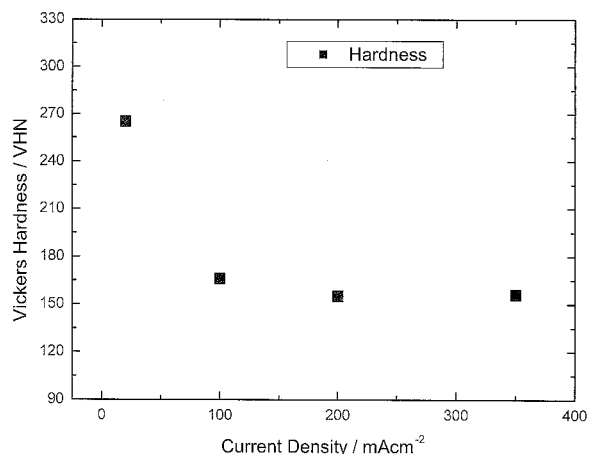


Fig. 2. Microhardness measured from the Ni electrodeposits obtained as a function of the current density.

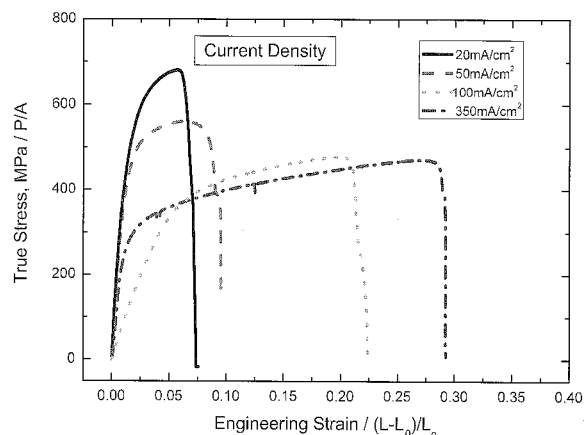


Fig. 3. Stress-strain curves measured from the Ni electrodeposits obtained as a function of the current density.

the current density in 60 °C. With the increase of the current density, the measured hardness and the strength

were decreased but the elongation was increased.

Total overpotential is composed of mainly an activation controlled polarization expressing the Butler-Volmer equation and a concentration polarization determining the limiting current density because an ohmic polarization is small in an aqueous system. As the current density increased, the concentration polarization increased due to an increase of the reaction rate leading to an increased concentration depletion at the interface of the electrodeposit/electrolyte. Hence, an insufficient supply of the reacting species at the interface reduced the nucleation rate during the electrodeposition and consequently, the grain size increased leading to a strength decrease (hardness decrease) but a ductility increase. There have been the reports^{12,13)} expressing a grain size coarsening of the electrodeposit by a concentration depletion as the current density and the on time increased.

Moreover it is possible that the fraction of a hydrogen reduction reaction decreases slightly as the current density increases within the range of this study, leading to an increase of the current efficiency. Hydrogen evolution is known to supply nucleation sites to the electrodeposit.¹⁴⁾ Therefore a large grain size at a high current density can also be caused by a fractional decrease of the hydrogen reduction reaction, which decreases the strength but increases the ductility.

Figs. 4 and 5 show microhardness and stress-strain curves for the Ni electrodeposits obtained as a function of the duty cycle at a constant peak current density of 111 mA/cm². As the duty cycle increases, the hardness value, YS (yield strength) and TS (tensile strength) decrease but elongation increases. Concentration of the reacting species at the interface of the electrodeposit/electrolyte is further depleted as the duty cycle increases because the off time to recover the depleted ion at the interface is decreased. Thereby a large grain sized electrodeposit could be obtained, caused by the reduction of the nucleation rate, which results in a hardness value and strength decrease but an elongation increase.

In addition, the current efficiency increases from about 85 to 89% with an increase of the duty cycle ($T_{on} / (T_{on} + T_{off})$) in the range of 0.3 to 0.9 meaning that the fraction of the hydrogen reduction reaction decreases. At a low duty cycle (T_{on} is small and T_{off} is large), during an on time, a hydrogen evolution reaction which is kinetically faster than a nickel reduction reaction occurs vigorously, followed by a relatively complete recovery of the hydrogen ion concentration at the interface of the electrodeposit/electrolyte during a relatively longer off time, which leads to a grain size refinement whereas at a high duty cycle, the fraction of the hydrogen evolution reaction can be

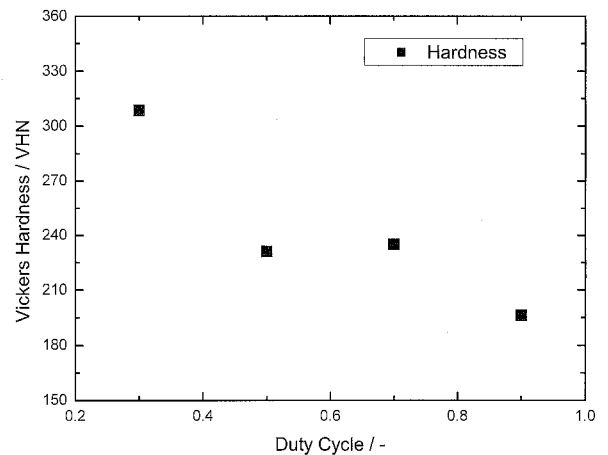


Fig. 4. Microhardness measured from the Ni electrodeposits obtained as a function of the duty cycle at a constant peak current density of 111 mA/cm².

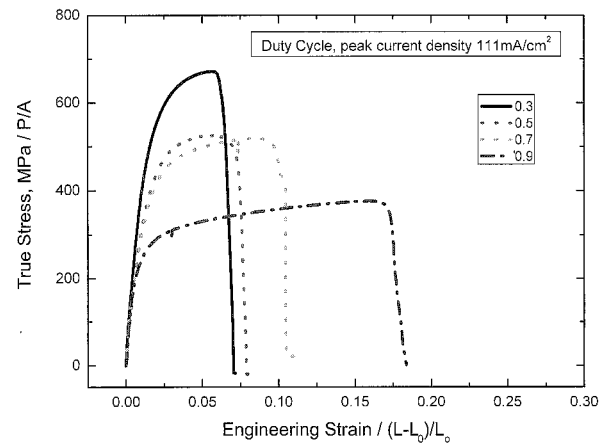


Fig. 5. Stress-strain curves measured from the Ni electrodeposits obtained as a function of the duty cycle at a constant peak current density of 111 mA/cm².

reduced because the off time is too small to be recovered completely at the interface of the electrodeposit/electrolyte.

Fig. 6 illustrates the potentiodynamic curves obtained as a function of the bath temperature with a scan rate of 10 mV/s. As the bath temperature increases, the limiting current of the cathodic curve regarding to the nickel reduction increases while the cathodic curves related to the hydrogen evolution reaction did not show a significant change, irrespective of the temperature. The current efficiency increases with the temperature from about 84 to 89%, caused by a relatively larger dependency of the limiting current density for the nickel reduction on the temperature. Diffusion coefficient increases with the temperature leading to an increase of the limiting current density as shown in Eq. (1). Consequently, the concentration depletion would be relieved at the interface of the

electrodeposit/electrolyte, which achieved a grain size refinement, accompanied by the YS and the TS increases as shown in Fig. 7. Additionally, it is also plausible that the reaction rate (the nickel reduction rate) at the interface of the electrodeposit/electrolyte could be accelerated with the bath temperature.

$$i_L = \frac{nFDC_B}{\delta} \quad (1)$$

where i_L , n , F , D , C_B , δ are the limiting current density, the valence number, the Faraday constant, the diffusivity, the bulk concentration and the Nernst diffusion length, respectively.

Fig. 8 presents the potentiodynamic curves obtained as a function of the bath pH with a scan rate of 10 mV/s. As the pH increased, the cathodic curves for the hydrogen evolution reaction shifted downward and the limiting

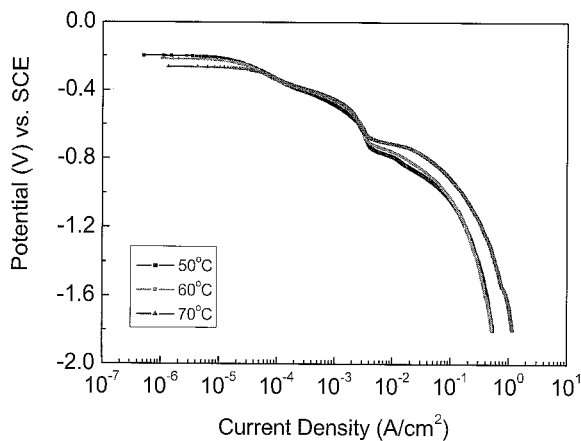


Fig. 6. Potentiodynamic curves obtained for the electroplating solution of pH 2 as a function of the bath temperature at a scan rate of 10 mV/s.

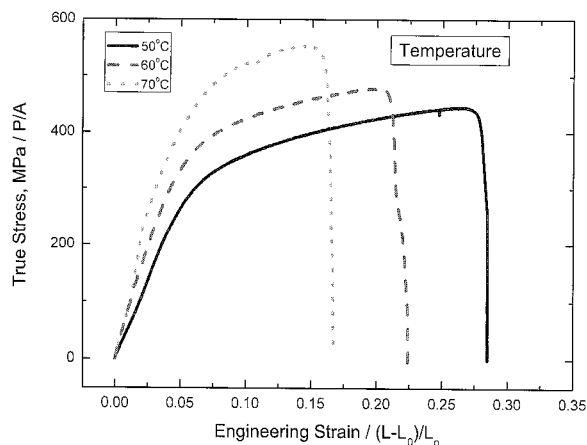


Fig. 7. Stress-strain curves measured from the Ni electrodeposits obtained as a function of the temperature.

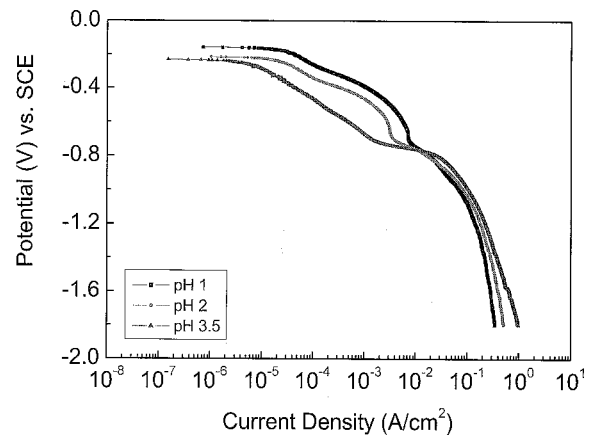


Fig. 8. Potentiodynamic curves obtained for the electroplating solution of pH 2 as a function of the bath temperature at a scan rate of 10 mV/s.

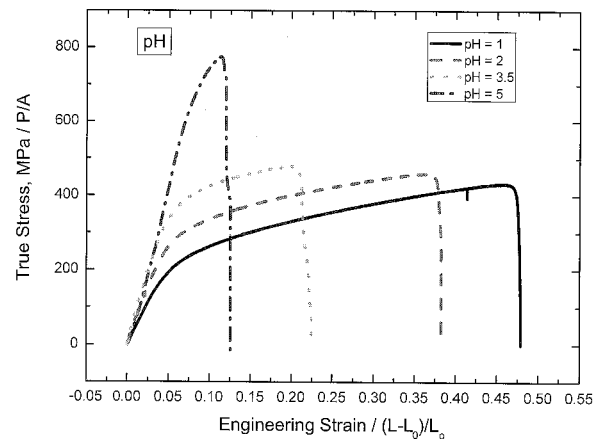


Fig. 9. Stress-strain curves measured from the Ni electrodeposits obtained as a function of the pH.

current density for the nickel reduction reaction increased. From the cathodic curves for the hydrogen evolution reaction, it was found that the limiting current density for the hydrogen evolution reaction decreases and the overpotential for the hydrogen evolution reaction increases due to a decrease of the hydrogen ion concentration in the solution. Unlike the hydrogen reduction reaction, the limiting current density for the nickel reduction increases with the pH. It is conceivable that the nickel ion transport through the solution to the electrodeposit surface is enhanced by a decrease of the hydrogen ion concentration in the solution with the pH. Consistently with the results of the potentiodynamic curves, the current efficiency increases from about 73 to 93% with an increase of the pH in the range of 1 to 5.

Fig. 9 represents the stress-strain curves for the Ni electrodeposits obtained as a function of the pH. As the pH increases, the YS and the TS increases but the elongation decreases. Recognizing that the limiting current

density for the nickel reduction reaction increases with the pH, it is expected that the concentration of the nickel ion at a higher pH is less depleted at the interface of the electrodeposit/electrolyte than that at a lower pH. This leads to a small grained microstructure having the material property of a high YS and TS but a low ductility.

4. Summary

This work investigated the effects of the applied current density, duty cycle ($T_{\text{on}} / (T_{\text{on}} + T_{\text{off}})$) of a pulse current, bath temperature and solution pH on the material properties of Ni electrodeposit obtained from a Ni sulphamate bath by analyzing the current efficiency, potentiodynamic curve, hardness and stress-strain curve. The results can be summarized as follows.

1. The hardness, the YS (yield strength) and the TS (tensile strength) decreased whereas the elongation increased as the applied current density increased. This was explained by a concentration depletion at the interface of the electrodeposit/solution, and a fractional decrease of the hydrogen reduction reaction.

2. As the duty cycle increased, the hardness, the YS and TS decreased while the elongation increased. During an off time at a high duty cycle, the concentration depletion could not be recovered sufficiently enough to induce a coarse grain sized electrodeposit.

3. With the solution temperature and the pH, the YS and TS increased while the elongation decreased. The strength and the elongation results for the electrodeposit could be expected from the results of the potentiodynamic curve

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