Proceedings of the Korean Nuclear Society Autumn Meeting
Yongpyong, Korea, 2003

The study on residual stresses of Ni alloy electrodeposits for steam generator tube repair

Moo Hong Seo*, Dong Jin Kim, and Joung Soo Kim

Korea Atomic Energy Research Institute
150 Dukjin-dong, Yusong-gu
Daejeon, Korea 305-353

Abstract

The effect of process parameters including alloying elements, additive, pH, temperature and current types on residual stresses of Ni-P, Ni-B, Ni-Fe, Ni-P-Fe and Ni-P-B alloy electrodeposited from a concentrated Ni sulphamate bath was investigated using a flexible strip bend method.

Form the results of alloying elements on residual stresses of the deposits, it was expected that the difference between Ni and alloying element in atomic radius caused the stresses of the deposits, and alloying elements having higher or lower atomic radius than Ni produced stresses compressively or tensively, respectively. As the pH of the electrolytes increased from 1 to 3.5, the current efficiency and stresses in the deposits increased. It seems to be concerned with the decrease of the hydrogen evolution reaction and hydrogen absorption, and the increase of NH_4 with increasing pH. Residual tensile stresses in the deposits decreased with increasing temperature of the electrolytes from 50 to 70^{o}C. The reason was that decreased hydrogen evolution by temperature elevation lowered hydrated material, leading to a decrease in the tensile stresses of the deposits. The measured stress values with current types decreased in the order of direct current (DC), pulse current (PC) and periodic reverse current (PRC). The compactness of the deposit produced by PC and the production of oxide occured during reverse current resulted in lower stresses.

Keyword: Residual stresses, Process parameters, Ni alloy electrodeposits, Sulphamate bath.

1. Introduction

Degradation of nuclear steam generator tubing due to localized corrosion such as stress corrosion cracking, pitting etc., often leads to costly forced outages and system derating [1]. A commonly applied approach to 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, the tube deformation and an introduction of stress onto the host tube which then usually requires stress relief to improve the in-service life. Therefore, the focus on sleeve design shifted to a repair method to eliminate the weak points.

An electrodeposited sleeve was developed as a repair method free from these weak points [2]. The electrodeposited sleeve provides a continuous bond of high-strength micro-alloyed nickel to the host tube, spanning the defective region. Since no deformation of the host tube occurs, post heat treatment for stress relief is not required, thus avoiding the associated heat affected zone. However, there is a limitation to the electrodeposited sleeve method which is that the sleeve made through electrodeposition is quite low in the sleeving rate compared with the intrusive sleeve method. Therefore, a great attention should be paid to nickel electrodeposition in view of a high electrodeposition rate and low residual stress.

Residual stresses in electrodeposits during plating are well-known phenomenon which affects the life of the deposited film. Residual stresses in deposits often lead to cracking, peeling and blistering of the deposits. Even stress corrosion, porosity and poor adhesion can be related to the stresses. Residual stresses in electrodeposition can mainly originate from foreign substances and impurities, but no overall theory of the causes of the stresses has been formulated to date [3].

Stress in electrodeposited Ni can vary over a wide range depending on solution composition and operating conditions. In general, Ni deposited from additive-free Watts baths exhibits a tensile stress that is 125 to 185MPa. Deposits from sulphamate baths display lower tensile stress within the range of 0 to 55MPa. Compressively stress Ni deposits are obtained from the baths that contain sulfur-containing organic additives. Owing to the importance of residual stresses of the deposits, intensive research has been conducted, but most research was focused on pure Ni than Ni alloy [4-6].

Therefore, present work was done to investigate the process parameters such as alloying elements, additive, pH, temperature and current types on residual stresses in Ni alloy electrodeposits from a concentrated Ni sulphamate bath containing higher Ni sulphamate concentration than convention Ni sulphamate bath of 0.93M.

2. Experimental

2.1. Electrochemical deposition

Ni sulphamate as a Ni source, Fe sulphamate as an Fe source, phosphorus acid as a P source, dimethylamine borane (DMAB) as a B source, Pt plated Ti as an anode and alloy 600 plate with a surface area of $3x10cm^2$ as a cathode were used in the Ni-Fe-P alloy electrodeposition.

Table 1 shows the bath compositions and process parameters used in this study. The pH was controlled and adjusted by sulphamic acid or ammonia.

Chemical compositions of the deposits were determined using GBC LAPTAM 8440 and sulfur content using LECO CS 444. Residual stresses in the deposits were measured through a flexible strip (Model 683EC, Specialty Testing & Development Co.). The Model 785EC Plating Cell was specifically designed for use with the Model 683EC Deposit Stress Analyzer to standardize plating parameters for the test strips.

2.2. Measurement of residual stresses in the deposits

One of the earliest, the simplest and the still widely used stress-measuring devices is the bent strip. It is a long, narrow metal strip plated on only one side by insulating the other. One end is clamped and the other free to deflect either during plating or afterwards. If the deposit is in a state of tensile stress, the free end deflects towards the anode. If the stress is compressive, the free end deflects away from the anode. The test strips are made from chemically etched beryllium-copper alloy and have spring like properties.

In order to calculate the deposit stress, it is necessary to know both the increments of spread of each leg from the center line on the measuring block scale and the deposit thickness. The deposit stress can be calculated as follows:

$$S(MPa) = 58.26 \times \frac{U}{3T} \times k \tag{1}$$

where, S the residual stress; U the number of increments spread; T deposit thickness in micrometer; k is the strip calibration constant.

3. Results and discussion

Fig. 1 shows residual stresses of Ni binary alloy deposits with the concentration of various alloying elements such as Fe, P and B in a Ni sulphamate bath. With increasing concentration of DMAB in the Ni sulphamate bath, the tensile stresses of the deposits increased rapidly and continuously. In Ni-Fe and Ni-P alloy deposits, an increased concentration of the corresponding alloying element in the baths slightly enhanced the tensile stresses in both of the alloy deposits. Current efficiency was reduced by lower hydrogen overvoltage due to higher concentration of alloying element source in the bath for all of the deposits. It is anticipated that alloying elements having atomic radius smaller than Ni produce tensile stress of the deposit and those having atomic radius larger than Ni do compressive stress of the deposit. Atomic radius of Ni and alloying elements was given in Table 2. However, the tensile stresses of the Ni binary alloy deposits for the low concentration of Fe and P was shown. The fact indicated that the stresses of the Ni-Fe and Ni-P alloy deposits with the initial low concentration of alloying element was attributed to the formation of hydrated material, which was known to cause tensile stresses, rather than alloying element [7]. For the Ni-P alloy deposits, the tensile stresses started to decrease from the addition of phosphorus acid 0.005M above. When Fe sulphamate concentration in 1.39M Ni + 0.018M P solution increased from 0 to 0.1M, tensile stresses of the deposits decreased continuously from 10 to about 0MPa as shown in Fig. 2. This describes that Fe increased the compressive stress of the deposits as well. Hadian and Gabe [3] reported that Fe concentration of above 10 wt.% in the Ni-Fe deposits obtained from Watts baths lowered the internal stresses. Therefore, the reduction in tensile stresses of the Ni-Fe deposits was expected at more than any concentration of Fe sulphamate in the bath.

Fig. 3 presents the stress values measured for the Ni-P-B electrodeposits obtained from the electrodeposition solutions having various saccharin concentrations as a stress reducer. The current efficiency slightly increased but sulfur content of the deposit rapidly increased as the stress reducer concentration in the solution varied in the range from 0 to 500mg/L. These describe that hydrated material was not increased with increasing the concentration of stress reducer, which was a source of sulfur having higher atomic radius than Ni. Hence, by increasing the stress reducer concentration, the residual stress decreased monotonously.

With comparison between this result and atomic radius, it seems that the difference between Ni and alloying elements in atomic radius caused the stresses of the deposits, and alloying elements having higher or lower atomic radius than Ni produced the stress compressively or tensively, respectively.

Residual stresses of the Ni-P-Fe alloy deposits as a function of the pHs in the electrolytes of 1.39M Ni + 0.007M P + 0.005M Fe are shown in Fig. 4. The tensile stresses of the deposits increased from 5.9 to 29.7MPa as bulk pH increased from 1 to 3.5. The decrease in the pH of the electrolytes during the Ni-P-Fe alloy deposition occurred due to the use of an insoluble anode, which was caused by the formation of the hydrogen ion at the anode according to the reaction (2) [8]. Thus, in this work, we monitored the change in bulk pH of the electrolyte every 30min and controlled it with ammonia. Increased ammonia enhanced the residual tensile stresses in the deposits [9]. Holm and O'KEEFE [10] reported that residual stresses of the deposits increased with increasing pH to 3.5 under the condition of a sulphate bath and insoluble anode like Pb.

$$H_2O \rightarrow 2H^+ + 1/2O_2 + 2e \qquad (2)$$

Fig. 5 shows residual stresses of the Ni-P-Fe alloy deposits as a function of temperature in the electrolytes of 1.39M Ni + 0.007M P + 0.005M Fe. In general, increased temperatures produce lower stress values. Also in this study, residual tensile stresseses in the deposits decreased from 14.3 to 2.3MPa and current efficiency increased from 75 to 95% with increasing temperature of the electrolytes from 50 to 70^{o}C. The reason was that decreased hydrogen adsorption by temperature elevation lowered hydrated material, leading to a decrease in the tensile stresses of the deposits.

Fig. 6 shows residual stresses of the Ni-P-Fe alloy deposits with current types at a constant average current density of 10A/dm^2. The pulse deposition parameters consisted of a duty cycle (θ) of 0.8 and peak current density (i_p) of 12.5A/dm^2. For periodic reverse current (PRC), θ=0.8, i_p=20A/dm^2 and reverse current density (i_r)=30A/dm^2 were used. The measured stress value decreased in the order of direct current (DC), pulse current (PC) and PRC. Pulse-deposited alloy exhibited lower tensile stresses than that produced with direct current. A smaller grain size in pulse-deposited alloys is generally found to lead to an increased coverage of the substrate, resulting in decreased porosity and increased density of the deposits. Therefore, the decrease in the stress of the deposits seems to be attributed to compactness. While a negative pulse current in PRC is applied, the cathode (which becomes the anode) is dissolved and oxidized. Because the electrode potential of hydrogen is higher than that of Ni, hydrogen is easier to discharge, the hydride content of the deposits becomes lower [11]. Consistently, it was found that tensile stress of the deposits was reduced due to the increase in the oxide. Grain size of the deposits obtained utilizing PRC was largest since nucleus site was removed with impurities such as hydrogen and sulfur during negative reverse current as well. Duty cycle and average current density in PC are defined as shown in the Eq.(3) and (4), respectively. In PRC, average current density is defined according to the Eq.(5).

$$\theta = \frac{T_{on}}{T_{on} + T_{off}} \tag{3}$$

$$i_{ave} = \theta \times i_p \tag{4}$$

$$i_{ave} = i_p \times t_p + i_r \times t_r \tag{5}$$

where, duty cycle; T_{on} pulse on time; T_{off} pulse off time; i_{ave} average current density; i_p peak current density; t_p time during peak current; i_r reverse current density; t_r is time during reverse current.

4. Conclusion

The effect of process parameters including alloying elements, additive, pH, temperature and current types on residual stresses of Ni-P, Ni-B, Ni-Fe, Ni-P-Fe and Ni-P-B alloy electrodeposited from a concentrated Ni sulphamate bath was investigated using a flexible strip bend method.

1. Form the results of alloying elements on residual stresses of the deposits, it was expected that difference between Ni and alloying elements in atomic radius caused the stresses of the deposits, and alloying elements having higher or lower atomic radius than Ni produced stresses compressively or tensively, respectively.
2. As the pH of the electrolytes increased from 1 to 3.5, the current efficiency and stresses in the deposits increased. It seems to be concerned with the decrease of the hydrogen evolution reaction and hydrogen absorption, and the increase of NH_4 with increasing pH. Residual tensile stresses in the deposits decreased with increasing temperature of the electrolytes from 50 to 70^{o}C. The reason was that decreased hydrogen evolution by temperature elevation lowered hydrated material, leading to a decrease in the tensile stresses of the deposits.
3. The measured stress values with current types decreased in the order of direct current (DC), pulse current (PC) and PRC. The compactness of the deposit produced by PC and the production of oxide occured during reverse current resulted in lower stresses.

References

[1]P. E. MacDonald, V. N. Shah, L. W. Ward and P. G. Ellison, NUREG/CR-6365, INEL-95/0383 (1996) 36.

[2]A. Robertson, U. Erb and G. Palumbo, NanoStructured Materials **12** (1999) 1035.

[3] S.E. Hadian, D.R. Gabe, Surface & Coatings Technology 122 (1999) 118.

[4] J.L. Marti, Plating 53, 1 (1966) 61.

[5] W. Kim, R. Weil, Surface & Coatings Technology 38 (1989) 289.

[6] D. Baudrand, Metal Finishing 94, 7 (1996) 15.

[7] B. Martin, Proc. Electroplaters' Soc. 32 (1944) 206.

[8] A. Brenner, Electrodeposition of Alloys, Academic Press, New York, 1 (1963).

[9] C.S. Lin, P.C. Hsu, L. Chang, C.H. Chen, J. Appl. Electrochem. 31 (2001) 925.

[10] M. Holm, T. J. O'KEEFE, J. Appl. Electrochem. 30 (2000) 1125.

[11] K.C. Chan, N.S. Qu, D. Zhu, J. Materials Processing Technology 63 (1997) 819.

Table 1 Electrodeposition baths and conditions.

Nickel sulphamate	1.39mol/L
Iron sulphamate	0~0.1mol/L
Phosphorus acid	0~0.03mol/L
Dimethylamine-borane	0~0.02mol/L
Boric acid	0.65mol/L
pH	1~3.5
Current density	5~15A/dm^2
Temperature	50~70^{o}C
Agitation	N_2 gas or magnetic stirrer

Table 2 Atomic radius of Ni and various alloying elements.

Elements	Ni	Fe	P	B	S
Atomic Radius	1.24	1.26	1.28	0.98	1.27

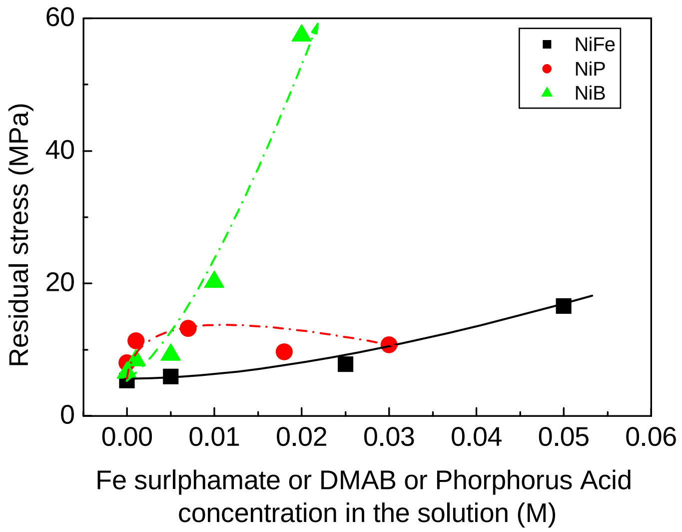

Fig. 1 Residual stresses of Ni binary alloy deposits with the concentration of various alloying element such as Fe, P and B in the sulphamate bath of 1.39M Ni under the condition of 50^{o}C, pH 1 and 15A/dm^2.

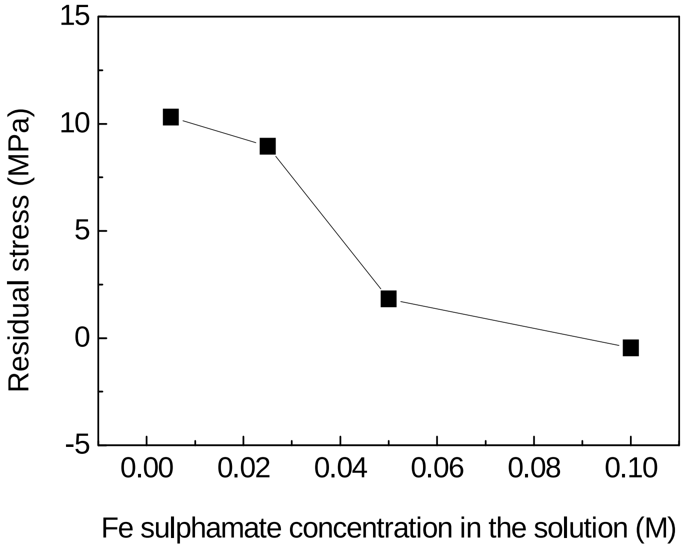

Fig. 2 Residual stresses of Ni-P-Fe alloy deposits as a function of Fe sulphamate concentration in the sulphamate bath of 1.39M Ni + 0.018M P under the condition of 50^{o}C, pH 1 and 15A/dm^{2}.

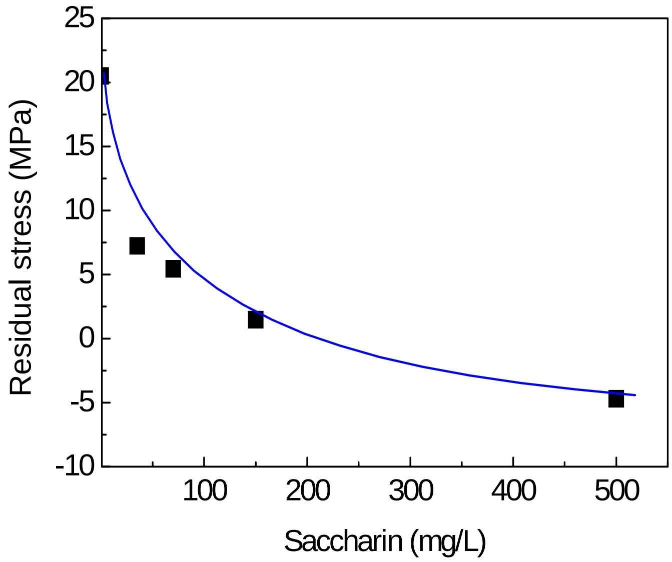

Fig. 3 Stress values measured for Ni-P-B alloy electrodeposits prepared from the baths containing various saccharin concentrations.

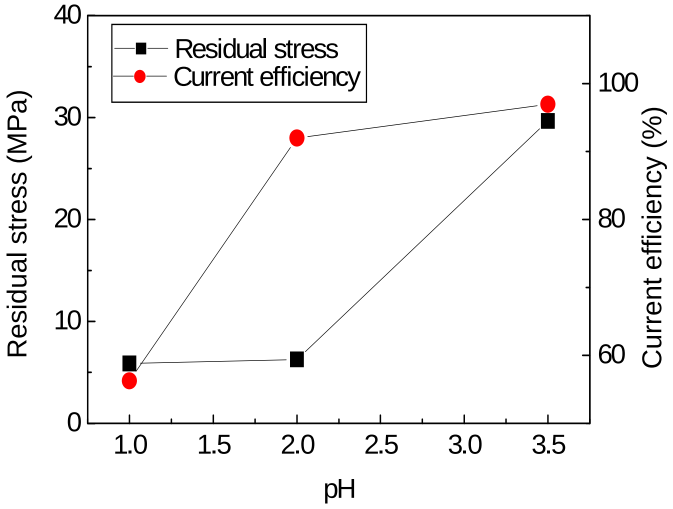

Fig. 4 Residual stresses of Ni-P-Fe alloy deposits with the pHs in the electrolytes of 1.39M Ni + 0.007M P + 0.005M Fe under the condition of 60°C and 5A/dm^2.

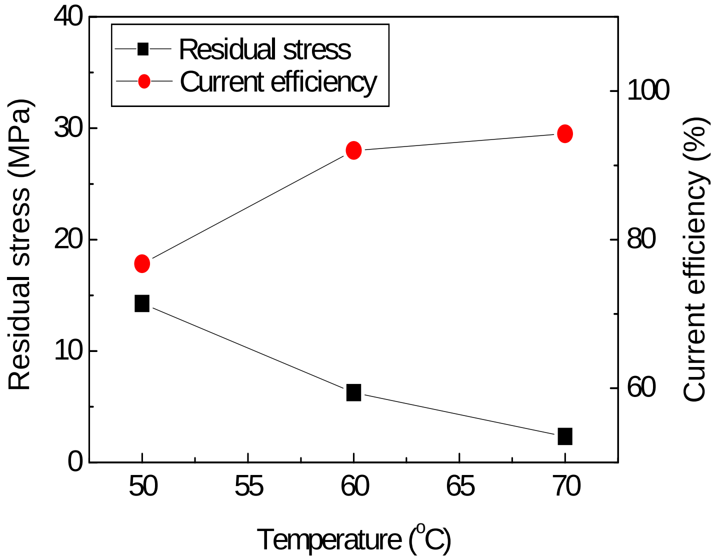

Fig. 5 Residual stresses of Ni-P-Fe alloy deposits with temperature in the electrolytes of 1.39M Ni + 0.007M P + 0.005M Fe under the condition of pH 2 and 5A/dm^2.

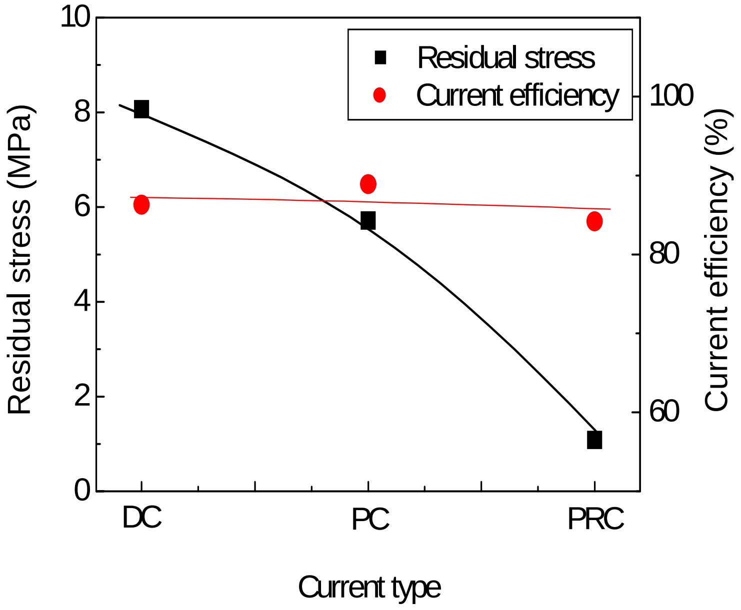

Fig. 6 Residual stresses of Ni-P-Fe deposits with current types at an average current density of $10A/dm^2$ in the electrolytes of 1.39M Ni + 0.007M P + 0.005M Fe containing various additives of saccharin, coumarin, sodiumlaruylsulfate under the condition of 60^oC and pH 2.