CORROSION SCIENCE AND TECHNOLOGY, Vol.2, No.4(2003), pp.197~201

Mechanical Properties and Microstructure of Nano Grain Nickel Alloy Deposit

Moo Hong Seo, Jung Su Kim, Seung Ho Kim, Jung Il Wyi*, Woon Suk Hwang*, Si Sung Jang, Hyun Kyu Jung, and Byung Sun Chun*****

Korea Atomic Energy Research Institute, Taejon, Korea
**Dept. of Metallurgy, Inha University, Inchon, Korea*
***Dept. of Surface Treatment, Jaeneung College, Inchon, Korea*
****Dept. of Metallurgy, Chungnam University, Taejon, Korea*

In this study, Ni-P layers were electroplated on the surface of stainless steel in order to investigate the effects of an additive and agitation on their mechanical properties and microstructure. The concentration of the additive in the plating solution increased, the pores formed in the layer decreased, while the residual stress developed in the layers during electroplating increased. Agitation of the solution during electroplating was observed to force to increase local pores in the layer, which lowers its tensile properties. Grain growth was suppressed due to very fine Ni_3P precipitates formed at its grain boundaries during heat treatment at 343 ℃ for 1 hr in air.

Keywords : *ni-p electroplating, pores, steam generator tube, additive, agitation, mechanical properties, microstructure*

1. Introduction

The long period of time operation of Pressurized Water Reactor(PWR) steam generators has been observed to result in localized corrosive attacks on the inside (primary side) or outside (secondary side) of steam generator tubing. The conventional approach to tube rehabilitation is to repair the damaged area of tubes via the insertion of tubular sleeves which are either welded or mechanically bonded at their extremities to the host tubing. Those method have the disadvantages like as parent tube deformation, requirement for PWHT(Post Weld Heat Treatment), corrosion concerns associated with weldments, etc.[1),2)] But, electrocladding technique using electroplating provides a continuous bond of high strength micro alloyed nickel to the parent tube internal diameter, spanning the defective region.[3)] No deformation of the parent tube occurs, and stress relief is not required.

Sulfamate solution for electroplating is used to make Ni-P alloyed sleeves. The sulfamate solution is low in stress and high in cathodic efficiency. Alloyed P is precipitated with Ni as Ni_3P which present Zener Drag effect of grain growth inhibition at high temperature. Due to magnetic properties of Ni-P alloy, ECT(Eddy Current Testing) can't be used to inspect the qualities of a Ni-P film plated on Alloy 600. REECT(Remote Field ECT) has been studied to overcome this disadvantage recently.[4)] In this paper, basic experimental had been conducted to develop the electrocladding technique for steam generator tube repair. Mechanical properties and microstructure evaluation of the Ni-P alloyed electrodeposits had been conducted.

2. Experimental

Ni sulfamate solution as a Ni source, phosphorous acid as a P source, Pt plated Ti as an anode and stainless steels as a cathode were used in Ni-P alloy electroplating. Table 1 shows the electroplating condition used in this study.

Table 1. Electroforming Process Conditions.

Sample No.	Solution	Current Density (A/dm^2)	Temp. (℃)	pH	RPP (Additive, ㎖)	Agitation	Heat Treatment
P1	Sulfamate	10	50	1	X	X	-
P2R					0.5	X	-
P2					0.5	0	-
P2H					0.5	0	343℃, 1hr
P3					2	0	-
P4					3	0	-

The bath composition were 1.39 M $Ni(SO_3NH_2)_2$, 0.65 M H_3BO_3, 0.018 M H_3PO_3; the pH of the bath was adjusted to be 1.0 by the Ni sulfamate solution.

Various contents of Reagent Pitting Protection(RPP) in the range of 0 ~ 3 ml / l were added in the plating solution to study its effect on mechanical properties and microstructure of Ni-P alloyed deposits. Agitation was conducted in the speed of 70 rpm using a stirrer bar to study its effect on Ni-P alloyed deposits. Tensile tests were performed using specimen machined by EDM(Electro Discharge Machining) method to reduce possible deformation which would induce residual stress. Tensile test was conducted in the condition of strain rate 0.1 mm/min using Instron 8872.

SEM and TEM microstructures of the specimen were investigated using Jeol JSM5200 and Jeol 2000FX equipped with Oxford Link(Model ISIS-5947) EDX respectively. Thin foil were prepared by jet polishing using 90% Acetic acid + 10% Perchloric Acid solution at 10℃, DC 20V.

3. Results and discussion

3.1 Mechanical properties and microstructure

The use of additives in aqueous electroplating solution is extremely important owing to the interesting and important effects produced on the growth and structure of deposits. Therefore, the effects of RPP on the mechanical properties associated with microstructure were mainly investigated in this study.

Fig. 1 shows the results of the tensile tests of the Ni-P film layers. The values of yield strength(Y.S), ultra tensile strength(U.T.S) and elongation of P1 specimen were 71.83 kgf/mm^2, 114.79 kgf/mm^2 and 5.66% respectively, while those of P2 specimen were 126.9 kgf/mm^2, 189.52 kgf/mm^2 and 6.48% respectively. The superior mechanical properties of P2 specimen which compared to those of P1 might be attributed to the decrease of surface pores by addition of RPP.[5)]

Fig. 2 shows the appearance of electrodeposits as a function of electroplating condition. The deposit (no RPP addition and agitation) shows surface pores formed on the surface. The deposit in (b) with only 0.5 ml RPP shows surface pores localized. This is because the additive undissolved in the plating solution was gradually sinking during the electroplating due to no agitation. The deposits in (c) ~ (e) show no surface pores on the surface but it buckled due to its high residual stress, which gradually increases as the content of RPP. It can be noted that the additive RPP used in this study increased suppression of the forming surface pores, surface brightness, and residual

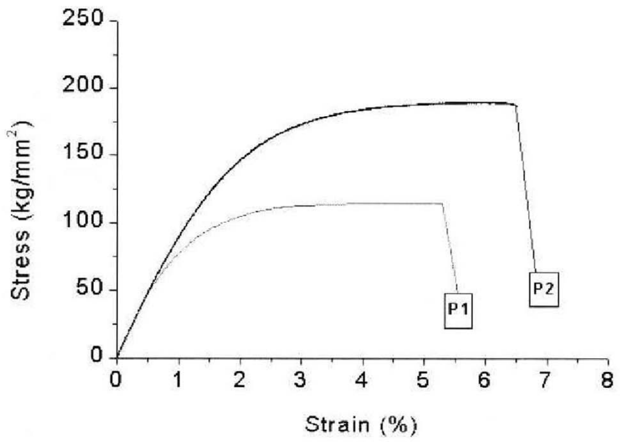

Fig. 1. Stress-strain curve for P1 and P2.

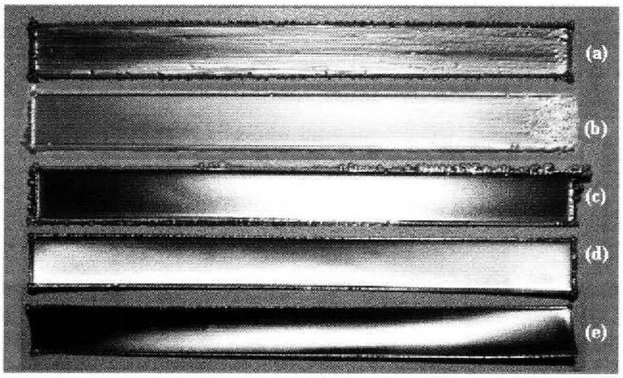

Fig. 2. The appearance of the Ni-P electroplated layers as a function of process condition; (a)P1, (b)P2R, (c)P2, (d)P3, (e)P4.

stress of the film layers.

Fig. 3 shows SEM microstructures of fracture surface of P1 (a), (b) and P2 (c) after the tensile tests. They show pores on the fracture surface in the specimen P1 and P2, while the pores formed in P2 were small and few compared to those of P1. It seems that fracture stress was concentrated on internal pores during tensile test as can be seen in Fig. 3 (c) which could result in the lower mechanical properties. In P1 and P2, it was confirmed that pores affected the mechanical properties. However P1 and P2 showed equal gradient in the elastic curve as can be seen Fig. 1. Both of P1 and P2 fractured rapidly after U.T.S and showed fracture in brittle manner without necking in the specimen during the tensile test. From the results of tensile test, it was thought that grain size and pores were the main factors in determining the mechanical properties of the film layers.

Fig. 4 shows TEM microstructures of P1, P2 and P2H. The grain sizes of P1, P2 and P2H were measured to be

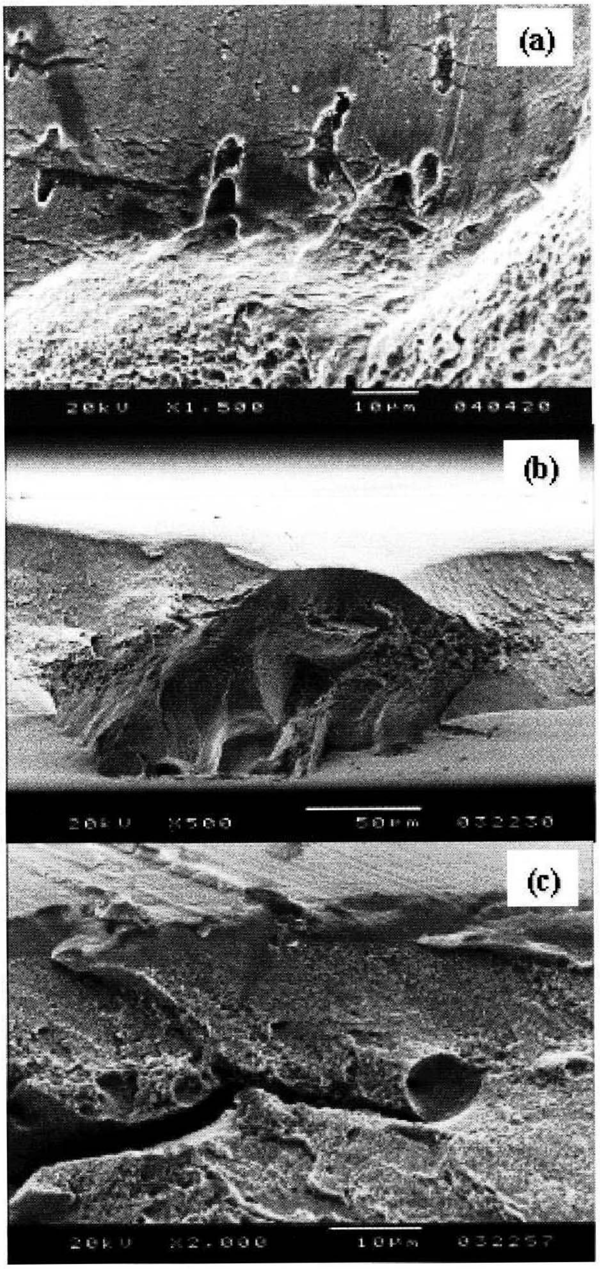

Fig. 3. Scanning electron micrographs showing fracture surface of P1(a), (b) and P2(c) after tensile test.

100 nm, 50 nm and 55 nm respectively on the average. It was thought that RPP was the main cause of smaller grain size in P2 compared to P1. Generally, additives make grain refined but agitation makes grain coarse.[6] A refinement of the deposit in regard to crystal size is found in all the cases of leveling and brightening additives. The dimensions of grains are determined by the number of grain-producing dislocation as well as by the number of nuclei which appear during electrodeposition. Consequently, the deposit will have a finer grain structure the larger the density of grain precursors, and therefore all

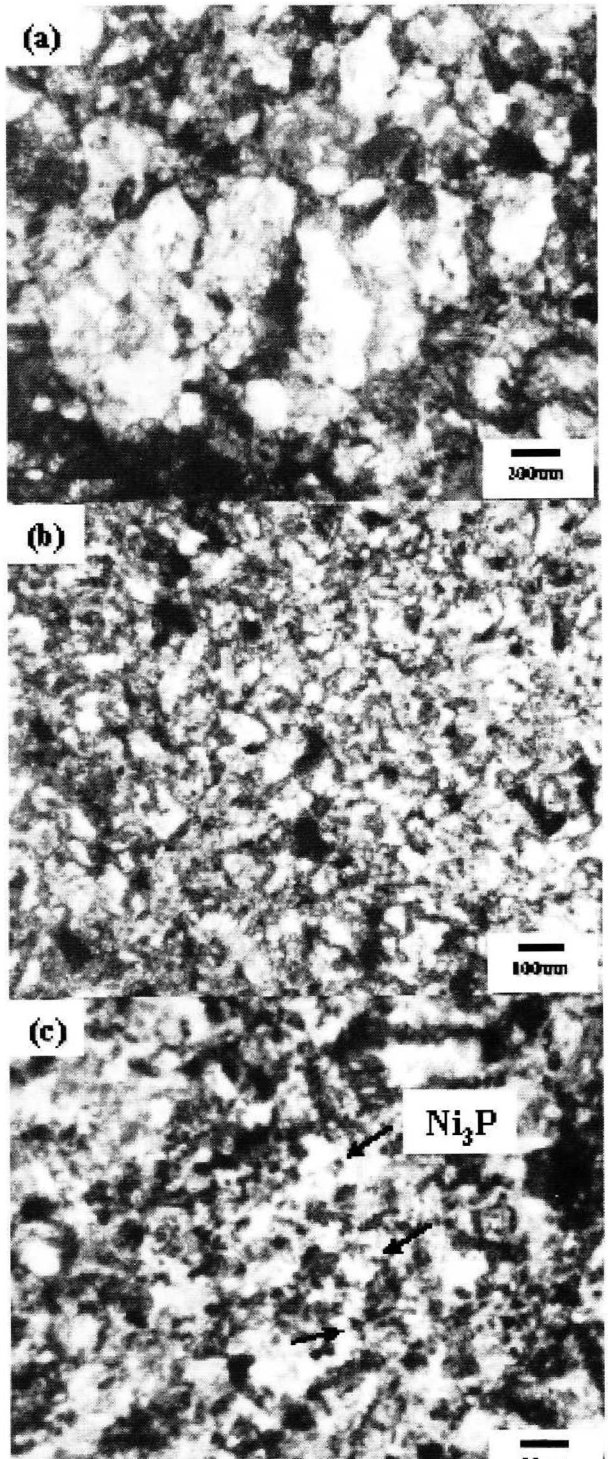

Fig. 4. Transmission electron micrographs showing grain size and precipitates in (a) P1, (b) P2 and (c) P2H.

the factors promoting formation of dislocations or nucleation contribute to reduction of the grain size.[7] Additives of these factors adsorbed at the surface create disorder in the incorporation of atoms into the lattice or inhibit surface diffusion of atoms towards growing centers.[8]

There were observed many small black spots in Fig. 4 (c). The spots seemed to be Ni_3P precipitates formed during the heat treatment at 343°C for 1hr. This obsevation is consistent with previous study. Boylan studied the microstructure of a Ni-1.2 wt%P electroplated layer and reported that Ni_3P precipitates appeared in the form of small second phase particles, the size of which was less than 5 nm after the annealing at 300°C for 10 min.[9] The Ni_3P precipitates formed at the grain boundary suppressed the grain growth by Zener Drag effect. In this study, grain size of P2H was nearly same as that of P2 by Zener Drag effect even though P2H was heat treated at 343°C for 1hr. Also, Boylan reported that above the temperature of 40 0°C, the Zener Drag effect became low and resulted in rapid grain growth.

3.2 Pores

Defects in electroplated layer are classified into cracks and pores. In this study, cracks were not observed in Ni-P alloyed film layer. The surface of a film layer were designed here for a moment in this study, the front surface contacted with the plating solution during electroplating, while the back surface contacted with the substrate. Lots of pores were observed on the both surface of P1 as can be seen Fig. 5. The average size of the pore formed on the front and back surface of P1 were measured to be 2.5 um and 5 um, respectively. Compared to the front surface, the back surface of P1 had high pore density. No pore was observed on the front surface of P2, while on its back surface, pores were formed to be 1 um in average size. In P2, the formation of surface pore was suppressed by RPP, but localized internal pores were generated by agitation as observed in Fig. 3 (c). Fig. 6 shows dependence of pore density as a function of the thickness of electroplated layers.[10] In the interface pore density is high, at greater thickness pore dropped exponentially with thick-

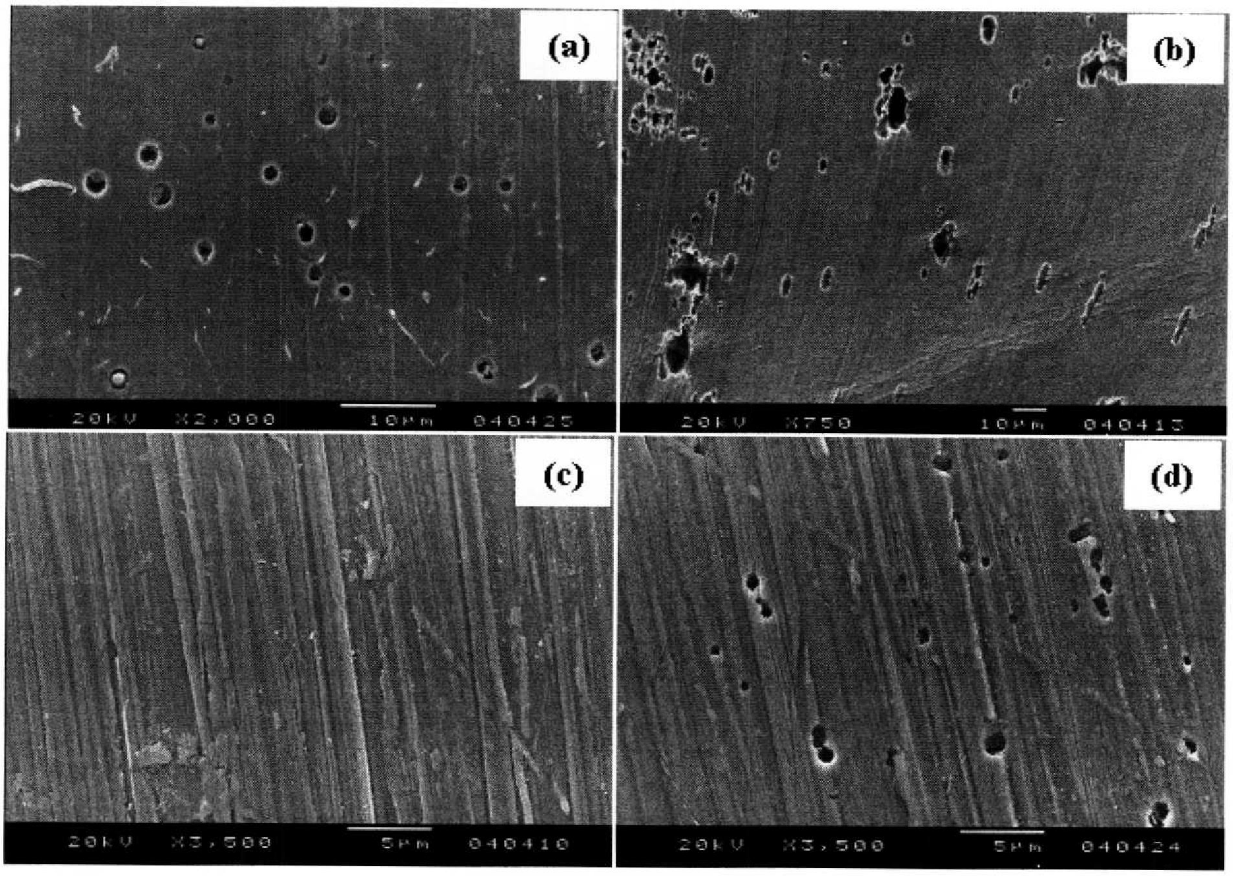

Fig. 5. Scanning electron micrographs showing specimen of surface P1(a), (b) and P2(c), (d) ; Front surface (a), (c), Back surface (b), (d).

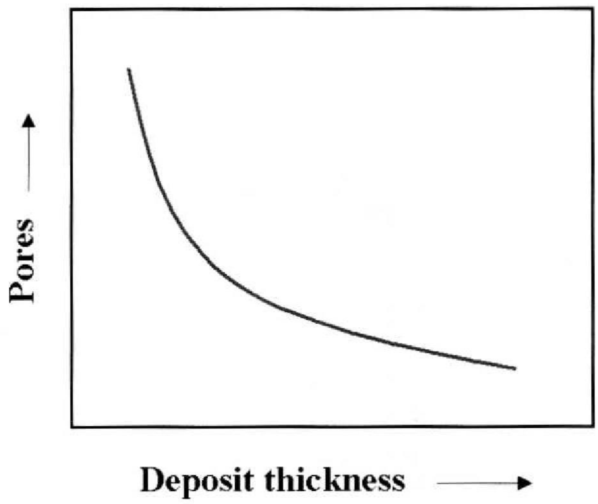

Fig. 6. Variation of pores as a function of thickness.

ness. In 1985, Morrissey reported that the sensitivity of pore to substrate and electroplated layer parameters.[11) Three distinct phases for electrodeposited unbrightened gold on a copper substrate were proposed, such as substrate dominated, transition, and coating dominated. The phenomena like this are closely connected with the cause of pore formation. Pores on the layer surface close to the interface between substrate/deposit are formed by nonconducting material during the early stages of the deposition. This condition persists up to a limiting thickness. Over the limiting thickness, pore of electrodeposited films is controlled by parameters relevant to the deposit itself. The thickness at which this sharp transition occurs varies with the deposit grain size. The form and position of the pores-thickness plots are affected by the deposit grain size, the crystallographic orientation and the ratio of nucleation rate to rate of grain growth.[12),13)]

4. Conclusions

Primary study on the electroplated layer in the sulfamate solution comes to conclusions as follows:

1. Addition of RPP 0.5 ㎖ to the electroplating solution increased Y.S and U.T.S of the electroplated layer by suppression of surface pore and grain refinement, but the content of RPP over than 2.0 ㎖ induced buckling the electroplated layer due to an increase of internal residual stress.

2. In the case of the electroplated layer formed in a solution with 0.5 ㎖ RPP and no agitation, surface pores were localized on the surface of Ni-P electroplated layers. In the electroplated layer formed in a solution with 0.5 ㎖ RPP and agitation, internal pores were observed.

3. Ni_3P precipitates were formed by heat treatment at 343C for 1hr and suppressed the grain growth at the temperature.

4. Additive RPP used in this study suppressed surface pore, and increased brightness and residual stress resulting in buckling.

References

1. F. W. Cooper, "In-Place Retubing and Sleeving of Nuclear Steam Generator", Paper presented at American Nuclear Society Meeting, Detroit, Michigan, June (1983).
2. Electric Power Research Institute, Workshop Proceedings, "Replacement and Repair of Steam Generator", Report No. EPRI NP-3207-SR, August (1983).
3. S. H. Kim, KAERI Report No. KAERI/AR-590/2001, (2001) 66-76
4. Y. M. Cheong, KAERI Report No. KAERI/AR-593/2001, (2001).
5. A. M. El-Sherik, U. Erb, G. Palumbo, and K. T. Aust, *Scripta Metall. et Mater.*, **27**, 1185 (1992).
6. J. W. Dini, Electrodeposition, Noyes Publications, New Jersey, 207 (1993).
7. A. R. Despic, "Deposition and Dissolution of Metals and Alloys, Part B, in Comprehensive Treatise of Electrochemistry, Vol. 7, Plenum, New York (1983).
8. L. Oniciu, L. Muresan, *J. Appl. Electrochem.*, **21**, 565 (1991).
9. K. Boylan, D. Ostrander, U. Erb, G. Palumbo, K. T. Aust, *Scripta Metall. et Mater.*, **25**, 2711 (1991).
10. D. R. Gabe, "Metallic Coating for Protection", Chapter 4 in coatings and surface treatment for corrosion and wear resistance, K. N. Strafford, P. K. Datta and C. G. Coogan, Editors, Ellis Horwood Limited, (1984).
11. R. J. Morrissey, Electrochemical Techniques for Corrosion Engineering, R. Baboian. Editor, National Association of Corrosion Engineers, Houston, Texas (1985).
12. A. M. Weisberg, H. Shoushanian and R. J. Morrissey, "Methods of reducing porosity in gold deposits", Proceeding Design and Finishing of Printed Wiring an Hybrid Circuits Symposium American Electroplater Soc., (1976).
13. R. J. Morrissey, A. M. Weisberg, "Some further studies on porosity in gold electrodeposits", Corrosion Control by Coatings, H. Leidheiser, Jr., Editor, Science Press (1979).