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Pulse plating of NiPB alloy for steam generator tube repair

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Abstract

This study deals with the effects of the duty cycle at the constant PCD of 20A/dm² and the peak current density at the constant duty cycle of 0.5 on the material properties of NiPB electrodeposits obtained from a sulfamate bath through inductively coupled plasma (ICP), transmission electron microscope (TEM) and the tensile test. With an increasing of the duty cycle at the constant peak current density during electrodeposition, the yield strength and ultra tensile strength decrease, and the elongation increases by the reduction of the minor alloying element contents, and the increment of the grain size in the NiPB alloy electrodeposits, which are dependent on an average current density. The coarse grain of the NiPB alloy electrodeposits can be obtained by the decrease of the hydrogen reduction reaction rate and the minor alloying element content such as phosphorus when the current density increases.

1. Introduction

Ni alloy electrodeposition has been widely studied to improve corrosion resistance, and the mechanical and magnetic properties of several materials [1-4]. Especially, Ni alloy electrodeposition is needed to repair the degraded nuclear steam generator tube, composed of Ni base alloy [5]. The Ni alloy electrodeposits for the repair of the degraded tube should have the structural strength to support the tube because its strength is presumed to be zero. Accordingly, the mechanical properties of the deposits are very important.

Pulse electrodeposition has been found to be an effective means of controlling the

mechanical properties by changing the microstructure and chemical composition of the electrodeposits. Therefore, a significant effort has been devoted to exploring how the pulse plating variables, i.e. duty cycle, θ , where $\theta = \text{on time} / (\text{on} + \text{off time})$, on time, off time and the peak current density (PCD), influence the material properties of the deposits [6-8]. However, there is no report about the effect of the duty cycle at a constant PCD to date. Most of the research refers to the duty cycle under the condition of a constant average current density (ACD), where $\text{ACD} = \theta \times \text{PCD}$. Regarding the PCD, there is a controversial argument. Kim and Weil [7] insist that the grain size decreases due to a high overvoltage, while Toth-Kadar et al. [8] asserts it increases owing to the depletion of the metal ion concentration at the interface of the electrodeposit/solution as the PCD increases. But, it needs more discussion because a high overvoltage generally induces the depletion of the metal ion concentration at the interface.

Hence, this study deals with the effects of the duty cycle at a constant PCD of $20\text{A}/\text{dm}^2$ and the PCD at a constant duty cycle of 0.5 on the material properties of the NiPB electrodeposits obtained from a sulfamate bath.

2. Experimental

Ni sulfamate, phosphorus acid and DMAB(dimethyl amine borane complex) are used as a Ni source, a P source and a B source, respectively. The bath is composed of Ni sulfamate of 1.39mol, phosphorus acid of 0.007mol and DMAB of 0.001mol. Boric acid of 0.65mol is added to the bath. Measured pH of the prepared bath was about 2. Pt deposited Ti and alloy 600 plates with a surface area of $3 \times 9\text{cm}^2$ were used as an anode and a cathode, respectively.

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

TEM microstructure of the specimen was investigated using a Jeol 2000FX equipped with an Oxford Link(Model ISIS-5947) EDX. Thin foil was prepared by jet polishing using a 60% methanol + 35% n-butyl alcohol + 5% perchloric acid solution at -30°C and a DC of 20.4V.

Tensile test was performed using INSTRON 8872 operating at a crosshead-speed of 3mm/min and at room temperature.

3. Result and discussion

Chemical composition and current efficiency of the deposits with the duty cycle are given in Table 1. P content in the deposits show a reduction, but the current efficiency increases as the duty cycle is varied from 0.3 to 1. A higher duty cycle increases the electrochemical driving force for the deposition by the increment of the ACD. Then, the Ni content increases

because the only Ni of the alloying elements is deposited electrochemically according to equations (1)~(3), and the P content decreases relatively. The NiP alloy has a high catalytic activity for the hydrogen evolution reaction and it increases with P (< 6.7wt.% P) [9]. Accordingly, the hydrogen evolution reaction of the deposits decreases at the higher duty cycle owing to the low P in the deposit. The B content is so small that its effect on the material properties could be ignored.



Fig. 1 illustrates the TEM photos with the duty cycle. Grain size is measured to be 300nm and 800nm at a duty cycle of 0.3 and 0.8, respectively, which means it increases when the duty cycle is increased. Restraining force against the grain growth by the particle per unit area of the boundary can be described by the following equation (4),

$$\tau = (3f\gamma)/(2r) \quad (4)$$

, where τ , f , γ and r are the restraining force against the grain growth, volume fraction of the particle, grain boundary energy and the radius of the particle, respectively [10]. Accordingly, it is obvious that the reduction in the volume fraction of the particles such as P and hydrogen causes grain coarsening by lowering the restraining force against the grain growth. Another possible reason for this is related to the on and off time during the pulse deposition. Nucleation and grain growth occur during the pulse on time, and nucleation sites are produced during the pulse off time [11]. Thus, a larger grain size is obtained from a shorter off time.

Fig. 2 shows the results from the tensile tests of the NiPB electrodeposits with the duty cycle at the constant PCD. With an increasing duty cycle, the yield strength (YS) and the tensile strength (TS) decrease, but the elongation increases. These phenomena are attributed to the chemical composition and grain size in the deposits. The degree of the solution of the P in the Ni is very low and most of the P in the deposit is segregated, which makes the elongation lower. Grain coarsening at a higher duty cycle reduces the YS and the TS, consistent with Hall-Petch relationship where YS is inversely proportional to the square root of the grain diameter.

Fig. 3 shows the fracture surface of the tensile tested specimens, indicating that the pore

size decreases but its density increases with an increasing duty cycle. Considering the elongation of the deposits, it seems that the pore size is more effective for its property than its density. It is presumed that the adsorbed hydrogens on the surface of the electrode are gathered during the off time and form a pore, becoming bigger at a longer off time.

Fig. 4 shows the TEM photos as a function of PCD at a constant duty cycle of 0.5. A coarse grain is obtained at a higher PCD. It is thought to be due to the current efficiency and the minor alloying element. As the PCD increases, the hydrogen reduction reaction rate and the minor alloying element decrease, resulting in a coarse grain by lowering the restraining force against the grain growth and the nucleation rate. Toth-Kadar et. al [8] report that HCOOH in the electrolyte and the impurities such as Fe and Co influence the microstructure. Hence, under a circumstance like this, it is presumed that the effect of the impurities such as P and hydrogen on the grain size of the NiPB electrodeposits is more dominant than that of an overvoltage.

4. Conclusions

This study deals with the effects of the duty cycle at a constant PCD of $20\text{A}/\text{dm}^2$ and the peak current density at a constant duty cycle of 0.5 on the material properties of NiPB electrodeposits obtained from a sulfamate bath.

1. With increasing the duty cycle at a constant peak current density during electrodeposition, the yield strength and ultra tensile strength decrease, and the elongation increases by the reduction of the minor alloying element contents, and the increment of the grain size in the NiPB alloy electrodeposits, which are dependent on the average current density.

2. The coarse grain of the NiPB alloy electrodeposits can be obtained by a decrease of the hydrogen reduction reaction rate and the minor alloying element content such as phosphorus when the current density increases.

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Table 1 Chemical composition and current efficiency (CE) with a duty cycle.

Duty Cycle	ACD(A/dm ²)	CE(%)	P(wt.%)	B(wt.%)
0.3	6	88	0.66	0.002
0.5	10	89	0.62	0.004
0.8	16	91	0.55	0.006
1	20	93	0.52	0.003

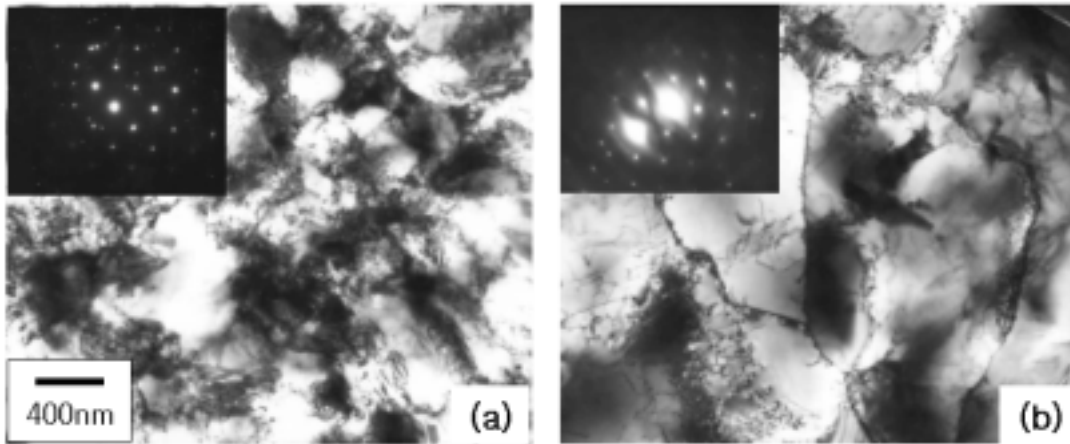


Fig. 1 TEM photos for the NiPB electrodeposits obtained at a duty cycle = 0.3 (a) and a duty cycle = 0.8 (b).

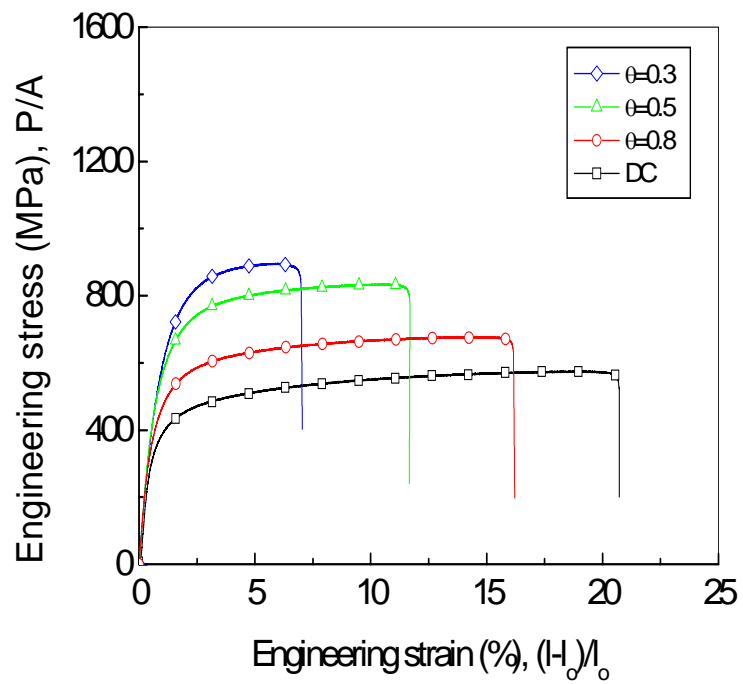


Fig. 2 Stress-strain curves for the NiPB electrodeposits obtained at various duty cycle.

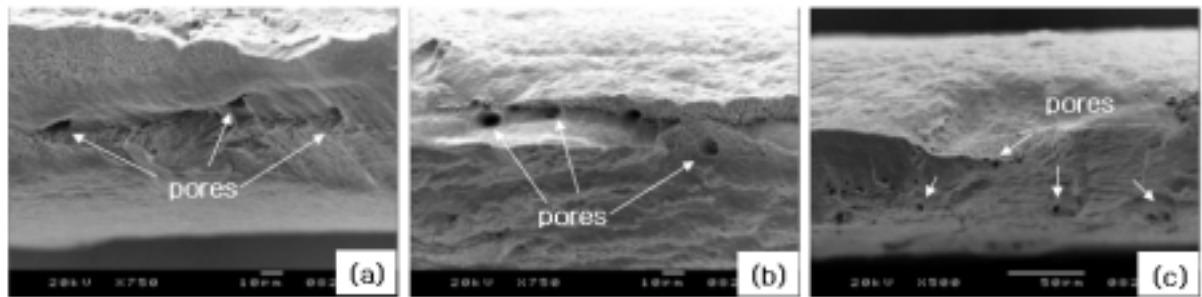


Fig. 3 Fracture surface of the electrodeposits obtained at duty cycle of (a) 0.3, (b) 0.5 and (c) 0.8.

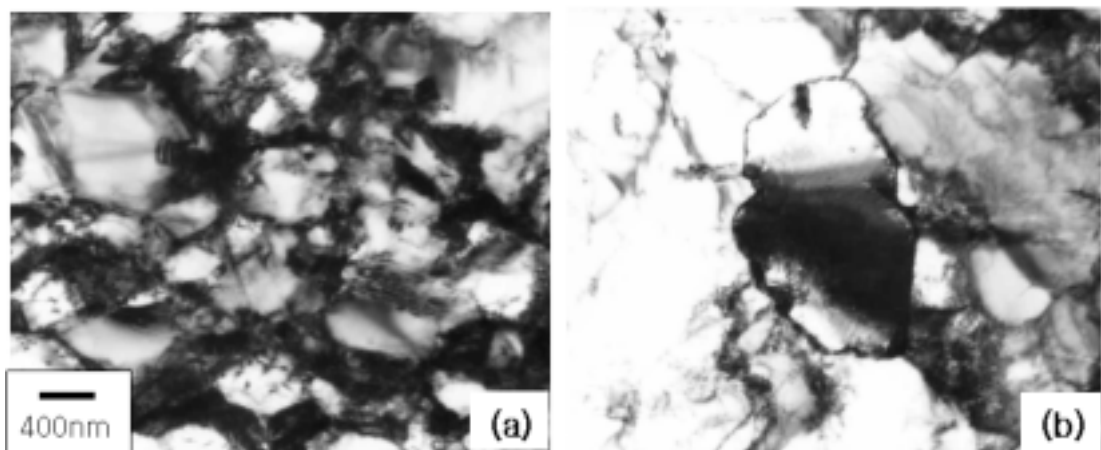


Fig. 4 TEM photos for the NiPB electrodeposits obtained at a PCD = $30\text{A}/\text{dm}^2$ (a) and a PCD = $40\text{A}/\text{dm}^2$ (b).