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Effects of Saccharin on the Electrodeposition of Ni-Fe Alloy Films

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Effects of saccharin on the electrodeposition of Ni-Fe alloy films from a sulfate-chloride bath has been studied. The polarization curve, differential capacity, the composition of Ni-Fe alloy films and the current efficiency were measured as a function of the plating time for the electrodeposition of Ni-Fe alloy films in the presence or absence of saccharin in the plating bath at 47°C. The adsorption of saccharin on the electrode resulted in a decrease of differential capacity, and the polarization curves were shifted towards more negative value giving a smooth and bright deposit. The Fe content of Ni-Fe alloy films increased with a decrease of coulombs passed in the electrodeposition of Ni-Fe alloy film. An addition of saccharin to the bath led to an increase of anomalous codeposition of Ni-Fe alloys.

1. Introduction

The commercial use of decorative Ni-Fe alloy deposits occurred more than 10 years ago.^{1,2)} A large number of physical and metallurgical properties of the Ni-Fe alloys depend on the plating variables but interdependence was not yet well understood.

The electrodeposition of Ni-Fe alloy was a system which displayed the phenomenon of anomalous codeposition.³⁾ Dahm and Crool⁴⁾ suggested that the high local pH can cause precipitation of $\text{Fe}(\text{OH})_2$ on the electrode surface. Such hydroxide precipitation may influence the discharge of other metal ions, and thus suppresses the rate of Ni deposition in the alloy.

Horkans⁵⁾ reported that the adsorption of H_3BO_3 on the electrode surface was apparently quite important in determining the deposit properties. Henstock⁶⁾ reported that the Fe content of Ni-Fe alloy films increased with a decrease of film thickness.

In the present study, polarization curve, differential capacity, the composition of Ni-Fe films and the current efficiency of deposition have been measured as a function of coulombs passed in the plating solution in the presence or absence of saccharin. The effect of saccharin on the electrodeposition of Ni-Fe films was discussed.

2. Experimental

Bath composition used in the present study was shown in Table 1. The cathode used for the polarization and differential capacity measurements was a commercial copper wire ($\phi 1.5$ mm) encapsulated in Araldite resin. The exposed area of the cathode was 0.018 cm^2 . The sulfur-activated nickel was used as an anode. An

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Table 1 Bath composition

NiSO ₄ ·6H ₂ O	85 g/l
NiCl ₂ ·6H ₂ O	135 g/l
H ₃ BO ₃	50 g/l
Citric acid	0.6 g/l
FeSO ₄ ·7H ₂ O	0–60 g/l
Saccharin	0.5 g/l

electrochemical cell of the standard H type was used for this work. The cross section of the copper wire was ground to 1500 grit finish and was electroplated with Woods nickel before each measurement. The electrode was inserted into the cell and pure nitrogen was passed through the solution before each measurement. The measurement of polarization curves in Ni and Ni-Fe electrodeposition was carried out by galvanostatic method. The differential capacity of the working electrode was measured by the current interrupter method.

For the determination of alloy composition, Ni-Fe films electroplated on copper-plated platinum sheet were dissolved in a small amount of concentrated HCl-H₂O₂ solution, and Fe and Ni were determined by atomic absorption spectroscopy. Total amount of electricity supplied for the electrodeposition of Ni-Fe alloys allowed the calculation of the current efficiency after analysis of the deposited Ni-Fe. The surface structure of the Ni-Fe alloy deposits were examined by scanning electron microscopy.

3. Results and Discussion

Total and partial polarization curves for the electrodeposition of pure Ni and Ni-Fe alloy films were shown in Fig. 1. The polarization curve of the Ni-Fe alloy film was similar to those obtained with pure Ni. By an addition of saccharin, total polarization curve was shifted towards more negative value at higher current density and was hardly affected at lower current density. With the addition of saccharin, partial polarization curves of Ni and Fe deposition except H₂ evolution were shifted towards more negative value. It was found that Ni deposition was suppressed remarkably with an increase of a current density and the partial current of H₂ evolution was increased with the addition of saccharin.

Figure 2 showed the effect of current efficiency of Ni, Fe and H₂, respectively in the electrodeposition of Ni-Fe films in the presence or absence of saccharin. In the absence of saccharin, the current efficiency of H₂ evolution decreased remarkably with increasing current density. Conversely, the current efficiency of Ni deposition increased remarkably with an increase of current density. The iron began to codeposit above the current density at which nickel began to deposit with high efficiency and the current efficiency of Fe deposition increased gradually with an increase of current density. The addition of saccharin led to an increase of H₂ evolution and resulted in a decrease of the Ni deposition. These results indicated that the presence of saccharin in the electrolyte increased the anomalous codeposition of Ni-Fe alloy films.

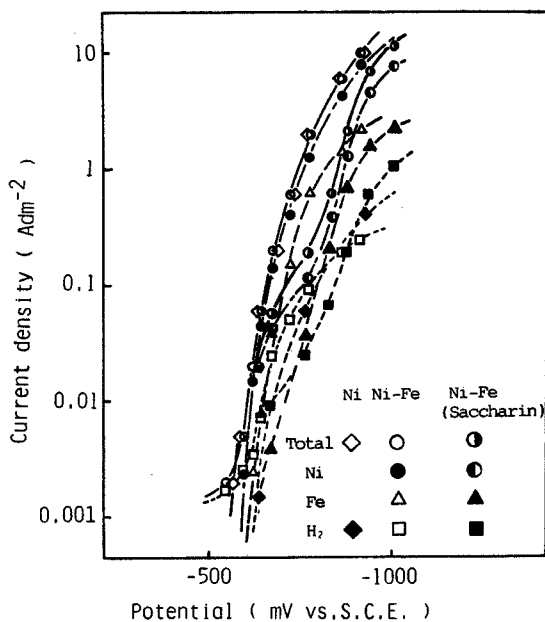


Fig. 1 Cathodic polarization curves in the electrodeposition of Ni and Ni-Fe films

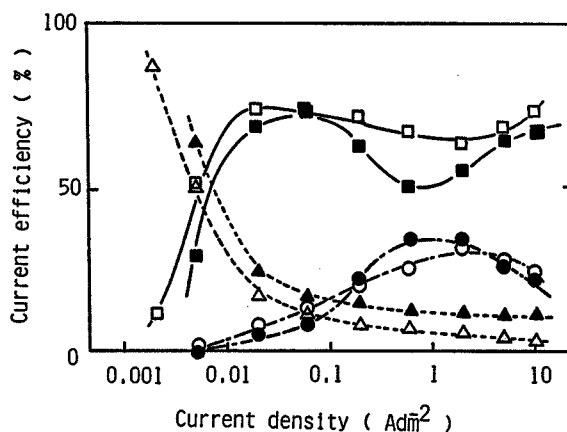


Fig. 2 Effect of current density on current efficiency in the electrodeposition of Ni-Fe coating

	Ni	Fe	H ₂
Ni-Fe	□	○	△
Ni-Fe (Saccharin)	■	●	▲

The effect of current density on the differential capacity in the electrodeposition of alloy was shown in Fig. 3. The current interrupter method was used to determine the slope of the potential decay curve of the electrode with a single pulse. From the slope of the potential decay curve, the differential capacity, C_{dl} was calculated from the following relationship:

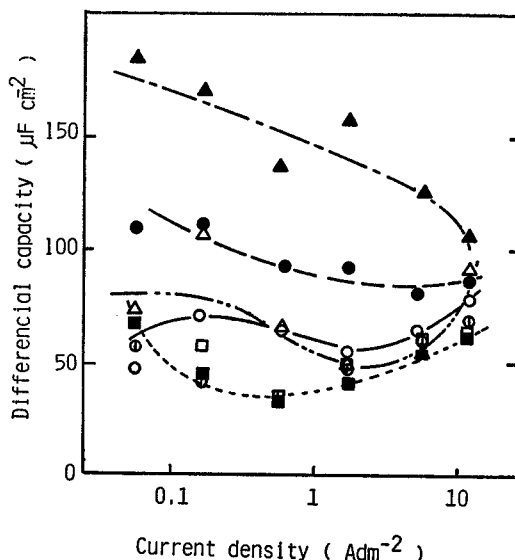


Fig. 3 Effect of current density on differential capacity of Ni and Ni-Fe deposits

	Q=0.22 Cdm ⁻²	44 Cdm ⁻²
Ni	○	●
Ni-Fe	△	▲
Ni (Saccharin)	⊙	⊗
Ni-Fe (Saccharin)	□	■

$$C = (dt/dE)_{t=0} \times i$$

The change of the differential capacity in Ni-Fe deposition with a current density was similar to those in Ni deposition at an early stage of electrodeposition. After the longer electrodeposition, however, the differential capacity in Ni-Fe deposition was found to be greater than those in the Ni deposition. This might be attributable to an increase of the surface area of the electrode or the change of adsorbed species on the electrode. The addition of saccharin in the Ni-Fe alloy plating bath led to a decrease of the differential capacity in Ni and also Ni-Fe deposition. These results imply that saccharin or its reaction products are strongly adsorbed on the electrode surface in the lower current density region in the electrodeposition of Ni and Ni-Fe. The potential shift in the negative direction in the polarization curves seemed to be attributed to the adsorption of saccharin.

Potential-current curves in the initial stage of electrodeposition of Ni and Ni-Fe films were shown in Fig. 4. For the electrodeposition of Ni-Fe films in galvanostatic method, at first the electrode potential changed abruptly towards more negative value by 100 mV and passed through a maximum. An appearance of the maximum in the polarization curves, indicated that the nucleation was hindered in the electrodeposition of Ni-Fe films. Therefore, the cathode polarization curves were shifted towards more negative value in the initial stage of electrodeposition of Ni-Fe alloy. With an addition of saccharin in the plating bath, polarization curves of the Ni deposition were affected greatly, but those of the Ni-Fe deposition were hardly

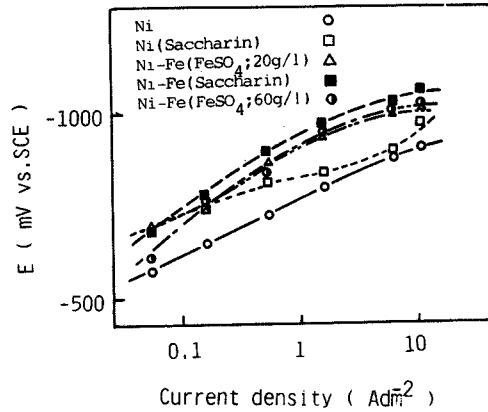


Fig. 4 Potential-current curves for electrodeposition of Ni and Ni-Fe

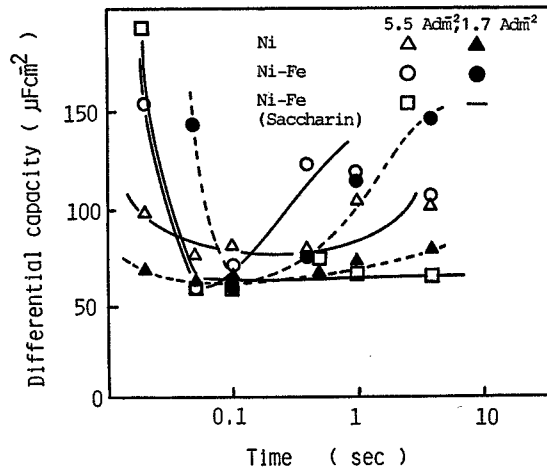


Fig. 5 Differential capacity-time curves for the electrodeposition of Ni and Ni-Fe films in the galvanostatic method

affected under the same conditions.

Figure 5 showed the differential capacity-time curves for the electrodeposition of Ni, Ni-Fe alloy films. The differential capacity which was measured from the potential decay curve of the electrode electrodeposited with a single pulse of various time were plotted against a pulse width. The differential capacity of the Ni electrodeposition does not seem to change with time, but that of the Ni-Fe electrodeposition was found to give a minimum value at a pulse width of 50 msec. The time to give the minimum value of capacity was dependent on the current density studied. This result indicated that adsorbed species might be absent on the electrode surface at an early stage of the electrodeposition of Ni-Fe films, however, the adsorbed species seemed to be accumulated on the electrode to give a minimum of the differential capacity. Therefore, in the electrodeposition of Ni-Fe alloys, the nucleation was hindered by the presence of Fe ions in the bath. The addition of saccharin in the

plating baths led to a decrease of differential capacity. An addition of saccharin to the Ni-Fe plating bath was found to give the smooth and bright surface of which seemed to be unchangable in the surface area.

Figure 6 showed the effects of coulombs passed on the Fe content of the Ni-Fe films and also on the current efficiency. The Fe content in Ni-Fe alloy film depends on the electricity supplied for the electrodeposition. The smaller the coulombs passed, the larger the Fe content of Ni-Fe was observed. The Fe content of Ni-Fe films obtained with 0.075 C cm^{-2} was found to be 55%. The current efficiency was found to increase with increasing coulombs passed. With the smaller coulombs passed, the current efficiency of the Ni-Fe alloy deposition was approximately 65–70%, and the current efficiency increased to 87–98% with the large amount of coulombs passed. It was thought that the change of the Fe content and the current efficiency in electrodeposition of Ni-Fe alloy may affect the differential capacity of the working electrode in the electrodeposition of Ni-Fe alloys. No sufficient data are available to determine precisely the factors affecting the differential capacity of the electrode in the electrodeposition of Ni-Fe alloys at the present time.

The effect of current density on the Fe content of Ni-Fe alloy films was shown in Fig. 7. The Fe content of the Ni-Fe alloys was found to give a maximum value at a current density of 2 Adm^{-2} on various film thickness.

Figure 8 showed the effect of coulombs passed on the Fe content of the Ni-Fe films and on the current efficiency in the electrodeposition of Ni-Fe alloys in the presence of saccharin. The Fe content was hardly affected by an addition of sac-

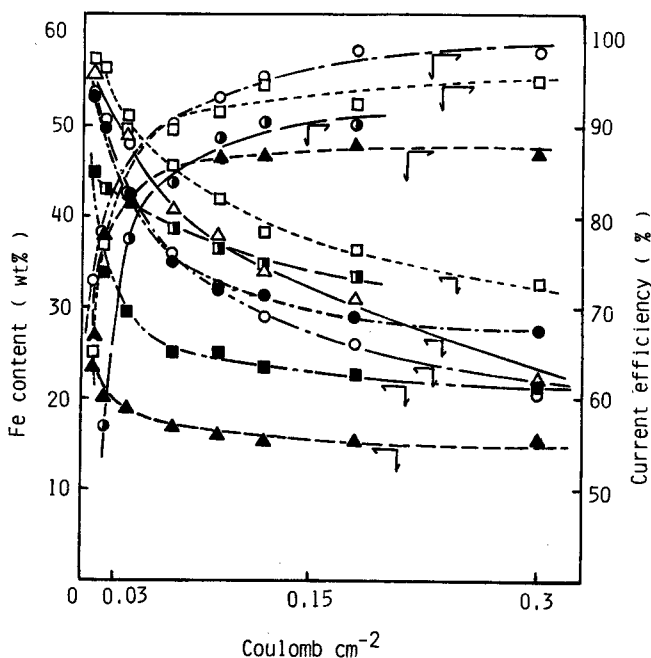


Fig. 6 Fe content in Ni-Fe and current efficiency vs. coulombs passed
Current density (Adm^{-2}) ○: 10, △: 6, □: 2, ●: 0.6, ■: 0.2,
▲: 0.06

charin, and the current efficiency decreased. The addition of saccharin in the Ni-Fe plating bath resulted in an increase of H₂ evolution and a decrease of Ni deposition.

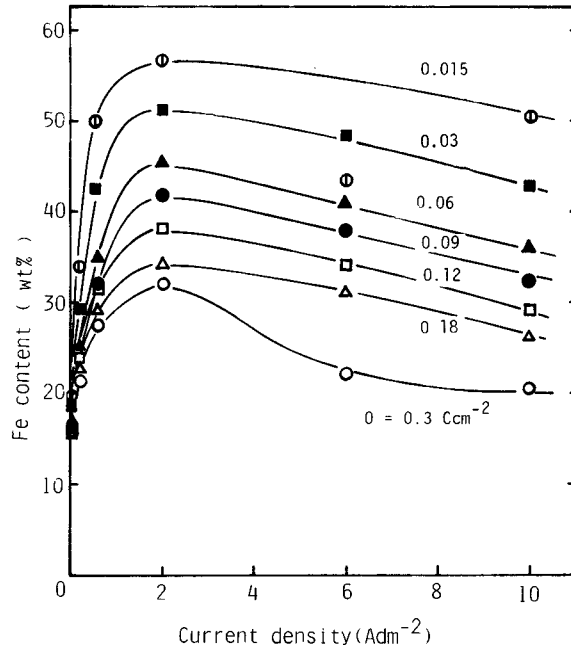


Fig. 7 Effect of current density on Fe contents in Ni-Fe alloy films

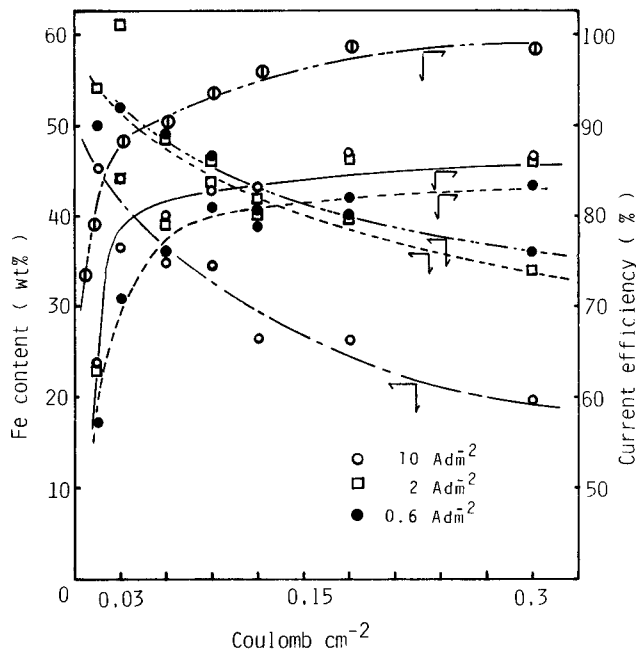


Fig. 8 Fe content in Ni-Fe and current efficiency vs. coulombs passed

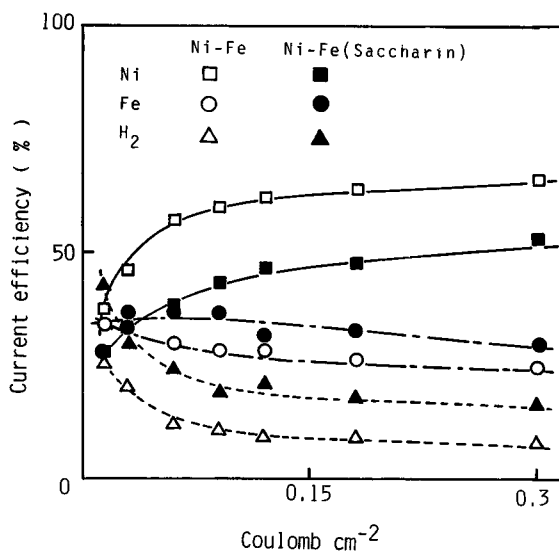


Fig. 9 Current efficiency vs. coulomb passed. Current density = 0.6 Adm^{-2}

Figure 9 showed the effects of coulombs passed on the current efficiency of Ni, Fe and H₂ deposition in the electrodeposition of Ni-Fe alloy films. With increasing coulombs passed, the current efficiency of Fe deposition was found to be unchanged. However the current efficiency of Ni deposition increased and that of H₂ evolution decreased with an increase of plating time. The addition of saccharin led to a decrease of the current efficiency of Ni deposition and to an increase of that of H₂ evolution.

Figure 10 showed the electronmicrographs of the Ni and Ni-Fe films electro-deposited at a current density of 10, 2 and 0.6 Adm^{-2} respectively. The Ni deposit was found to have the uneven sharp-pointed grains and the deposit obtained at a current density of 2 Adm^{-2} was largest. The addition of Fe ion led to the fine grains with a uniform grain size. It was suggested that the nucleation may occur at once due to the high overpotential at an early stage of the electrodeposition. Further addition of Fe ion to the bath led to the cracking fracture due to the internal stress. The current density seemed to affect seldomly to a grain size of the Ni-Fe deposits. With an addition of saccharin, the Ni-Fe deposits were found to give a uniform ultra fine crystal.

4. Conclusions

The polarization curve of the Ni-Fe alloy film was similar to those obtained with pure Ni. By an addition of saccharin, total polarization curve was shifted towards more negative value at higher current density and was hardly affected at lower current density. The addition of saccharin in the electrolyte increased the anomalous codeposition of Ni-Fe alloy films.

The change of differential capacity in Ni-Fe deposition with a current density was similar to those in Ni deposition. However, the differential capacity of the Ni-Fe electrodeposition was found to give a minimum value at a pulse width of

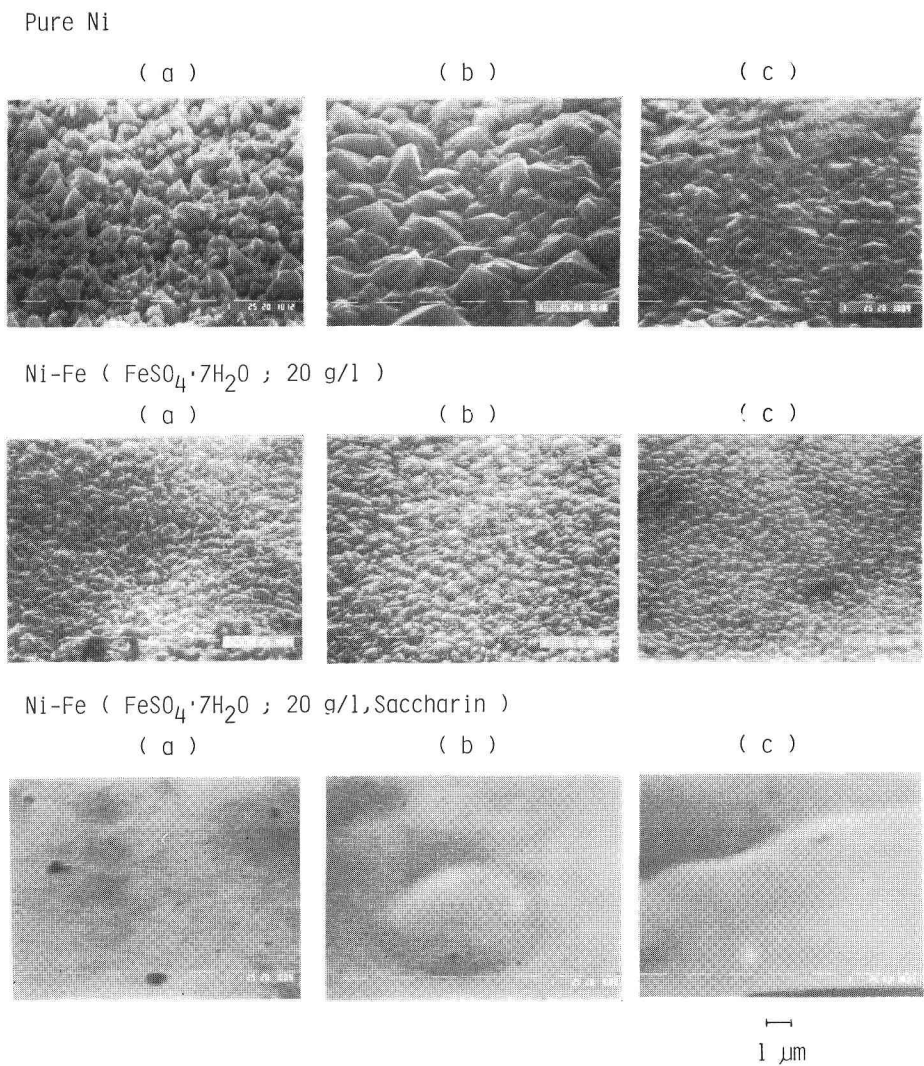


Fig. 10 Scanning electron micrographs of the surface of Ni and Ni-Fe films.
Current density (a); 0.6 Adm^{-2} , (b); 2 Adm^{-2} , (c); 10 Adm^{-2}

50 msec.

The Fe content in Ni-Fe alloy films depends on the electricity supplied for the electrodeposition. The Fe content of Ni-Fe films obtained with 0.075 C cm^{-2} was found to be 55%. The Fe content of Ni-Fe film increased as a result of a decrease in the current efficiency of Ni deposition with decreasing electricity supplied for the electrodeposition.

The addition of Fe ion led to the fine grains with an uniform grain size. Further addition of Fe ion to the bath led to cracking fracture due to internal stress. With an addition of saccharin, the Ni-Fe deposits were found to give an uniform ultra fine crystal.

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