

# Electrodeposition of Ni-Cr-P Alloys In the Presence of Additives

By R. Bindlish, B.N. Popov and R.E. White

Electrochemical d-c methods were used to study the electrodeposition of Ni-Cr-P alloy in the presence of organic and inorganic additives. It is shown that these additives help obtain deposited alloys with a higher percentage of chromium. They also improve the surface morphology of the electrodeposited alloy. A new formulation of a plating bath for Ni-Cr-P alloy is given.

Ni-Cr-P alloy has good corrosion-resistance characteristics. It resists corrosion much more effectively than Ni-P alloy or pure nickel. Addition of chromium to the basic Ni-P alloy results in an improvement in the passivity of the alloy.<sup>1,2</sup> Guilinger has developed a bath for electrodeposition of this alloy, which is a modification of Lashmore's bath for Ni-Cr alloy, and is based on chloride salts of the metals and completing agents.<sup>1</sup> The failure of composite coatings produced by electrodeposition is a result of the differences prevailing between the reduction potentials of the dissimilar metals.<sup>3</sup> These differences in electrochemical potentials can be controlled, resulting in improvement in corrosion performance. Citrate ion is employed as a completing agent to reduce the difference between nickel deposition potential and chromium deposition potential, so that nickel and chromium codeposition occurs more easily.<sup>4</sup>

The bath has two major problems associated with it. The first is the low current efficiency of the electrodeposition process; the second is instability. The low current efficiency is a result of a significant amount of energy being consumed by the accompanying hydrogen evolution reaction.<sup>1</sup> This reaction may be poisoned by incorporation of certain additives in the plating bath for Ni-Cr-P alloy. It has been shown that fluoride, thiourea and citric acid are essential additives in the plating bath for the deposition of black chromium from concentrated chromic acid solutions.<sup>5</sup> Saccharin relieves the stress in the deposited material.<sup>6</sup> Fluoride anion acts as a catalyst for the electrodeposition of chromium.<sup>7</sup> An attempt has been made to decrease the hydrogen evolution reaction and increase the relative chromium content by using additives. The additives studied are potassium fluoride (KF), sodium salt of saccharin ( $C_7H_4NO_3SNa$ ), thiourea ( $CH_4N_2S$ ) and camphor ( $C_{10}H_{16}O$ ). These additives are adsorbed on the surface of the electrode and block the sites for hydrogen evolution.

## Experimental Procedure

### Cyclic voltammograms

In order to establish the influence of the additives on the reduction processes when Ni-Cr-P alloy is deposited, cyclic voltammetry measurements were made. Platinum wire was used as the working electrode and platinum gauze as the counter electrode. The area of the platinum wire was controlled by using a masking tape. The potential of the working electrode was measured against a standard calomel electrode (SCE). The cell was connected to a potentiostat/galvanostat<sup>8</sup> by using a differential electrometer cell.<sup>9</sup> The potentiostat/galvanostat was connected to a computer.<sup>10</sup> The solution was mixed by magnetic stirrer, the pH determined,<sup>11</sup> then de-aerated by bubbling with nitrogen prior to the experiment.

### Electrodeposition Experiments

A copper disk was used as the working electrode, with platinum gauze as the counter electrode. The working electrode was rotated at 500 rpm. A potentiostat/galvanostat supplied the constant current for the electrodeposition process. The working electrode was cleaned mechanically by rubbing it on various grades of abrasive paper moistened with methanol. After cleaning, the working electrode was placed in a 1 (l-percent pickling HCl solution to remove the oxide layer from the surface. Then it was cleaned with acetone and washed with distilled water. The solution was de-aerated by bubbling with nitrogen prior to the experiment. With a current density of 250 mA/cm<sup>2</sup>, the effect of additives and current density on the composition of the alloy was observed.

### Corrosion Tests

The corrosion tests were performed in three-percent NaCl solution. The copper disk with the deposited alloy was used as the working electrode, with platinum gauze as the counter electrode. The potential of the working electrode was measured against SCE.

## Results and Discussion

### Cyclic voltammograms

The formulations of the baths used for the cyclic voltammetry experiments are given in Table 1. The bath used for electrodeposition of the Ni-Cr-P alloy has a very narrow pH range

Table 1  
Bath Composition for Cyclic Voltammograms

Component, g/L	Fig. 2	Fig. 3	Fig. 4	Fig. 5	Fig. 6	Fig. 7	Fig. 8	Fig. 9	Fig. 10
NH <sub>4</sub> Cl	50	50	50	50	50	50	50	50	50
H <sub>3</sub> BO <sub>3</sub>	35	35	35	35	35	35	35	35	35
NiCl <sub>2</sub>				30		10			
KF		5	1	1					
Saccharin		0.5	0.5	0.5	0.5	0.5			
Thiourea								0.2	

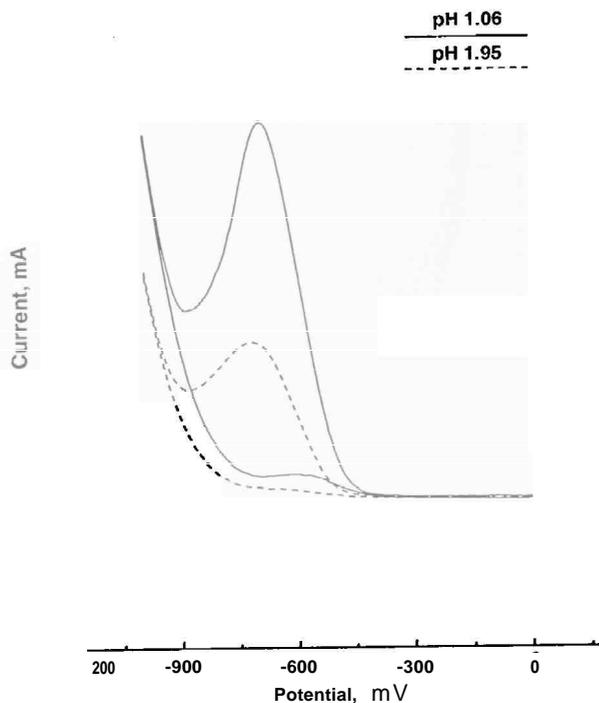


Fig. 1—Effect of pH on the hydrogen evolution peak.

over which the alloy can be deposited. At higher pH values, the bath is unstable because of the ongoing complexation reactions. At lower pH values, the electrodeposition process is very inefficient, in terms of energy, because the accompanying hydrogen evolution consumes most of the current.

The effect of pH on the hydrogen evolution reaction was studied. In Fig. 1, the peak observed near -700 mV (vs. SCE) corresponds to the hydrogen evolution reaction. It is found that the peak height at -0.7 V increases as the solution pH

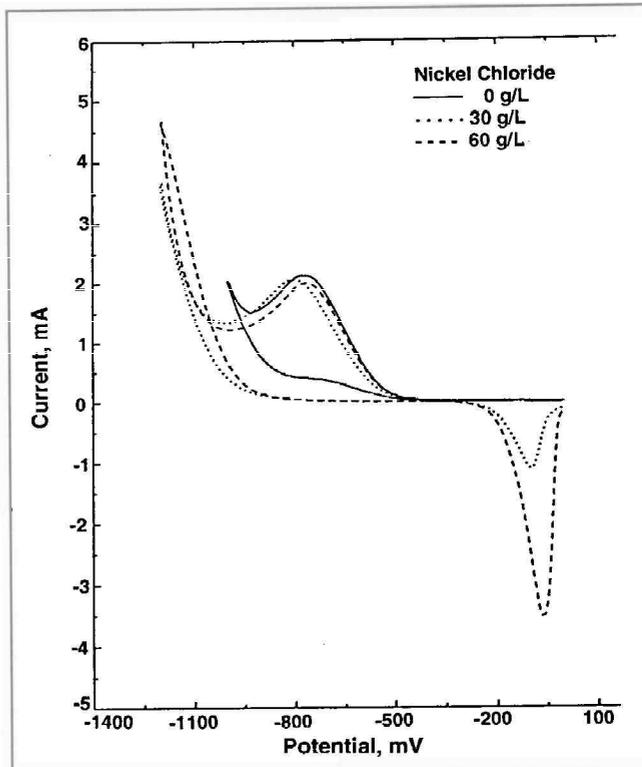


Fig. 2—Effect of nickel chloride on the anodic nickel peak.

decreases. The pH is lowered by adding 10-percent hydrochloric acid. The cathodic peak caused by the reduction of chromium is overshadowed by the hydrogen evolution from solvent breakdown, which occurs around -1300 mV. Phosphorus is deposited by a chemical reaction. The cathodic peak from nickel is covered by the hydrogen evolution peak. The anodic peak resulting from the stripping of the electrodeposited nickel, however, can be observed during the reverse scan. In order to determine qualitatively if the electrodeposition of nickel is a mass-transfer-controlled process, the effect of the concentration of nickel chloride and the scan rate on the anodic nickel peak was studied.

Figure 2 shows that the anodic peak of nickel increases with an increase in the concentration of nickel chloride. If the electrodeposition of nickel is a mass-transfer-controlled reaction, then more nickel will be deposited and subsequently stripped at a lower scan rate. It can be seen from Fig. 3 that the anodic peak of nickel increases with a decrease in scan rate. It can be concluded qualitatively that the electrodeposition of nickel is a diffusion-controlled reaction.

The effectiveness of different concentrations of potassium fluoride in suppressing the hydrogen evolution reaction was also studied to determine the optimum concentration of potassium fluoride, which can be used as an additive in electrodeposition.

It can be seen in Fig. 4 that the hydrogen evolution peak decreases as the concentration of potassium fluoride increases until a concentration of one g/L is reached, where the minimum occurs. This result can be explained by taking into account that the fluoride anion gets incorporated into the solvation sheath of the chromium complexes,<sup>18</sup> and forms a bridge between the cathode film and the chromium cation in the solution. The hydrogen evolution reaction is lowest when the concentration of the additive is sufficient to exceed the minimum fractional coverage of the surface. At a higher concentration than one g/L of potassium fluoride, the fluoride anions are in excess in the solution, where they may reduce

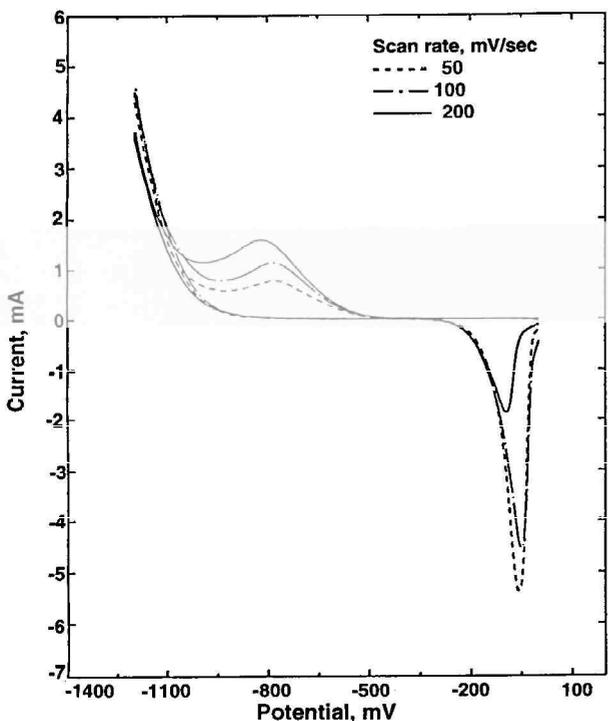


Fig. 3—Effect of scan rate on the anodic nickel peak

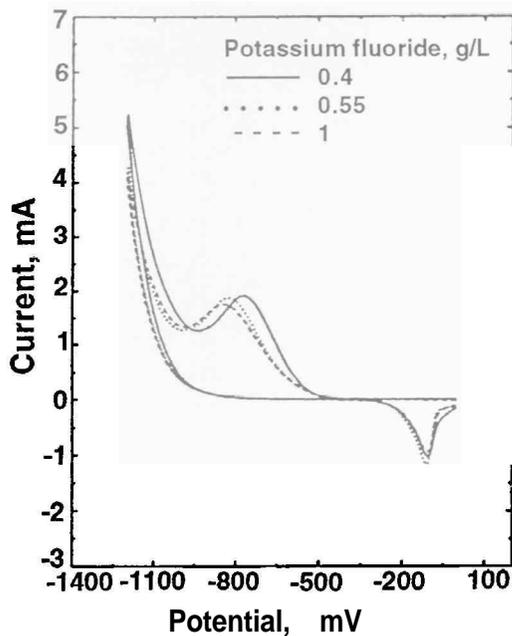
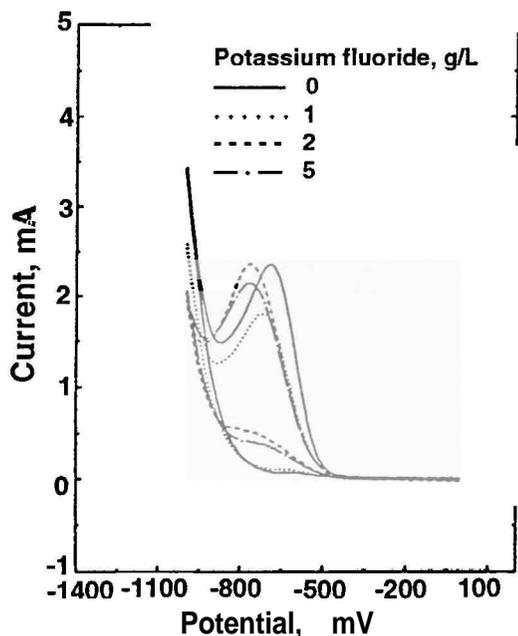


Fig. 4—Effect of potassium fluoride on the hydrogen evolution reaction.

the passivity of the deposited material and thereby increase the hydrogen evolution reaction.

The effect of the sodium salt of saccharin, camphor and thiourea on the hydrogen evolution peak was included in the study. It can be observed from Fig. 5 that the hydrogen evolution peak decreases to a certain extent because of the introduction of saccharin or camphor. This decrease in hydrogen evolution follows from the fact that saccharin or camphor is adsorbed on the surface of the cathode. The effect of higher concentrations of camphor on the hydrogen evolution peak was not investigated because the volatility of camphor in the aqueous solution is very low.

Figure 5 shows that the peak height increases as the concentration of thiourea increases. This is because the deposition of sulfur increases as the concentration of thiourea increases. Thiourea, a sulfur-containing compound, is responsible for the incorporation of sulfur in the deposit.

#### Electrodeposition Experiments

The effect of these additives and the current density on the composition of the deposited alloy was also investigated. The composition of the electrodeposited alloy was determined by using EDS. The effect of current density on the composition of the alloy deposited by using the bath without any additives, is given in Fig. 6. The relative content of chromium in the deposit increases with an increase in current density. Because phosphorus is deposited chemically, the phosphorus content in the deposit does not depend upon the current density, as do nickel and chromium. Therefore, the relative content of phosphorus should decrease with an increase in current density. It can be seen from Fig. 6 that the relative content of phosphorus decreases with an increase in current density. This decrease is consistent with the results reported in the literature for Ni-P deposition.<sup>6</sup>

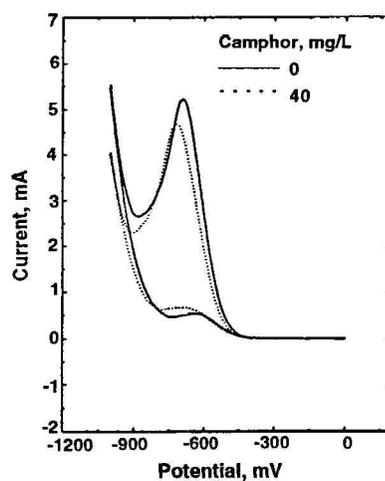
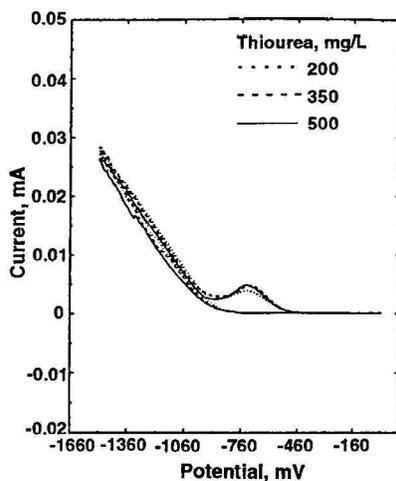
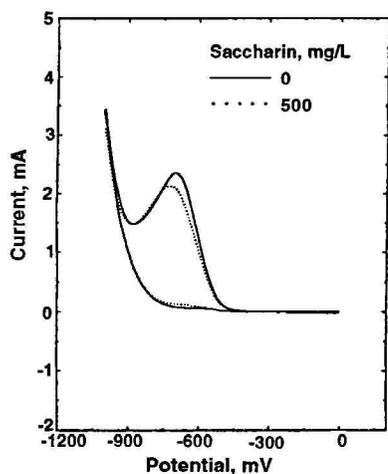


Fig. 5—Effect of sodium salt of saccharin, camphor and thiourea on the hydrogen evolution peak.

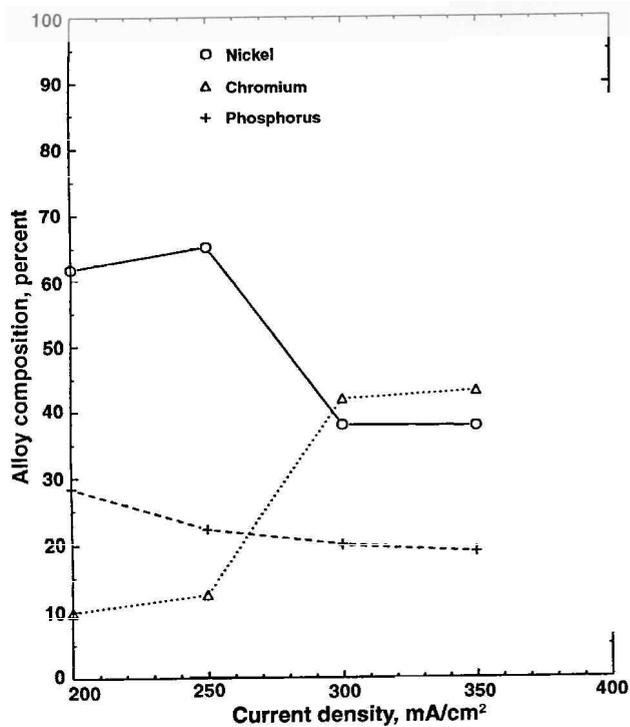


Fig. 6—Effect of current density on composition of the alloy (Ni-Cr-P bath).

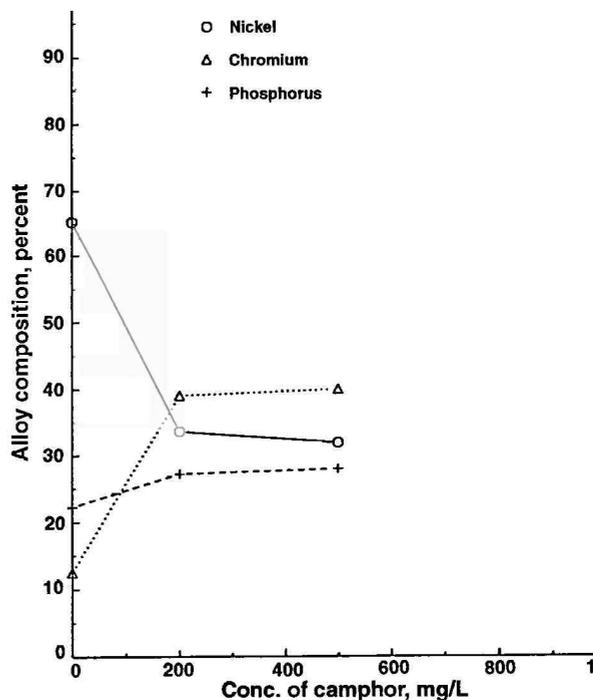


Fig. 7—Effect of camphor on composition of the alloy.

In Fig. 7, the relative content of chromium is seen to increase while that of nickel decreases with the introduction of camphor because of adsorption on the surface of the electrode, blocking the sites for hydrogen evolution, as mentioned earlier. Therefore, the overall rate of electrodeposition of the alloy increases. Because electrodeposition of nickel is a diffusion-controlled process, less area is available for deposition

when camphor is introduced. Accordingly, the relative content of nickel in the alloy decreases with introduction of camphor.

Electrodeposition of chromium is a kinetically controlled reaction, and is not adversely affected by coverage of the surface by camphor. Consequently, the relative content of chromium increases in the alloy with the introduction of camphor, as deposition of nickel declines. Further increase in the concentration of camphor does not affect the composition of the deposited alloy because of the extremely low volatility of camphor in aqueous solution.

The effect of fluoride on the composition of the alloy was also studied. It can be observed in Fig. 8 that an increase in the concentration of potassium fluoride results in an increase in the relative content of chromium and a decrease in the relative content of nickel. Fluoride anion acts as a catalyst for electrodeposition of chromium.<sup>7</sup> It enables the approach of chromium ions to the cathode through the cathode film. In the first stage, fluoride anion substitutes into the solvation sheath of the chromium cation, such as  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ , or into the coordination sheath of complexes bound into the cathode film. After that, there is bridging between the cathode film and the chromium cation in the solution. This is followed by expulsion of the fluoride anion, which was the bridging ligand. Further cross-linking of the complex with the cathode film leads to incorporation of chromium cations in the cathode film. The cations are reduced and deposition of chromium in the film results. Deposition could be expected to be favored in regions where the cathodic film is the thinnest because the potential will be higher in these regions. Because the fluoride anion is small and mobile, it is not expected to be trapped in the deposit.<sup>7</sup> Therefore, the addition of fluoride enables increase in the relative content of chromium in the deposit without incorporating fluoride.

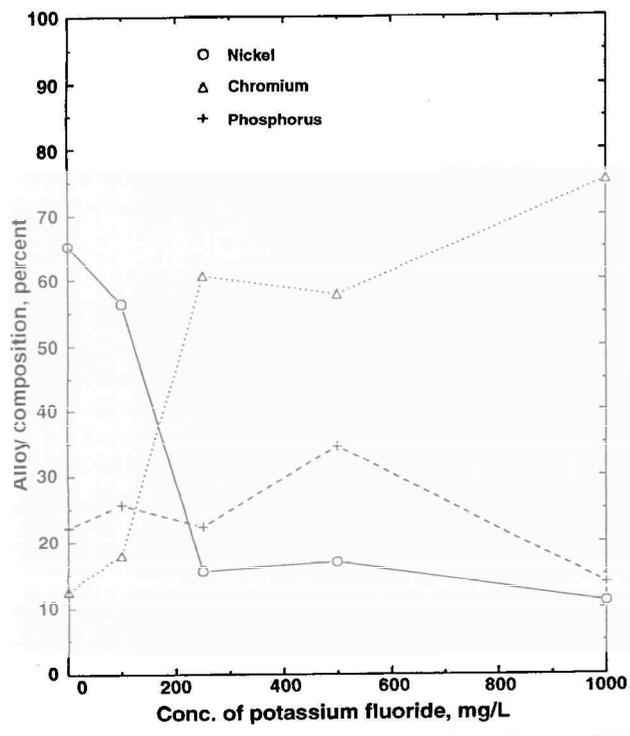


Fig. 8—Effect of potassium fluoride on composition of the alloy.

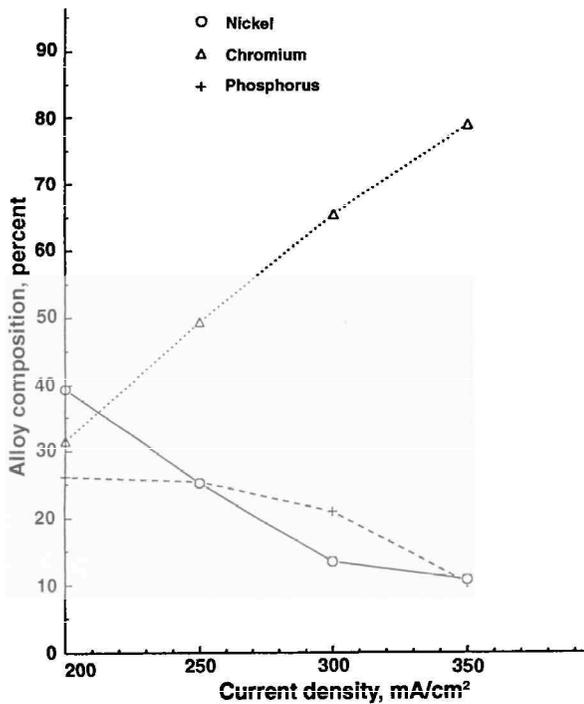


Fig. 9—Effect of current density on composition of the alloy (Ni-Cr-P bath with additives).

**Table 2**  
**Bath Formulation**

**For Ni-Cr-P Alloy Electrodeposition**

Component	Concentration
NiCl <sub>2</sub> ·6H <sub>2</sub> O	30 g/L
CrCl <sub>3</sub> ·6H <sub>2</sub> O	100 g/L
HCOOH	35 mL/L
KBr	17.3 g/L
NH <sub>4</sub> Cl	50 g/L
Na <sub>3</sub> (Cit) ·H <sub>2</sub> O	80 g/L
H <sub>3</sub> BO <sub>3</sub>	35 g/L
NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O	30 g/L
KF	1 g/L
Saccharin	0.5 g/L

The alloy bath formulation is modified by incorporating potassium fluoride and saccharin as additives in Guilinger's bath (see Table 2). The concentration of potassium fluoride is one g/L and that of saccharin is 500 mg/L. According to Fig. 4, one g/L of potassium fluoride is the most effective concentration for suppressing the hydrogen evolution reaction. Saccharin does not affect the composition of the alloy greatly. Its role is relieving stress in the deposit and making it much more uniform. As the current density of the deposition process is increased, the percentage of chromium can be as high as 80 in the deposit.

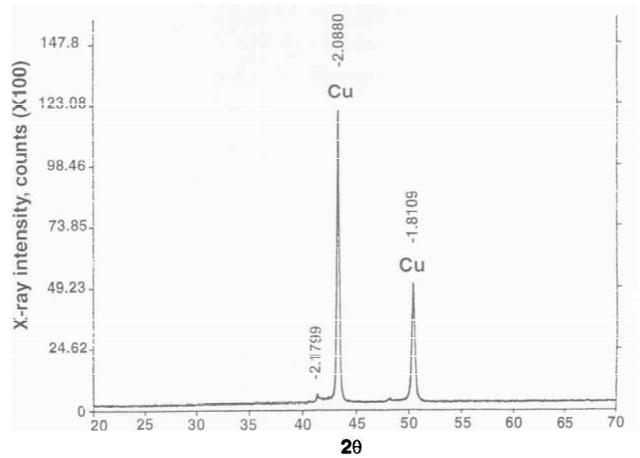


Fig. 10—X-ray diffraction pattern of the deposited alloy.

Figure 6 shows that the relative content of chromium is about 10 percent at a current density of 250 mA/cm<sup>2</sup> in the absence of additives. It can be seen in Fig. 9 that the relative content of chromium increases to about 50 percent at a current density of 250 mA/cm<sup>2</sup> in the presence of additives. Therefore, it is possible to obtain deposits of very high concentration of chromium by employing fluoride anions as a catalyst. The deposit composition can be controlled over a much wider range by using additives in the bath and by varying the current density for deposition of the alloy.

**Corrosion Tests**

The averaged results of the corrosion experiments are given in Table 3 and show that the corrosion resistance characteristics of the alloy improve with an increase in relative chromium content in the deposited alloy.

**Structure of the Alloy**

The amorphousness of the deposited alloy was analyzed by X-ray diffraction. The diffraction patterns are similar for the Ni-Cr-P alloy deposited under different conditions. A typical XRD pattern is shown in Fig. 10. The pattern shows two peaks, which arise because of the copper substrate. There are two small peaks resulting from nickel phosphide. There are no peaks corresponding to nickel, chromium or phosphorus. Therefore, the deposit is highly amorphous, with a few microcrystals of nickel phosphide.

**Conclusions**

The bath formulation for the electrodeposition of Ni-Cr-P alloy has been modified by incorporating potassium fluoride, saccharin, camphor and thiourea and observing their respective effect on the deposition process. These additives suppress hydrogen evolution by adsorption on the surface of the cathode. They also increase the relative content of chromium in the

**Table 3**  
**Effect of Chromium**  
**On the Corrosion Resistance Characteristics of the Alloy**

Percentage of Cr in the deposit	Polarization resistance, kΩ/cm <sup>2</sup>	Corrosion current, μA/cm <sup>2</sup>	Corrosion rate, MPY
42	2.2977	9.45	2.68
79	4.2462	5.11	1.45

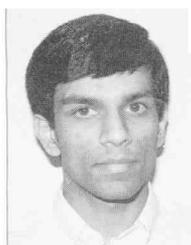
deposited alloy, while saccharin relieves stress. Potassium fluoride is most effective in suppressing hydrogen evolution and increasing the relative chromium content in the alloy. The Ni-Cr-P bath has been modified by adding one g/L of potassium fluoride and 500 mg/L of saccharin. A desired composition of the alloy can be obtained by employing the appropriate current density during the deposition process. The electrodeposited Ni-Cr-P alloy is highly amorphous in nature and contains a few microcrystals of nickel phosphide. The additives enable the deposition of Ni-Cr-P alloys with a very high chromium content. They result in deposition of alloys with improved corrosion resistance characteristics.

### Acknowledgment

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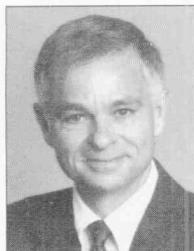
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