Electrodeposition of Iron-Chromium-Nickel Alloy

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An iron alloy containing 18 percent chromium and 8 percent nickel was electrodeposited with a current efficiency of 50 to 60 percent in a sulfate bath containing glycine and boric acid. The inferior quality of the deposit was attributed to unfavorable, diffusion-controlled proton discharge, a corresponding increase in the pH of the catholyte layer, and precipitation of metal hydroxides.

ernary alloys of iron, chromium, and nickel fabricated by a thermal process have excellent resistance to many chemicals and corrosive environments. Among these alloys, stainless steel with 18 percent chromium and 8 percent nickel has been adopted for many industrial uses. Electrodeposition of such an alloy could offer economic advantages.

A number of unsuccessful attempts have been made to obtain commercially feasible Fe-Cr-Ni deposits. Comprehensive reviews on electroplating of the ternary alloys have been published. ¹⁴ Poor coating quality due to internal stress and hydrogen em brittlement has been the main problem. The internal stress triggers the cracking observed in thick alloy deposits. The standard redox potential indicates that hydrogen discharge is thermodynamically more feasible than reduction of metal ions. In general, the current efficiency for alloy deposition is less than 50 percent, and the main portion of the applied current is consumed by hydrogen evolution, which raises the pH in the catholyte layer and leads to precipitation of hydroxides unless effective completing agents are present in the catholyte layer. Codeposition of the basic salts leads to inferior electrodeposits.

Recently, the buffering and completing capabilities of additives were comprehensively discussed by Lashmore.⁵ Because hydrogen evolution raises the pH by several units in the depletion layer adjacent to the cathode surface, additives are necessary for improving the buffering action of the solutions. The effects of a number of additives (e.g., urea, ⁶ citrate, ⁷ triethanolamine, ⁸ glycine, ⁹ and EDTA¹⁰) have been examined.

In our study, both glycine and boric acid were employed to improve the quality of Fe-Cr-Ni deposits. Because



Fig. 1—Changes in current efficiency and alloy composition as a function of currant density. All baths contained 0.5M H₂BO₃ and 1.0M glycine and were maintained at pH 2.0. In addition, Bath 1 contained 0.1 M Cr³⁺, 0.2M Ni²⁺, and 0.2M Fe²⁺; Bath 2,0.2M Cr³⁺, 0.4M Ni²⁺, and 0.4M Fe²⁺; Bath 3, 0.3M Cr³⁺, 0.6M Ni²⁺, and 0.6M Fe²⁺; Bath 4, 0.4M Cr³⁺, 0.8M Ni²⁺, and 0.8M Fe²⁺.



Fig. 2—Changes in current efficiency and alloy composition as a function of current density. All baths contained 0.5M H,BO,, 1.0M glycine, and 0.2M Cr at pH 2.0. In addition, Bath 1 contained 0.4M Ni and 0.4M Fe; Bath 2, 0.45M Ni and 0.35M Fe; Bath 3, 0.5M Ni and 0.3M Fe.

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glycine functions not only as a buffer but as a completing agent, it is useful for preventing the codeposition of basic salts. The maximum buffering action of glycine could be expected at pH 2.35 and 9.78, corresponding to pK and pK, respectively. The stability constant of the glycine complexes seems to be high enough to prevent the formation of hydroxides even if a rise in pH occurs in the cathode film (Fe: log B_2 = 7.63, Ni: log B_3 = 13.95, Cr: log B_3 20.5, where B represents the overall stability constants and the subscripts correspond to coordination numbers). The effect of glycine concentration, other plating parameters (e.g., current density, pH, and temperature), and hydrodynamic conditions on the quality and composition of the alloys was examined.

Experimental Procedure

The plating solution was a mixture of potassium chromium sulfate, $KCr(SO_4)_2$ •12H₂O; boric acid, H₃BO₃; and glycine, C₂H₅NO₂. Varying amounts of nickel and iron sulfates (NiSO₄.6H₂0, FeSO₄.7H₂0) were added. A fresh solution was prepared for each experiment and aged more than one night. An H-type cell, in which anolyte and catholyte were separated' from each other by a sintered glass diaphragm, was used to prevent contamination of the catholyte solution with oxidation products (e.g., Cr⁶⁺ and Fe³⁺) formed in the anolyte. Copper" strips or rotating cylinders (1 cm²) were used as cathodes while an insoluble platinum strip was employed as the anode. The alloys were plated at 25° C under galvanostatic conditions.

The cathode potential was measured against the saturated calomel electrode. The ternary alloys were stripped from the substrate with 6N hydrochloric acid, and the metal content was determined by atomic absorption. The potential sweep method was also employed to measure the limiting current density of proton discharge by using an iron rotating cylinder as the working electrode. The potential was swept linearly at 10 mV/sec. The magnetic

properties were qualitatively examined by observing the interaction between a magnetic bar and the alloy deposits. Corrosion resistance of the alloys was also briefly evaluated by immersion in 6N HCI.

Results and Discussion

Kudryavtsev et al.⁹ prepared Fe-Cr-Ni alloys from a glycine bath with a high ratio of Cr³⁺ to Ni²⁺ and Fe²⁺. The nickel content of the alloys was restricted to less than 5 percent. Good-quality Fe-Cr-Ni alloys could only be obtained over the narrow low-current-density range of 5 to 12 A/dm². Alloy composition and current efficiency were affected by forced convection. To overcome such disadvantages, the concentration of trivalent chromium salts in a glycine bath was varied while the molar ratio of Ni²⁺ to Cr³⁺ and Fe²⁺ to Cr³⁺ was kept constant at 2.

Increases in current density increased the chromium content of the alloys and decreased the iron content (Fig. 1). Except for Bath 1, the nickel content also decreased with increasing current density. The current efficiency for alloy deposition increased significantly to more than 60 percent when the total concentration of metal ions was increased. In general, current efficiency was improved by increasing the current density, except for Bath 4 in which the reverse effect was observed and attributed to a drop in the concentration of free glycine, as will be discussed.

In all cases, the iron content of the alloys increased in proportion to the Fe²⁺ concentration. By contrast, the Ni and Cr content was depressed when there was an increase in the concentration of the corresponding metal ion. In general, the nickel content of the deposits was lower than the percentage of nickel in solution—a feature characterized by the anomalous codeposition of iron. The preferential deposition of the less noble metal is attributed to the formation of a hydroxide film on the electrode surface. Evidence for the incorporation of Fe(OH)₂ in Fe-Cr-Ni deposits was presented by Ishihama and Hayashi.¹⁰



Fig. 3—Changes in current efficiency and alloy composition with glycine concentration as a function of current density. All baths contained 0.1 M Cr³⁺, 0.2M Ni²⁺, 0.2M Fe²⁺, and 0.5M H₃BO₃at pH 2.0. in addition, Baths 1 through 3 contained 1.0M, 1.5M, and 2.0M glycine, respectively.



Fig. 4-Changes in current efficiency and alloy composition with pH as a function of current density. Baths contained 0.3M Cr^{*}, 0.8M Ni^{*}, 0.4M Fe^{*}, 5M H,BO₃, and 1.5M glycine at pH 1.5 (Bath 1), pH 2.0 (Bath 2), and pH 2.3 (Bath 3).

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The coating obtained at 20 A/dm² (Bath 1, Fig. 1) contained about 18 percent chromium and 8 percent nickel,' but was deposited at low current efficiency (40 percent) and had many cracks. To obtain better 18 Cr/8 Ni deposits at a higher current efficiency, intermediate levels of chromium and nickel were combined with lower Fe²⁺ concentrations, ranging from 0.3 to 0.4M (Fig. 2). At 15 to 20 A/dm², deposits containing about 18 percent Cr and 8 percent Ni were obtained with a current efficiency of about 50 percent. However, the results of corrosion tests in 6N HCl were unsatisfactory due to cracking. Also, the deposits



Fig. 5—Changes in current efficiency and alloy composition with temperature as a function of current density. Baths contained 0.2M Cr³⁺, 0.5M Ni²⁺, 0.3M Fe²⁺, 1.0M glycine, and 0.5M H₃BO₃ at pH 2.0 and 20° C (Bath 1), 25° C (Bath 2), and 30° C (Bath 3).

were magnetic and therefore differed from the austenitic stainless steel produced by the thermal process.

Increasing the concentration of glycine reduced the current efficiency and tended to depress the chromium and nickel content of the deposit (Fig. 3). On the other hand, a higher (2M) concentration of glycine prevented crack formation (although the surface of the deposit was non-uniform), especially in low-current-density regions.

Lowering bath pH from 2.3 to 2.0 or 1.5 reduced current efficiency considerably (Fig. 4), especially at low current densities. At higher current densities, the deposits were dull and granular.

Increasing the temperature of the solution containing 1M glycine had no significant effect on current efficiency (Fig. 5). Chromium deposition was inhibited slightly and the Fe and Ni content increased. At the higher temperature, the cracks decreased in number but were not completely eliminated.

Figure 6 shows the surface appearance of typical thick alloy deposits obtained froma 1 M glycine bath at pH 2 after passing 4500 and 9000 coulombs of electricity. The surfaces were rough and cracked.

Use of a rotating cylindrical cathode in a similar solution produced bright alloy deposits with a uniform appearance but cathode efficiency was greatly reduced and chromium deposition inhibited (Fig. 7). This more or less duplicated the effects of reducing bath pH or increasing the glycine concentration.

Horkans¹² reported that the diffusion coefficient of hydrogen ions in a sulfate solution was higher than that in a chloride electrolyte and observed higher current efficiency for nickel deposition from the chloride bath. The role of chloride ions in the deposition of Fe-Cr-Ni alloys was therefore studied. When nickel sulfate was replaced with nickel chloride, current efficiency increased (Fig. 8). Consequently, the reduced efficiency caused by a high agitation rate may be effectively prevented by adding chloride.



Fig. 6—Typical surface appearance of Fe-Cr-Ni alloys from bath containing 0.3M Cr³⁺, 0.8M Ni²⁺, 0.4M Fe²⁺, 0.5M H₃BO₃, and 1.0M glycine at pH 2.0.



Fig. 7—Changes in current efficiency and alloy composition with rotation speed of cylinder electrode as a function of current density. Baths contained 0.3M Cr³⁺, 0.8M Ni²⁺, 0.4M Fe²⁺, 0.5M H₂BO₃, and 1.0M glycine at pH 2.0. Rotation speed was 0 rpm for Bath 1,1800 rpm for Bath 2, and 4000 rpm for Bath 3.

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Limiting Current Density

Due to the influence of hydrogen evolution and the corresponding rise in the pH of the catholyte layer during the deposition of Fe-Cr-Ni alloys, factors affecting the limiting current density of proton discharge at the surface of-a rotating electrode were investigated. A sodium sulfate solution with a pH of 2 was selected. The plateaus at -1.1 to -1.6 V (Fig. 9) represent the limiting current densities at different electrode rotation rates. The rise in current after each plateau is attributed to water decomposition.

The diffusion-controlled limiting current density for the rotating cylinder electrode is given by the following equation":

 $I_{L} = (0.79zF) (D^{0.664}) (v^{-0.344}) (r^{0.4}) (C) (w^{0.7})$

where zF is the faradic equivalence; D, the diffusion constant; v, the kinematic viscosity, r, the radius of the cylinder C, the bulk concentration of protons; and w, the angular velocity.

The limiting current densities in Fig. 9 plotted, against ψ^r gave straight lines (Fig. 10), indicating that the reduction rate of protons was diffusion controlled. The dependence of the limiting current density on the glycine concentration is shown in Fig. 10. All factors raising the limiting current density of proton discharge (e.g., an increase in the glycine concentration, a reduction in pH, or an increase in the rate of electrode rotation) resulted in a decrease in current efficiency for Fe-Cr-Ni alloy deposition.

During galvanostatic deposition of the alloys, depolarization caused by proton discharge shifted the electrode potential to a more noble direction and raised the pH in the catholyte layer. This affected the composition of the alloys and the quality of the deposits. The limiting current density decreased with the addition of chloride, agreeing with the observation that the current efficiency for Fe-Cr-Ni alloy deposition was increased by adding chloride ions.



Fig. 8—Changes in Current efficiency and alloy Composition with rotation speed of cylinder electrode as a function of current density. Baths contained 0.3M Cr³⁺, 0.8M NiCl₂, 0.4M Fe²⁺, 0.5M H₂BO₃, and 1.0M glycine at pH 2.0. Rotation speed was 0 rpm for Bath 1,1800 rpm for Bath 2, and 4000 rpm for Bath 3.

Conclusions

A bright alloy containing iron, 18 percent Cr, and 8 percent Ni was electrodeposited from a glycine bath. The corrosion resistance in 6N HCI was poor compared with that of stainless steel alloy produced by a thermal process. Also,



Fig. 9-Linear sweep voltammogram for iron cylinder electrode in 1.0 Na so, at pH 2.0.



Fig. 10-Effects of glycine and NaCl concentration on limiting current density for proton discharge in 1.0M Na,SO,at pH 2.0.

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the plated alloy had magnetic properties, whereas the austenitic stainless steel produced by the thermal process aid not.

The study indicated that proton discharge plays an important role in determining the composition and quality of the coating as well as current efficiency. Factors affecting diffusion to the catholyte layer correlated with changes in deposition potential due to the discharge of protons and pH variation in the catholyte layer. A more effective combination of addition agents for preventing hydrogen em brittlement and precipitation of metal hydroxides is needed.

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