ELECTRODEPOSITION OF IRON–NICKEL ALLOY FROM SULPHATE SOLUTIONS

***Ram Murti, Nusrat Javidani and Neerja Razdan**

Department of Applied Chemistry, Regional Engineering College, Hazratbal, Srinagar 190006, INDIA

The electrodeposition of Iron-nickel alloy was investigated from anodic sulphate bath containing $FeSO_4 . 7H_2O$ = 55.6 g/L $NiSO_4 . 6H_2O$ = 2.62 to 52.4 g/L; H_3BO_3 = 6.18 g/L; $MgSO_4 . 6H_2O$ = 22.8 g/L and sodium citrate = 75 g/L. The polarization curves, the percentage composition and the current efficiency of the electrodeposited alloy were determined as a function of electrolytic conditions such as pH, current density, temperature of the bath and citrate additions.

Iron-nickel alloys are known to possess a high degree of corrosion resistance and excellent mechanical properties. The standard electrode potentials of iron ($Fe^{2+} + 2e = Fe$; $E^\circ = -0.44V$) and nickel ($Ni^{2+} + 2e = Ni$; $E^\circ = -0.25V$) are only 0.19V apart and consequently the codeposition of Fe-Ni alloys is possible from acidic solutions of their simple salts. Some studies for electrodepositing this alloy have been made <1-4> where different bath compositions are used. Tsu <5> found that thiourea brings about a sharp change in the composition of the deposite. (The alloy composition changes from 8% Ni+92%Fe to 95% Ni + 5% Fe when 0.2g g/L thiourea was added to the bath). The addition of thiourea also changes the alloy structure from body centered to face centered.

De-Mars <6> has also reported the similar effect of thiourea on the composition changes of the deposited alloy.

The present studies were undertaken with a view to investigate the electrodeposition of this alloy further and to determine optimum conditions for electrodepositing it.

EXPERIMENTAL

The experiments were condcted in a H-shaped glass electrolytic cell with a porous diaphragm to seperate the two limbs. Each limb has a side tube. A cylinderical iron (MS. 152073/62) cathode (10 mm dia) was inserted through one of the side tubes via an air tight rubber cork. The electrode was welded to an insulated copper wire for external contact. The working surface of the electrode was polished by emery polishing paper. The iron electrode was then connected to a saturated calomel electrode through a lugin capillary just touching the surface of the electrode. Lead-silver(1% Ag) plate anode was placed in the other limb of the H-type electrolytic cell. The potential of the cathode w.r.to SCE was measured with a potentiometer (OSAW VP 6595) to an accuracy of 1 mV. The temperature of the cell and the calomel electrode were controlled in a water thermostat. Steady D.C. supply was obtained from a rectifier. The solutions used for electrodepositing parent metals and alloys were prepared from analytical grade chemicals (BDH) and distilled water.

The cathode current efficiency experiments were conducted in the same cell by replacing the iron cathode by a platinum cathode (2 cm^2 area). The cathode current efficiency calculations were based on the weight of the copper deposited in the coulometer and the gain in weight of the platinum cathode. Since the equivalent weights of Fe and Ni are very nearly equal (28 & 29 respectively), a mean equivalent weight of 28.5 was used for calculations of cathode current efficiency. After depositing the alloy on the platinum cathode, the cathode was washed with distilled water, alchol and then dried at 105°C in an air oven. The iron content in the alloy was determined volumetrically by Zummermann-Reinhard method <7>. The difference in the weight of the deposited alloy and the amount of iron gave the weight of nickel in the alloy.

RESULTS AND DISCUSSION

Polarization Curves

Fig(1) shows the cathodic polarization curves for the electrodeposition of iron, alloy and nickel from the baths having pure ferrous sulphate, mixture of nickel and ferrous sulphates and nickel sulphate respectively. The examination of the

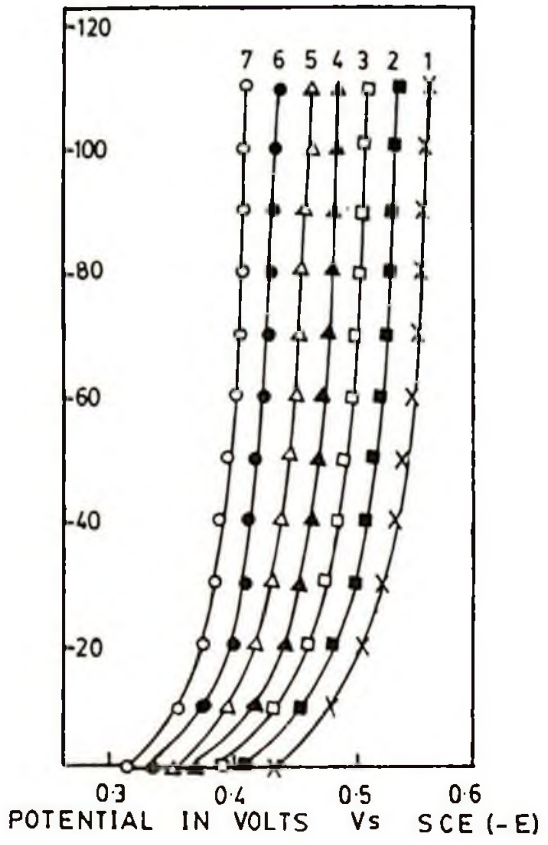


Fig. 1 Polarization in volts vs sce (E) and Ni elecrodeposition from baths (1) 1M $FeSO_4$. $7H_2O$ (2) 0.01M $NiSO_4$ $6H_2O$ + 1 M $FeSO_4$. $7H_2O$ (3) 0.05 M $NiSO_4$. $6H_2O$ + 1 M $FeSO_4$. $7H_2O$ (4) 0.1 M $NiSO_4$. $6H_2O$ + 1 M $FeSO_4$ $7H_2O$ (5) 0.2 M $NiSO_4$.$6H_2O$ + 1M $FeSO_4$. $7H_2O$ (6) 0.4 M $NiSO_4$. $6H_2O$ + 1M FeS_4. $7H_2O$ (7) 1M $NiSO_4$. $6H_2O$ at pH 3.0, t° = 30°C + 1°C.

figure reveals that the addition of nickel sulphate to the ferrous sulphate solutions shifts the cathodic polarization curves towards more positive direction thereby facilitating the codeposition of Ni and Fe The electrodeposition of Fe is attended by the highest polarization and polarization curve of the alloy deposition is always at a more positive potentials than that of iron, the position of which depends upon the amount of nickel sulphate in the bath.

On the otherhand, nickel in the alloy gets deposited at more negative potentials than it does from the solutions containing only nickel ions. This is perhaps due to the time lag in the formation of the complex alloy crystal lattice. This increases the polarization and that may account for greater negative potentials for alloy deposition.

As the temperature of the bath is raised, the polarization curves of Ni-Fe deposition shift to the positive direction. The temperature coefficient per degree of the shift of polarization curves is slightly more at lower temperatures than in the temperature range of 60° to 80°C. This can perhaps be attributed to the non-uniform composition changes during the alloy deposition in different temperature ranges. It is advisable to conduct electrodeposition of the alloy at higher temperatures because of the good quality of the alloy deposited. Higher temperatures increase the conductance of the bath and enhance the solubility of the salts. Also at higher temperatures, the diffusion layer thickness decreases due to the good agitation brought by convection currents.

The pH value could not be raised beyond 5.5 due to the commencement of the hydrolysis. Within the experimental region, the increase of pH of the bath brings a positive shift in the polarization curves. The evolution of hydrogen was more intense at lower pH values than at higher ones.

Alloy Composition

The alloy was deposited by varying conditions of concentration, temperature, pH and current density. Sodium citrate was used as an additive. Boric acid was used in all the experiments to control the pH changes which occur due to the discharge of hydrogen ions. Mg SO_4 was also added to the bath for increasing the conductance.

Effect of Nickel Sulphate

As is seen in fig 2, the cathode current efficiency increases from 75 to 79% when the nickel sulphate concentration is increased from 2.6 to 52.4 g/L and nickel content increases from 22 to 31% while the iron content drops marginally from 53 to 48%. The deposits obtained were silvery bright in appearance at higher nickel sulphate concentrations. It has been observed that the amount of iron in the alloy predominates in spite of the fact that an examination of the individual polarization curves suggests that nickel should predominate in the alloy.

Effect of Temperature

Increase of temperature raises the nickel content of the alloy and decreases that of

iron whereas the overall current efficiency rises from 79 to 82%. The shapes of curves are similar to that in Fig.2. This is due to the shift of polarization curves

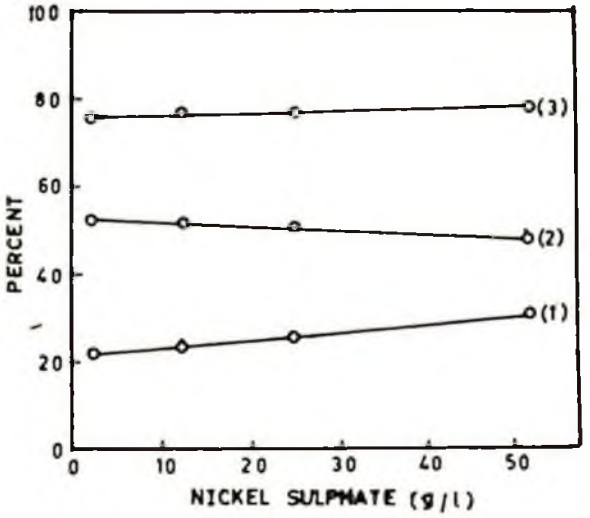


Fig. 2 Effect of nickel sulphate (g/L) on NiFe alloy composition in the bath. ($FeSO_4.7H_2O$ =55.6 g/L * $MgSO_4$ $7H_2O$ = 49.26 g/L) t°=25°C ± 1°C, pH = 2.5, c.c.d = 50 ma/cm²
(1) % of Nickel vs $NiSO_4$ in the bath
(2) % of Iron vs $NiSO_4$ in the bath
(3) Cathode current efficiency vs $NiSO_4$ in bath

in the favourable direction for the discharge of nickel ions and for decreasing the alloy deposition overpotential as compared to that of hydrogen ion discharge. Silvery bright deposits were obtained at 60°C. At lower temperatures they were dark and grey.

Effect of pH

The percentage of Ni in the cathode deposite is the lowest (30.5%) at pH=2.5 and the highest (34%) at pH=5.5. The current efficiency of the alloy deposition at pH 2.5 is 78.6% and increases somewhat as the pH is increased. The iron content in the alloy decreases (from 50% to 45%) with the increase of pH from 2.5 to 5.5. (The graphs are similar to that in fig.2). This can be attributed to the shift of cathodic polarization curves to more favourable +ve direction for the electro desposition of Ni. The deposits obtained at pH 5.5 were brighter and of silvery appearance. The experiments could not be performed beyond pH 5.5 as the solutions start hydrolysing.

Effect of Current Density

The iron content in the alloy decreases slightly with the increase in c.d; but the nickel content of the alloy increases from 27% to 31% when c.d is raised from 10 to 50 mA/cm². (The grpahs are similar to that in Fig.2).- The iron content in the alloy decreases slightly with the increase in c.ds; nickel content increases from 27% to 31% when the c.d is raised from from 10-50 mA/cm². (The graphs are similar to that in Fig.2). The current efficiency increases very little (80 to 82%). The current efficiency increase is due, perhaps to the smaller increase in overpotential of the alloy deposition than that of Hydrogen. The alloy deposits at lower c.d were dull and grey but at higher values were black which on rubbing became bright. The black colour of the deposits at higher c.d is perhaps due to the bigger and irregular crystals which on rubbing become bright. The black colour may also be attributed to the co-deposition of Ni black or oxide of iron or nickel or both.

Effct of Sodium Citrate on the percentage composition of the Alloy

It is clear from the fig 3 that nickel content decreases in the alloy with the

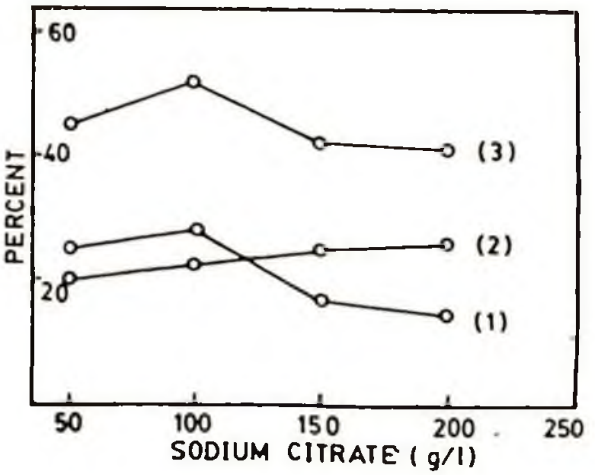


Fig. 3 Effect of sodium citrate additions (g/) on iFe alloy composition in the bath (55.6 g/L $FeSO_4.7H_2O$, 52.4 g/L $NiSO_4.6H_2O$ & 49.2 g/L $MgSO_4.7H_2O$) t° = 25°C + 1°C, pH = 2.5, c.c.d. = 50 ma / cm²
(1) % of Nickel
(2) % of Iron
(3) Cathode current efficiency

increase in addition of sodium citrate while iron content increases. The current

efficiency on the whole at first increases and becomes maximum and then decreases. This decrease may be attributed to the complex formation with Ni and Fe which reduces the activity of the metals. This act favours more intense evolution of hydrogen at the cost of alloy deposition.

CONCLUSION

The Ni-Fe alloy is best deposited under the following conditons

$FeSO_4.7H_2O$= 55.6 g/L; $NiSO_4.6H_2O$=52.4 g/L;

$MgSO_4.6H_2O$= 22.8 g/L; H_3BO_3 =6.18 g/L;

o.c.d = 50 mA/cm², t = 50°C; pH = 3.5 and sodium citrate= 75 g/L.

Anodic and cathodic compartments should be seperated by a porous diaphragm.

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