Effect of Inorganic Impurities in Nickel-Iron Plating Baths

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Studies on the effect of metallic impurities in nickel and nickel-iron baths indicate that the latter is more tolerant to chromium, copper and zinc contamination in addition to its inherent tolerance to iron contamination. Of the two nickel-iron baths studied, citrate bath showed more promising results than gluconate bath.

Nickel-iron alloy deposition is receiving much attention in decorative field as a cost saving technology for nickel(1-4). This is generally carried out in presence of a suitable complexing agent. In the earlier communications(6,9), the authors have discussed about the performance of trisodium citrate, sodium gluconate, and sodium sulphosalicylate as suitable complexing agents for the alloy deposition(10). It is found that gluconate gives favourable results with respect to mechanical and physical properties like internal stress, hardness, levelling, reflectivity, rate of deposition etc.

It is well known that substances present in small amounts as contaminants have a marked effect upon the physical properties of deposits and current efficiency of the electrolytic process(11). As a rule, bright plating processes are much more sensitive to presence of contaminants than dull plating process. In this paper, the authors discuss the effect of inorganic impurities like copper, zinc and chromium in nickel-iron baths containing citrate or gluconate as stabilisers and compare the results with that obtained in bright nickel bath.

EXPERIMENTAL

The bath compositions given in Table-1 are used for depositing bright nickel and nickel-iron alloy. The solutions were made up with laboratory grade chemicals and the pH level was adjusted. The solutions were given activated carbon tratment to remove the organic impurities and low current electrolysis treatment to remove the metallic impurities. In the case of nickel solution, high pH treatment was also given to get rid of iron impurities After filtration, the pH of the above solutions were readjusted. Rolled nickel anode for nickel plating and dual anodes for nickel-iron plating were used. A brightener composition consisting of saccharin, Butyne-1,4-diol and nephtalene trisulphonic acid were used (Table 1). The bath was operated at 60°C. Stock solutions of Ferrous sulphate, copper sulphate, chromic acid and zinc sulphate were prepared using AR grade chemicals at concentrations of 1 g/l, 1 g/l, 1 g/l and 5 g/l respectively.

A 267 ml glass Hull cell was used for determining the effects of inorganic contaminants in the above three baths. The Hull cell was kept in a water bath to maintain the solution at the desired temperature. Mechanical agitation with a glass rod near the cathode was resorted to at the rate of 2 strokes/minute. A cell current of 1 A was applied for 5 minutes. Cathode current efficiency.

TABLE 1

BATH COMPOSITIONS USED FOR BRIGHT NICKEL AND NICKEL-IRON ALLOY

	Nickel	Nickel-iron	Nickel-iron
Nickel sulphate g/l	250	75	75
Nickel Chloride g/l	30	75	75
Ferrous sulphate g/l	---	15	15
Stabiliser:-			
Trisodium citrate g/l	---	30	--
Sodium gluconate g/l	---	--	30
Boric acid g/l	40	45	45
Brightener:-			
Saccharin g/l	1	3	3
Butyne diol g/l	0.4	0.4	0.4
Naphthalene trisulphonate (sodium salt) g/l	1	1	1
Condition:-			
Current density A/dm^2	4.2	4.2	4.2
pH	4	3	3
Temperature °C	60	60	60

was determined using brass cathodes. Internal stress of the deposits was measured using Hoar and Arrowsmith method and hardness of the deposits were measured using knoop indendation method at 25 grams load.

RESULTS AND DISCUSSION

The most striking feature of nickel-iron bath is that one need not worry about iron contamination. In nickel-iron baths, iron contents varying from 2-5 g/l is added to produce alloys having 15-35% iron. Here iron is co-deposited with nickel to produce the alloy. Because of the presence of effective complexing action, iron exists in the ferrous state and any ferric iron formed is converted to slouble complex state which allows easy codeposition of iron with nickel with out loss of ductility and cohesion.

Nickel electrolyte does not contain any complexing agent. So insoluble ferric iron formed at the cathode, solution interface results in brittle and semibright deposits (Fig. 1) even at 50 ppm

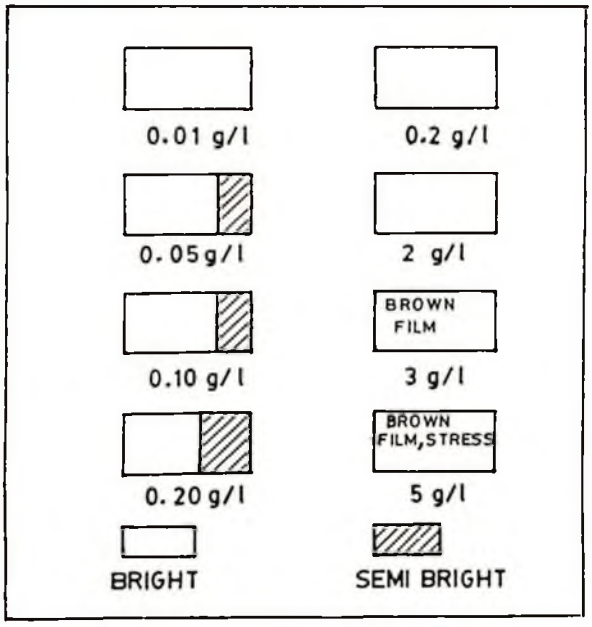


Fig. 1 Effect of iron impurity in bright Nickel and Nickel-Iron bath.

concentration level. Iron impurity as $Fe(OH)_3$ in the colloidal or precipitated state causes roughness (12, 13) of the deposit and gives rise to enhanced internal stress as indicated in Fig. 2, in addition to increase in porosity and reduction in cathode current efficiency considerably (Table-2). Table-3 gives the hardness values obtained with nickel and nickel iron deposits obtained in presence of iron. In spite of higher hardness values, nickel-iron deposits have lower stress and higher ductility.

Chromium contamination is one of the most harmful impurity in bright nickel and nickel-iron baths at all current densities (14, 15). In nickel bath in the absence of any complexing agent, the hydrogen evolution reaction results in hydroxide formation. In the medium current densities, a bloom is observed and cracked streaks appear in the coating while in low current densities, the deposit tends to be brown in colour and under extreme conditions no deposit could be obtained at all.

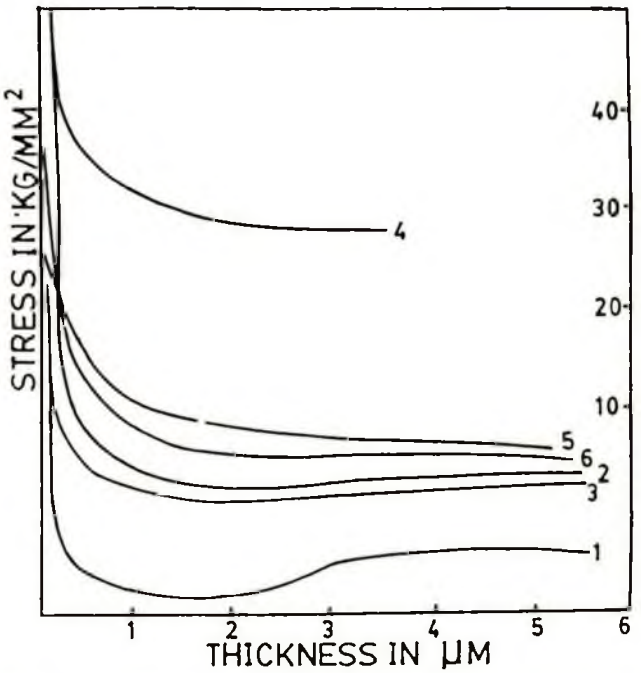


Fig. 2 Effect of iron addition on internal stress in bright Nickel and Nickel-Iron baths.

TABLE 2

EFFECT OF METALLIC IMPURITIES ON THE CATHODE EFFICIENCY IN BRIGHT NICKEL AND NICKEL-IRON BATHS

	Concentration g/l	Cathode Current Efficiency % Ni	Ni-Fe citrate	Ni-Fe gluconate
	-	99	90	94
Cu	0.05	98	90	90
Zinc	0.10	98	90	88
Iron Fe^{2+}	1.0	90	92	92
Fe^{3+}	0.10	80	90	90
Cr^{6+}	0.05	55	58	58

TABLE 3

HARDNESS VALUES WITH IRON ADDITION IN BRIGHT NICKEL AND NICKEL IRON BATHS

Concentration of iron g/l	Hardness VHN	
	Nickel	Nickel-iron
0	580	660
0.100	620	660
0.200	650	''
0.300	680	''
1	Stressed	680
2	''	700

Macnaughten and Hammond (16) have recommended a procedure for the removal of chromium, which consists of the addition of ferrous sulphate in an amount sufficient to reduce all hexavalent chrominum to less harmful trivalent state followed by high pH treatment to remove the precipitated hydroxides. Since in nickel-iron baths, ferrous sulphate is present in appreciable quantity, reduction of hexavalent chromium is a continuous process, making the baths more tolerant to chrominum contamination than nickel baths. Of the two alloy baths,gluconate bath is more susceptible to chromium contamination than the citrate bath which can be attributed to the lower current efficiency and higher rate of hydrogen evolution experienced in citrate baths which results in the quicker reduction of hexavalent chromium.

The internal stress measurements made with nickel and nickel-iron baths with chromium addition also indicate that higher stress values are obtained in nickel bath even with slightest traces of chromium and with nickel-iron baths it is slightly lesser.

Copper is another most deleterious impurity in nickel and nickel-iron baths It enters into the solution by the dissolution of busbar contacts and also through impure salts and anode. Copper in bright nickel solutions causes dull dark deposits in low current densities and a general fogging in other regions. Deposits obtained were satisfactory upto 0.05 g/l copper contamination, but above 0.1 g/l,roughness and darkness appear. This effect is more predominant in plating intricate shaped objects, wherein the dark deposits not only spoil the appearance and enhance rejects, but they lessen the corrosion resistance of the deposit, due to the porous nature.

As experienced in earlier cases, nickel iron citrate bath shows more tolerance to copper impurity than the gluconate bath. This may be attributed to the lesser complexing ability of the gluconat ion than the citrate ion. Presence of copper does not appreciably alter the internal stress of the deposits in all the three baths within the concentration limits under investigation.

Zinc enters the plating solution during plating of zinc die castings, or through the impure salts and anodes. As little as 0.05 g/l of zinc as impurity causes slight dullness in the low current density region and at concentrations above 0.1 g/l zinc causes blackness with striations. This behaviour is more predominant in bright nickel and nickel-iron gluconate baths than in citrate bath which is tolerant upto 200 ppm zinc contamination. J.K.Dennis and J.J.Fuggle (17) state that such behaviour arises only in saccharin containing solutions and in presence of high chloride concentration in a bright nickel bath, such striations do not appear under the same concentrations of saccharin and zinc ions. They attribute this effect to the complexation of zinc ions with excess chloride ions which prevents interaction with saccharin. We can attribute the higher tolerance of citrate bath to the more efficient complexation of the impurities than the gluconate bath. In confirmation with this fact, slow precipitation of ferric iron starts in gluconate baths on storage which is not experienced in the case of citrate bath.

Though the above confirm that citrate bath shows more tolerance to metallic impurities than gluconate bath, due to the efficient complexation, the same fact makes the removal of impurities slightly difficult when their concentration limit exceeds the recommended limit. In the case of gluconate bath, copper and zinc impurities are easily removed by low current density treatment at the operating pH. But in citrate bath, the above treatment should be carried out at somewhat lesser pH levels (pH 2-2.5) in order to make the complexes less stable.

CONCLUSIONS

Studies on the effect of metallic impurities in nickel and nickel-iron baths indicate that the latter is more tolerant to chromium, copper and zinc contamination in addition to its inherent tolerance to iron contamination. Of the two nickel-iron baths studied, citrate bath showed more promising results than gluconate bath.

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