

ELECTRODEPOSITION OF CHROMIUM-NICKEL-IRON ALLOY COATINGS FROM NON-TOXIC ELECTROLYTES

N. V. Shanmugam^a and S. John^b

Central Electorchemical Research Institute, Karaidudi 630 006, India.

a) nvshartmuqam@cecric.res.in b) sjohnimf@cecric.res.in

ABSTRACT

Maximum corrosion resistance among iron group alloys has been observed for 50Ni50Fe and 70Co30Ni binary alloys depending upon deposit composition and microstructure, which are controlled by solution composition and deposition variables. Renewed interest has been shown on the development of environment-friendly electroplating baths enabling one to apply chromium-nickel coatings.

Chromium-nickel-iron alloy plating from non-toxic acetate based trivalent electrolyte, has been examined under different Hull cell current values. The resulting deposits were examined for their elemental content, micro hardness and their surface topography with SEM. This alloy contains chromium 3%, nickel 65% and iron being 32%.

KEYWORDS : Alloy electrodeposition, Cr-Ni-Fe

INTRODUCTION

Chromium-nickel-iron alloy electrodeposits have gained great importance [1-4] in recent years as they provide an economical substitute for stainless steel without prejudice to the functional advantages. The Fe-Ni-Cr samples electrodeposited using a chloride bath along with DMF [5,6], resulted in deposits with an average composition of 25% Cr, 25% Ni and 50% Fe. Electrodeposited iron alloy film (8-10% Ni and 17-19% Cr) corresponding to SS303 stainless steel from a bath containing chromium sulfamate, nickel sulfamate and ferrous sulfamate in a specified molar ratio has been claimed by a Japanese patent [7].

Alloys containing 20 % iron in addition to chromium are produced by co-depositing chromium carbide from a nickel-iron based solution and heat treating in hydrogen to form nickel-iron-chromium alloys. Hardness after heat treatment is 215 HV. Approximately 0.8% C remains in the nickel iron-chromium alloy, which may account for its higher hardness of 332 HV.[8]

Inconel 600 is a standard engineering alloy for use in severely corrosive environments at elevated temperatures [9]. It is a Ni-Cr-Fe alloy containing 15.5% Cr, and 8% Fe. Further, an American patent [10] discloses an aqueous plating solution containing a trivalent chromium salt, formic and / or acetic acid salt, a bromide, borate and ammonium ions. The advantages of the trivalent chromium processes over the hexavalent chromium process are fewer environmental concerns due to the lower toxicity of trivalent chromium, higher productivity, and lower operating costs. Use of trivalent chromium also reduces waste disposal problems and costs.

Despite frequent claims to the contrary, especially in the patent literature, all these attempts have proved unacceptable in commercial practice. A commercially acceptable plating

solution must provide a more or less even deposit over the whole work piece. To overcome burning at high current density areas and inability to plate into recessed areas, it has been proposed to form complexes.

A process and bath for electroplating Ni-Cr alloys from an electrolyte containing 50-125 g/L of Chromium chloride, 10-125 g/L of nickel chloride, 10-115 g/L of formic acid, 25-50 g/L of boric acid; and 50-100 g/L of sodium citrate at pH of 1-5 and at 20- 60°C has been claimed by Lashmore [13, 14]. Co-deposition of Cr particles during Fe-Ni plating, followed by heat treatment, is mentioned.

Typical iron group alloy plating solutions are operated using sulfate or mixed sulfate-chloride baths containing stress reducing and grain refining agents, at room temperature around a pH of 3 [15].

The mechanical properties of electroformed Ni-Fe microstructures [16], are superior to those of microstructures formed by casting or powder metallurgy. The potential properties of thin and thick deposits of nickel-chromium-iron alloys are discussed by Sitnikova et.al [17]. Recently, residual stresses in electrodeposits of nickel and nickel-iron alloys have been reported by Hadian and Gabe [18]. Structure-property relationships of iron group alloys were studied in detail by Myung and his team [19-22]. The electrodeposition of these Fe-Ni alloys is characterized by so called anomalous behavior; the less noble metal, in this case iron, deposits more readily out of the plating bath than the more noble nickel. This phenomenon is not yet fully understood and requires a more rigid control of the plating conditions [23].

Alloys containing 20-40% Cr, balance Fe were deposited at 100-300 mA/cm² in formate solutions containing chromium chloride, ferrous chloride, glycine and boric acid with a current efficiency of 55-65%, that is kept at a pH of 2.8. The influence of current density temperature and pH on the composition and characteristics of the alloy deposits is described [24]. Effect of aluminum chloride in chloride baths has been studied by Domnikov [25].

EXPERIMENTAL PROCEDURE

The potential properties of thin deposits of nickel-chromium-iron alloys are discussed using Hull cell studies. The operating parameters were studied at 1, 2 & 5 A for 5 minutes at temperature of 50°C and Hull cell patterns were recorded.

To study the hardness of the alloy deposits, coatings were prepared on copper panels of size 25 x 100 x 3mm³ after proper pretreatment. The hardness of alloy plated at a CD of 60mA/cm² for a period of 60 minutes on copper substrates (20-25 µm thick) under a load of 50 g was measured, using a conventional Vickers micro hardness tester SHIMADZU HMV, Japan and an average of three readings was taken from this experimental test.

The topography of samples plated from the electrolytes used for hardness measurements, were also examined for their secondary electron image at 1000x using HITACHI 3000H, Scanning Electron Microscope.

Surface composition was studied using X-ray analytical microscope, XGT 2700 model, and Horiba make, Japan. The surface composition of various elements present in the

LEGENDS FOR RECORDING HULL CELL PATTERNS

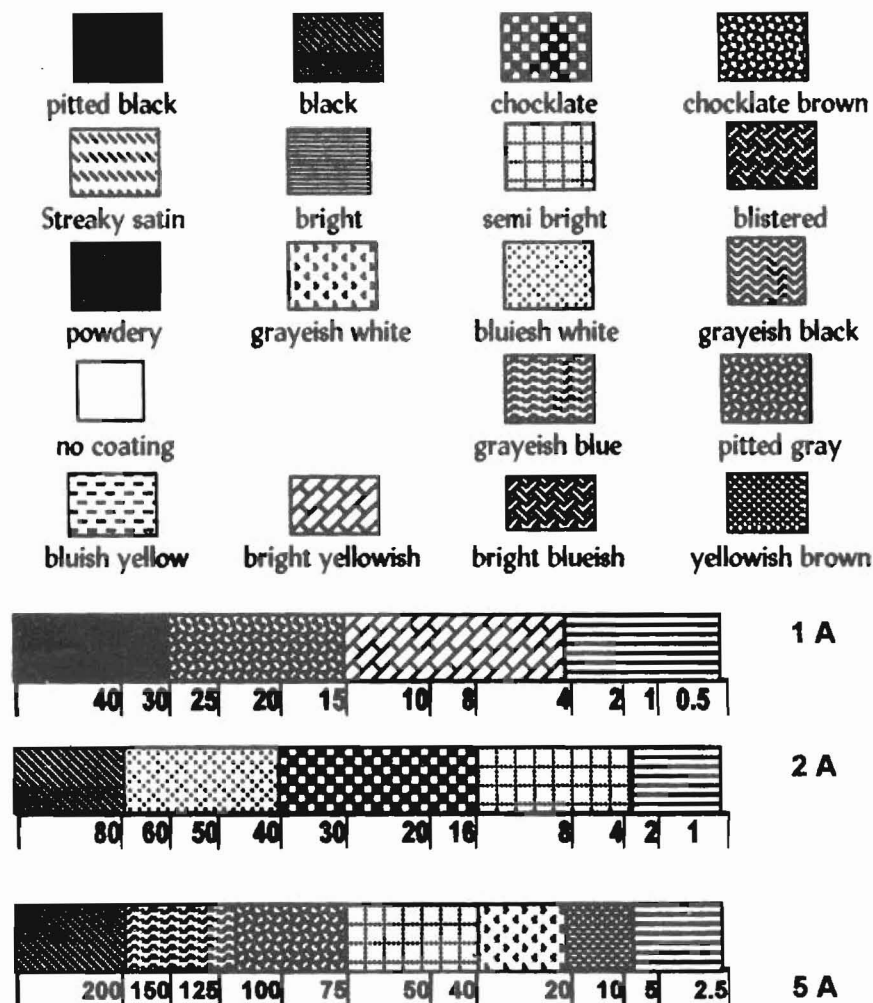


Fig. 1 : Appearance of Hull cel panels obtained at different cell currents for 5 minutes from solution containing Nickel acetate 10 g/L, Chromium acetate, 24 g/L, Ferrous ammonium sulfate, 80 g/L, Boric acid, 30 g/L, Ascorbic acid, 60 g/L, Temperature 50-C

alloy deposits, obtained from these electrolytes are examined and the results are recorded.

RESULTS AND DISCUSSION

Fig 1. Shows the appearances Cr-Ni-Fe deposits obtained over Hull cell panels plated at different cell currents of 1,2 & 5A for 5 minutes from Cr-Ni-Fe plating solution having higher iron salt along with ascorbic acid containing nickel acetate 10 g/L, chromium acetate

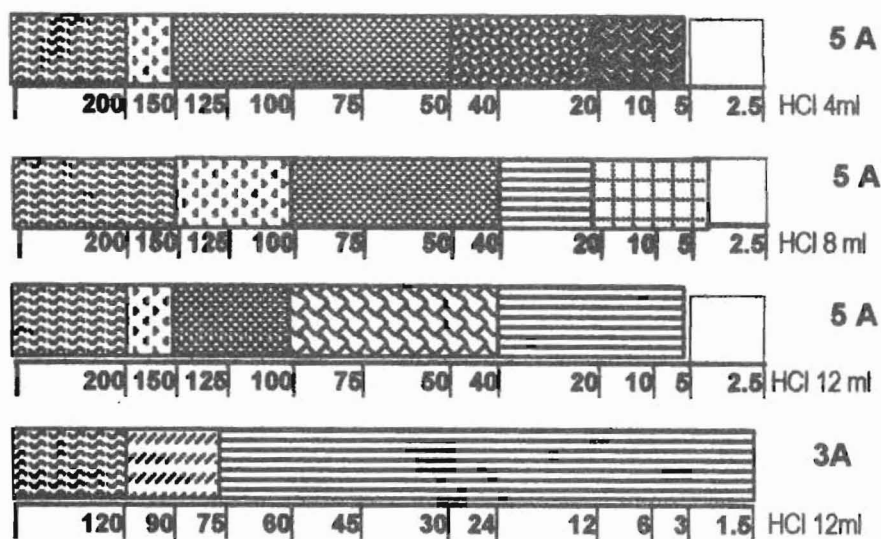
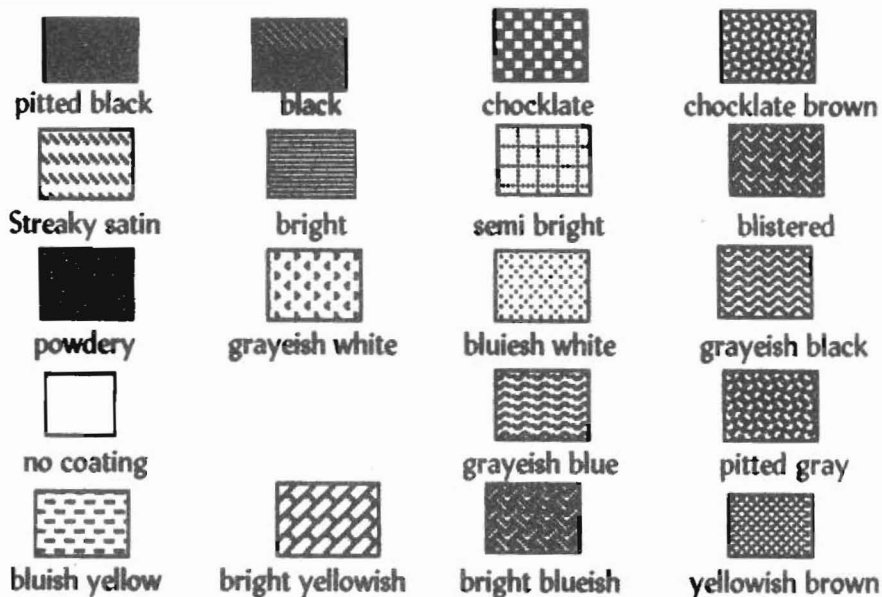


Fig. 2 : Influence of Hydrochloric acid on the appearance of Hull cell panels obtained at different cell currents for 5 minutes from solution containing Nickel acetate, 10 g/l, Chromium acetate, 24 g/l, Ferrous ammonium

24 g/L, ferrous ammonium sulfate, 80 g/L, boric acid 30 g/L, ascorbic acid 60 g/L, temperature 50°C.

1 A Hull cell panels indicate that bright Cr-Ni-Fe alloy deposit could be obtained at low CD values namely 0-4 mA/cm² region. Yellowish bright coatings are obtained between 4-15

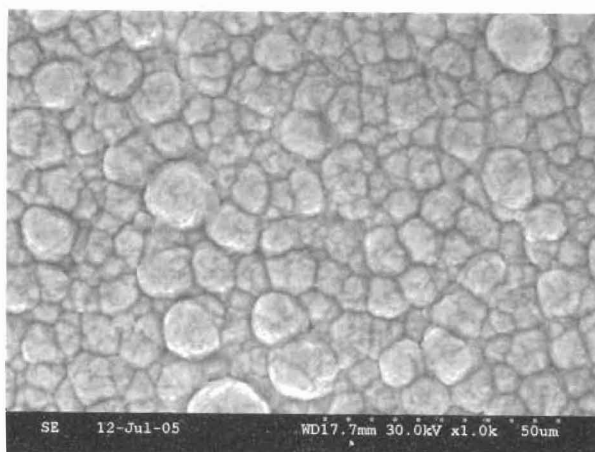


Fig. 3 : Secondary electron image of Cr-Ni-Fe deposit at 1000 x plated at a CD of 60mA/cm² for 15 minutes, from Acetate based Nickel - Chromium - Iron bath containing Nickel acetate 12 g/l, Chromium acetate 100 g/L, Ferrous ammonium sulfate 12 g/L, Boric acid 30 g/L, Ascorbic acid 60 g/L, at 50°C



Fig. 4 : Effect of chloride addition on the Secondary electron image of Cr-Ni-Fe deposit at 1000 X, plated for 15 minutes duration at a CD of 60 mA/cm², from solution containing Nickel acetate 10 g/l, Chromium acetate 24 g/l, Ferrus ammonium sulfate, 80 g/l, Boric acid 30 g/l, Ascorbic acid 60 g/l, Hydrochloric acid 4, 8 & 12 ml/l respectively, at 50°C

Effect of HCl addition - 12 ml /L at 3A cell current

3A Hull cell panel indicate that bright Cr-Ni-Fe alloy deposit could be obtained at low CD values namely 0-75 mA/cm² region. Streaky and satin like deposits are obtained between a CD range of 75-120 mA/cm². Grayish blue coatings are obtained at and above 120 mA/cm².

STUDIES ON HARDNESS

The hardness of the deposits from acetate and acetate-chloride electrolyte electrolytes are shown in Table 1, and 2 respectively.

Table 1 - The elemental analysis and hardness of the deposits obtained from acetate based electrolytes at different CD values plated for 5 minutes.

Acetate bath	Current Density, mA/cm ²	% of element in deposits			Hardness Kg/mm ²
		Cr	Ni	Fe	
					VHN _{50g}
	60	1.75	66.08	32.17	Not measurable
	12	1.64	65.17	33.19	
	300	3.92	69	27.08	

Table 2 : The effect of chloride addition on hardness of the deposits from acetate-chloride electrolytes at a Current Density of 60 mA/cm² plated for 5 minutes

Acetate bath + HCl	Current Density, mA/cm ²	% of element in deposits			Hardness Kg/mm ²
		Cr	Ni	Fe	
					VHN _{50g}
4mL/L	300	3.09	65.77	31.14	183
8mL/L	300	3.21	65.53	31.26	
12mL/L	300	3.2	65.5	31.3	
12mL/L	180	3.19	65.82	30.99	

STUDIES ON TOPOGRAPHY USING SEM

The topography of samples plated for hardness measurements, were examined for their secondary electron image (sei) at 1000X using Hitachi 3000H, Scanning Electron Microscope, Canada and are shown in Fig 3 -4 respectively,

Acetate based nickel - chromium - iron bath produced fine grained deposits as shown in Fig 3 whereas the addition of chloride resulted in fine grained deposits with agglomeration of grains as seen in Fig 4, probably owing to the increased iron content of 22%.

STUDIES ON ELEMENTAL ANALYSIS OF SURFACE COMPOSITION

The surface composition of various elements present in the alloy deposits, obtained from XRF analysis produced in various electrolyte are shown in Table 1-2.

The percentage of chromium remains around 1-2% for acetate based solutions under study, whereas the addition of chloride resulted in an slightly increased value of 3%. Similarly the iron content in the deposit gets increased from 10-20% to 31 % at a CD values of 300 mA/cm². The percentage content of Ni & Fe do not show any regular trend with CD values.

CONCLUSION

Chromium - nickel - iron alloy plating bath has been examined for the production of alloy deposit and their operating condition under different Hull cell current values from a non-

toxic trivalent electrolyte from acetate based electrolytes and with the addition of chloride. The resulting deposits were examined for their elemental content from these electrolytes. Thick deposits were produced when plated at a cathode CD of 60 mA/cm² for 60 minutes: the micro hardness and their surface topography were analyzed with SEM.

Based on the above experimental results, a mixed acetate electrolyte with little addition of hydro chloric acid was formulated and their operating characteristics and hardness and other surface properties were reported. This alloy contains chromium 3%, nickel 65% and iron being 32% and exhibit a hardness value of 183 VHN_{50g}

BIBLIOGRAPHY

1. S. Gowri, B.A. Shenoj, and P.L Elsie, Metal Finishing Journal. Oct 1971.p254.
2. W. Machu, and M.F.Ghandour, Werks tooffe und Korrosion , 11,[1960] 420.
3. L.A. Zytner et.al., J. Appl. Chem, USSR, 35, [1962] 1020
4. L. Szira"ki, E. Kuzmann, M. EI-Sharif, C.U. Chisholm, G. Principi, C.Tosello, A.Ve'rtres, Electrochemistry Communications 2 [2000], 619-625
5. M. EI-Sharif, A. Watson, C.U. Chisholm, Trans. IMF 64 [1988], 149
6. M. EI-Sharif, A. Watson, C.U. Chisholm, Trans. IMF 66 [1988], 34
7. Ishiguro Takayoshi, JP62238389, [1989]
8. S.Alec Watson, Nickel Development Institute, Toronto. Ontario Canada <http://www.pfonline.com/articles/119604.html>
9. <http://www.roymech.co.uk/Useful Tables/Matter/Nickel.html>
10. Gyllenspetz, J. andd Renton, S. (to Albright + Wilson) U.S. Patent 3,954,574 [1976]
11. Bride J.E. (to DuPont), US Pat. 3,706,636 (1972).
12. J. C. Saiddington et al., Plating, pp. 923-930, Oct. 1974.
13. Lashmore, D.S. US Pat. 4461680 (1984)
14. ASM Handbook, Surface Engineering, 5 [1994] 270-273
15. A.Brenner, Electrodeposition of Alloys, Principle and Practice, vol. II, Academic Press, New York, 1963, Chapter 31, p. 239.
16. J.T.Ravnkilde, V.Ziebart, O. Hansen and H. Baltes, "Mechanical characterization of electroplated nickel-iron", Sensors and Materials 12, 99-108 (2000).
17. Sitnikova T.G., Sitnikov A.S., Protection of Metals, 39, 3 [2003] , 241-244
18. S. E. Hadian and D. R. Gabe, Surface and Coatings Technology,122, 2-3, [1999], 118-135
19. N. V. Myung and K. Nobe, " J. Electrochem. Soc., 148(3), C133-C144,2001.
20. D. Kim. D.-Y. Park, B. Y. Yoo, P. T. A. Sumodjo, N. V. Myung, Electrochim. Acta, 48, 819-830, 2003.
21. N. V. Myung, D.-Y. Park, E. Urgiles, T. George Electrochim. Acta 49, 4394-4404, 2004
22. K. M Yin, H. F Huang, Y.T Lin, Trans. IMF, 83, 2 [2005], 82-90.
23. Metal Finishing Guidebook And Directory Issue '93k, Volume 91, Issue 1A, Elsievier Science Publishing Company, Inc., New York, January 1993.
24. T . Hayashi, A Ishihama, Plating and Surface Finishing. Vol. 66, no. 9, pp. 36-40. Sept. 1979
25. Larissa Domnikov, Met. Finish., 2,[1979] 57-63