International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.5, No.5, pp 2405-2409, July-Sept 2013

Optimization Of Black Coatings By Electro Deposition And Evaluation Of Optical Properties

P.A.Jeeva[1], S.Karthikeyan[2]*, S.Narayanan[1]

[1] School of Mechanical Building Sciences, VIT University,Vellore-632014,India
[2] Centre for Nanobiotechnology, VIT University,Vellore-632014,India

*Corres. Author : skarthikeyanphd@yahoo.co.in

Abstract: The optical properties of black coatings obtained by trivalent chromium and Ni-Cu-Co based electro plating baths were evaluated. The formulations of black coatings were arrived by incorporating of extraneous metals into chromium and nickel. The influence of plating time, bath ingredients, pH and current density were studied. SEM images confirmed the presence of chromium, nickel, copper and cobalt metals in the coatings. The hardness values of black coatings were altered after annealing at 300^{o}C.
Keywords: Black coating, absorption, emission.

Introduction

The development of trivalent chromium coatings deserves much attention because of its eco-friendliness and optical properties for solar energy applications. The trivalent chromium coated metals exhibit high hardness, wear and corrosion resistance[1-3] incomparable with Hexavalent chromium. However, the development of black coatings based on trivalent chrome throws much light in recent years[4]. The stability of plating bath as well as the intensity of black colour is a challenging factors when formulating trivalent chrome based black coatings. The use of nickel alloys in black coatings found less important owing to its powdery deposit after annealing[5-6]. Hence, the development of black coatings based on trivalent chrome and nickel based alloys pay much consideration in recent days. In this paper, we have attempted to formulate trivalent chrome black coatings and nickel alloy deposition by incorporating copper and cobalt metals in an optimized plating bath. The results are presented and discussed.

Experimental

Mild steel of area 2 cm x 5 cm with the following composition was used. Mn=0.05%; C=1.2%; Si=0.05%;Fe=remainder. The mildsteel panels were mechanically polished and degreased by acetone. Then, the panels were subjected to nickel deposition by Wurtz-strike bath for one minute which is preferred undercoat for selective black coatings[7-8]. The steel samples were removed and washed with distill water. Finally, electro depositions of trivalent black chrome coatings were carried out.

The optimized bath was arrived after trial and error experiments from nearly six formulations. The composition of trivalent chrome bath(chromium was added in the form of its chloride salts) used in the present study is given in table 1. The hardness of the resultant black coatings were evaluated by Vickers micro hardness tester at a load of 100 g. An indentation was made on coatings, from the diagonal of indentation hardness was evaluated. The absorption and emission values were obtained from UV-Visible Shimadzhu spectrometer in the frequency range of 10 to 700 nm for measuring absorption. The reflectance in the IR region was taken as emission of the black coatings[9].

Surface analysis of the optimized coatings was examined using SEM analysis. The SEM was instrumented with Silicon solid state X-ray analyzer and a system for qualitative and quantitative analysis of metals in the coatings.

Results and discussion

Influence of plating time and current density

In this test, the time of plating process has been varied from 20 to 350 seconds while keeping all other parameters as fixed values. The absorption and emission values of coatings varied with respect to plating time. The electro deposition of trivalent black chrome coatings were carried out in 267 ml capacity of Hull cell to optimize the current density, pH and plating time.

The optimized current density was 400 mA/cm^2. The obtained film contains 99.1% chromium and 0.9% cobalt by weight. A comparative study between A/E ratio of black films obtained in chromating solutions with varied concentrations of bath ingredients were conducted and the results are presented in table 2. It was noticed that the plating time has significant effect on the optical properties of the coatings. As the thickness of the coatings increases, both absorption and emission increase to some extent.

Influence of pH

The pH of the plating process was followed regularly during deposition. The solution pH after mixing of all bath constituents was maintained by the addition of dilute H_2SO_4 and dilute NOH. If the pH is low(less than 2.5), the deposit was yellowish colour. When the pH is 3.5, the deposit was grayish black and non-uniform. An intensive black was visualized when the pH was 4.6. beyond that concentration, the plating bath became turbid due to the precipitation of chromium and cobalt as their hydroxides. At higher pH values, the deposit was non-uniform and blue.

Influence of Cobalt

Keeping the bath composition with other plating factors intact, the concentration of cobalt metal was varied between 1gram and 7 gram per litre in a bath. The cobalt addition were done in the form of sulphate and nitrate salts. It was observed that as the concentration of cobalt increases, the absorption values (α) first and decreased. There is no direct relationship was found between cobalt metal concentrations and emission. The optimum values of optical properties were got at the concentration of cobalt was 6.75 gram per litre.

Hardness values

Micro hardness of the as plated trivalent chromium bath was 380 V.H.N which was enhanced to above 450 after annealing at 300^{o}C. The enhancement of hardness values may be due to precipitation hardening process of Cr-Co.

Surface morphologies

Figure 1 and 2 represent the SEM images of uncoated and coated mild steel taken at the magnification of X,500. Figure 2 showed that the uniform, layered formation of chromium and cobalt deposits. The existence of cobalt has not altered the structure of coating matrix. However, the cobalt metal remarkably contributed for intensification of black colour which resulted the enhancement of A/E ratio of black coatings.

Table 1 Formulation of various trivalent chromium baths

S.No	Trial baths	Optimized bath
1.	$CrCl_3$ = 22 g/l H_2SO_4 = 22 g/l H_2O_2 = 53 g/l FAS = 0.25 g/l $CoSO_4$ = 2.1 g/l NH_4HF_2 = 1.8 g/l pH = 2-2.5 Current density= 200-450 mA/cm^2 Plating time = 4-5 min.	Cr metal(Trivalent) = 54.45 g/l Co metal = 6.75 g/l NaH_2PO_4 = 6 g/l NaF = 21 g/l pH = 4.6 Current density= 200-450 mA/cm^2 Plating time = 7 min.
2.	$CrCl_3$ = 263 g/l $CoSO_4$ = 15 g/l NaH_2PO_4 = 4 g/l NaF = 21 g/l pH = 3-3.5 Current density= 200-450 mA/cm^2 Plating time = 4-5 min.	
3.	$CrCl_3$ = 263 g/l $CoSO_4$ = 15 g/l $Co(NO_3)_2$ = 12 g/l NaH_2PO_4 = 2 g/l NaF = 21 g/l pH = 3.5-4 Current density= 200-450 mA/cm^2 Plating time = 4-5 min.	
4.	$CrCl_3$ = 40 g/l $CoSO_4$ = 10 g/l $Co(NO_3)_2$ = 10 g/l NaH_2PO_4 = 8 g/l NaF = 8 g/l pH = 3.5-4 Current density= 200-450 mA/cm^2 Plating time = 4-5 min.	
5.	$CrCl_3$ = 240 g/l $CoSO_4$ = 15 g/l $Co(NO_3)_2$ = 12 g/l NaH_2PO_4 = 6 g/l NaF = 21 g/l pH = 4-4.5 Current density= 200-450 mA/cm^2 Plating time = 4-5 min.	

Table 2

Bath	Absorption(~)	Emission(£)	Nature of coatings
Trail 1	0.81	0.04	Yellowish black
Trail 2	0.83	0.06	Grayish black
Trail 3	0.84	0.07	Semi black
Trail 4	0.85	0.07	Grayish black with non-uniform
Trail 5	0.90	0.08	Dull black
Optimized bath	0.94	0.09	Intensive black

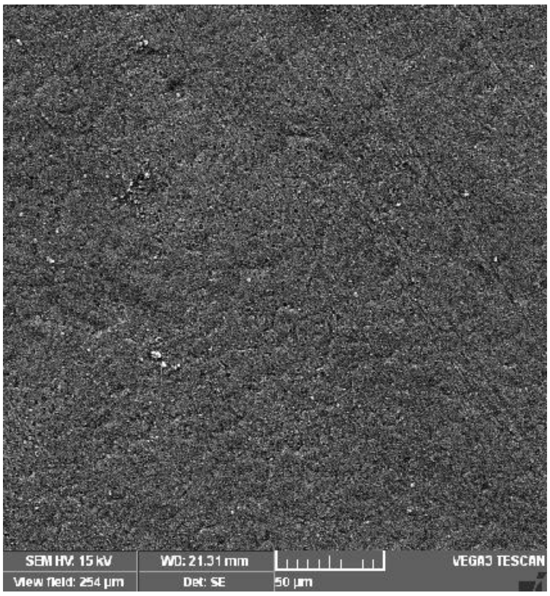

Figure 1. SEM images of uncoated mild steel

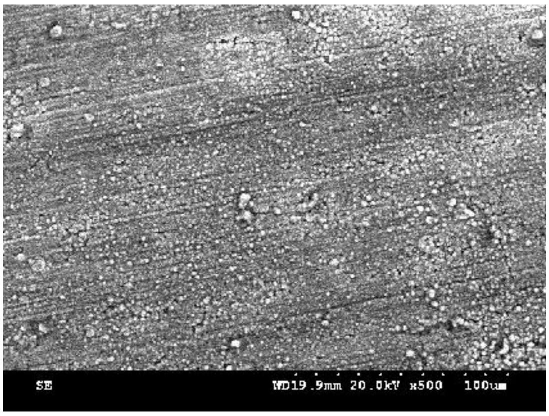

Figure 2. SEM images of mild steel with coating

Conclusions

1. A suitable plating bath has been formulated from six different plating compositions.
2. The influence of pH and cobalt metal directly contributed for the optical properties of the coatings.
3. SEM images confirmed the existence of chromium in the black coatings.

References

1. M. Nikolova, O. Harizanov, P. Steftchev, I. Kristev, S. Rashkov, Surf. Coat. Technol. 34(1988) 501.
2. S. Surviliene, L. Orlovskaja, S. Biallozor, Surf. Coat. Technol. 122 (1999) 235.
3. M. Aguilar, E.Barrera, M. Palomar-Pardavé, L. Huerta, S. Muhl, J. Non Cristal. Sol. 329 (2003) 31.
4. Z. Abdel Hamid, Surf. Coat. Technol. 203(2009) 3442.
5. C. Anandan, V.K. William Grips, K.S. Rajam, V. Jayaram, Parthasarathi Bera, Appl. Surf.Sci. 191 (2002) 254.
6. M. R. Bayati, M. H. Shariat, K. Janghorban, Renewable Enery. 30 (2005) 2163
7. R. Constantin, P.A. Steinmann, C. Manastereski, Revêtements PVD decorative in Nanomatériaux, traitement et fonctionnalisation des surfaces, J. Takadoum (ed), p.141, Hermes, Lavoisier, Paris 2008.
8. M.F. Quaely, Plating, 9 (1953) 982.

9. A. Grill, Wear, vol. 168(1–2) (1993),143.
10. S.J. Bull, Diamond Related Materials, 4(5–6) (1995) 827.
11. J.M. Chappé, F. Vaz, L. Cunha, C.Moura, M.C. Marco de Lucas, L. Imhoff, S. Bourgeois,J.F. Pierson, Surf. Coat. Technol. 203 (2008) 804.
12. A.K. Graham, Proc. Amer. Electroplaters Soc. 46 (61) (1959) 61.
13. T. Le Huu, H. Zaidi, D. Paulmier, P. Voumard, Thin Solid Films, (290–291) (1996) 126.

*****