Low-cost black Cu–Ni alloy coatings for solar selective applications

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Abstract

The development of the Cu–Ni alloy coating as a selective surface for solar energy use is reported. The coatings were deposited by electrodeposition using Hull cell. Effects of electrolyte concentration and operating parameters on the appearance and optical properties of the coating were studied. Deposition parameters were optimized to achieve high solar absorptance $\alpha = 0.94$ and low emittance $\epsilon = 0.08$. The elemental composition and morphology were evaluated by SEM and energy dispersive X-ray diffraction analysis (EDAX). The coating may be promising for solar collector panels used in domestic water heaters.

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1. Introduction

It is generally understood that the current pattern of energy supply is non-sustainable and the harnessing of solar energy is bound to play a major role in near future [1–3]. Terrestrial solar radiation is a low-intensity variable energy amounting to about 1000 W/m^2 . The widespread use of solar energy requires the development of optically efficient solar selective coatings. The economic feasibility of the conversion process depends upon low cost of production and durability of the coating under severe service condition along with efficient collection and storage characteristics. In this direction several solar selective coatings have been developed and used as flat-plate collector.

Solar selective coatings can be prepared by various techniques. Matsubara has reviewed the manufacturing methods and properties of various solar selective absorber coatings [4]. Diverse techniques such as sputtering [5,6], chemical vapor deposition [7,8], thermal oxidation [9,10], pyrolysis [11], chemical conversion [12–14], electroless

plating [15–17] and electroplating [18,19] are in vogue to deposit black solar absorber coatings.

Electroplating method is gaining importance over other method simply because of its commercial viability and practicability for large-scale production. A number of efforts have been made to electrodeposit black chromium [20–25], black nickel [26–35], black cobalt [36–38], black molybdenum [39–43], black copper coatings [44–46] and black aluminum [47–51]. Other known black coatings are Ni–Sn [52], Ni–Cd [53], Co–Sn [54], Co–Cd [55], Mo–Cu [56] and Fe–P [57].

Certain oxide films of Cu or Ni grown in situ thermally are found to be selective absorber materials. However, they are not commonly considered as very successful coatings since their preparation requires fairly high temperature from 600 to 1000° . The process involves difficulties to control the film thickness, which is crucial for deciding thermal emittance [58]. Though the better optical properties, absorptance (α) > 0.9 and emittance (ϵ) < 0.1 are offered by electrochemically prepared black coatings of copper and nickel but their utility under humid conditions and at elevated temperatures is not encouraging. In addition, the other successful competitor like black chromium involves operating difficulties for a full sized collector owing to the use of high current densities ($> 20 \text{ A/dm}^2$) and its toxic impacts on environment. Hence, it is felt to deposit Cu–Ni coatings which can exhibit good

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corrosion resistance [59,60] with desirable solar selective properties. This article reports the electroplating of black Cu–Ni coatings from a low-concentration plating bath solution for solar collector panels used in domestic water heaters. The coating produced was thick enough to achieve low thermal emittance ϵ with high solar absorptance (α) to suit solar applications.

2. Results and discussion

2.1. Hull cell studies

To optimize the bath composition and plating variables to obtain good quality black coatings, the experiments

Table 1
Formulation used in Hull cell studies

Optimum composition Operating conditions	Range
CuSO ₄	0–20 g/L
NiSO ₄	0–30 g/L
TEA	0–30 ml/L
H ₃ BO ₃	20 g/L
PH	3.0–8.0
Temperature	20–50 °C

Fig. 1. Codes for recording Hull cell pattern.

Fig. 2. Hull cell patterns with different concentrations of CuSO₄, NiSO₄ (20 g/L), TEA (20 ml/L), H₃BO₃ (20 g/L) and pH 5.0 (a) without; (b) 5 g/L; (c) 10 g/L and (d) 20 g/L.

Fig. 3. Hull cell patterns with different concentrations of NiSO₄, CuSO₄ (10 g/L), TEA (20 ml/L), H₃BO₃ (20 g/L) and pH 5.0 (a) without; (b) 10 g/L; (c) 20 g/L and (d) 30 g/L.

Fig. 4. Hull cell patterns with different concentrations of TEA, NiSO₄ (20 g/L); CuSO₄ (10 g/L), H₃BO₃ (20 g/L) and pH 5.0 without; (b) 10 ml/L; (c) 20 ml/L and (d) 30 ml/L.

Fig. 5. Hull cell patterns obtained at different pH values NiSO₄ (20 g/L), CuSO₄ (10 g/L), TEA (20 ml/L) and H₃BO₃ (20 g/L) (a) 3.0; (b) 5.0 and (c) 8.0.

were carried in a 267 ml capacity Hull cell at a fixed current density of 2 A. The effect of addition of CuSO_4 , NiSO_4 and TEA in different quantities was studied by following the formulations and conditions given in Table 1. The results were represented using the codes shown in Fig. 1. In all the cases, H_3BO_3 was used as a buffering agent to minimize the hydrogen evolution during the electrodeposition [61]. The choice of substrate and their pre-treatment play a decisive role on the optical properties and thermal stability of the coatings [62,63]. In the present study, copper sheets (99%) were used as substrates to electrodeposit black coatings. They were solvent degreased in an ultrasonic bath of trichloroethylene and mechanically polished on 4/0 emery paper with ethanol as lubricant. Finally, they were

Fig. 6. Hull cell patterns obtained at different electrolyte temperature NiSO_4 (20 g/L), CuSO_4 (10 g/L); TEA (20 ml/L) and H_3BO_3 (20 g/L) 20 °C; (b) 30 °C and (c) 50 °C.

Table 2
Optimum bath composition and operating conditions to deposit black Cu–Ni alloy coating

Composition		Operating conditions
CuSO_4	10 g/L	Substrate–Cu foil
NiSO_4	20 g/L	Anode–SS 316
TEA	20 ml/L	Temperature–30 °C
H_3BO_3	10 g/L	pH–5.0
		cd–1 A/dm ²
		Time–30 s

Table 3
Dependence of optical properties on the deposition time

Deposition time	Optical properties		Selectivity factor (α/ε)
	α	ε	
10	0.84	0.12	7.00
20	0.90	0.09	10.00
30	0.94	0.08	11.75
60	0.96	0.11	8.72
90	0.86	0.14	6.14
120	0.82	0.18	4.55

Fig. 7. Variation of selectivity factor (α/ε) with deposition time, deposited at cd of 1 A/dm², temperature 30 °C.

Table 4
The effect of copper content in the bath solution on copper content in the deposit and optical properties

Cu_{bath} (%)	$\text{Cu}_{\text{deposit}}$ (%)	Optical properties	
		α	ε
2.5	4	0.84	0.09
5.0	7.2	0.90	0.09
10	11.8	0.94	0.08
15	18.5	0.88	0.10
20	23.2	0.82	0.12

Fig. 8. Variation of solar absorbance with copper (●) nickel (▲) salt at a cd of 1 A/dm², temperature 30 °C.

chemically polished in a bath solution (20 mL H_2SO_4 , 2 mL HCl , in 70 mL H_2O saturated with CrO_3) for 6 min [64], and then washed with 10% H_2SO_4 solution, rinsed thoroughly with distilled water and used immediately for electrodeposition of black coatings. Optical properties (α) and (ϵ) of the deposited black coatings were evaluated.

2.1.1. Effect of CuSO_4

Hull cell experiments were carried out using NiSO_4 (20 g/L), TEA (20 mL/L) and H_3BO_3 (20 g/L) at pH 5.0 and 30°C with varying amount of CuSO_4 (0–20 g/L). Fig. 2

Fig. 9. Variation of solar absorbance with annealing temperature as a function of time: ■— 100°C , ●— 200°C and ▲— 300°C .

shows the results from different bath solutions in the Hull cell. It shows that in the absence of CuSO_4 , black deposit could be obtained only at higher current densities ($> 8 \text{ A/dm}^2$). The good quality black deposit was obtained at a wide range of current density (Fig. 2(c)) with 10 g/L of CuSO_4 . Further increase ($> 10 \text{ g/L}$) in the concentration of CuSO_4 black deposit with poor adherence results in the higher cd range. Hence, 10 g/L was chosen as optimum concentration.

2.1.2. Effect of NiSO_4

Hull cell experiments were carried out using CuSO_4 (10 g/L), TEA (20 mL/L) and H_3BO_3 (20 g/L) at pH 5.0 and 30°C with varying amount of NiSO_4 (0–30 g/L). The results (Fig. 3) indicate that increase in nickel sulfate gives compact black coatings (Figs. 3(b) and (c)). Further increase in the nickel sulfate content ($> 20 \text{ g/L}$) results in an increase (Fig. 3(d)) in deposition current density of black coating. Hence, an optimum concentration of 20 g/L was chosen. However, it is also noted that use of nickel ammonium sulfate instead of nickel sulfate does not give good quality black coating in a wide range of current density.

2.1.3. Effect of TEA

Hull cell experiments were carried out using CuSO_4 (10 g/L), NiSO_4 (20 g/L), and H_3BO_3 (20 g/L) at pH 5.0 and 30°C with varying amount of TEA (0–30 mL/L). It is observed that (Fig. 4) black deposit could be obtained at a wide range of current density with a minimum of 20 mL/L TEA (Fig. 4(c)). Increase in TEA concentration ($> 20 \text{ mL/L}$) produces a streaky black coating (Fig. 4(d)) with poor adherence. In the absence of TEA no quality black deposit is obtained.

Fig. 10. Energy dispersive X-ray diffraction analysis of as deposited Cu–Ni alloy.

2.1.4. Influence of pH

The pH of the solution was adjusted using dilute H_2SO_4 /NaOH and was varied from 3.0 to 8.0 for the bath solution containing CuSO_4 (10 g/L), NiSO_4 (20 g/L), TEA (20 mL/L) and H_3BO_3 (20 g/L). Fig. 5 shows the Hull cell patterns obtained at different pH values. At pH 3.0 the deposits were gray in color and quality black coating were obtained at pH 5.0 (Fig. 5(b)) only. Increasing pH to 6.5, increases the black coating deposition current density and at pH 8.0, a black coating containing a dull metallic deposit of copper (Fig. 5(c)) was obtained. Hence, the pH 5.0 was considered as optimum pH to obtain black Cu–Ni coatings.

2.1.5. Influence of temperature

The effect of bath solution temperature on the nature of Cu–Ni alloy was studied using a bath solution containing CuSO_4 (10 g/L), NiSO_4 (20 g/L), TEA (20 mL/L) and H_3BO_3 (20 g/L) at pH 5.0. The temperature of the bath was varied between 20 and 50 °C. The typical results are shown in Fig. 6. It is noted that the best black deposits could be obtained in the temperature range of 20–30 °C (Fig. 6(b)). Increase in temperature above 50 °C led to decomposition of the bath solution. For ease of temperature control in the laboratory 30 °C was chosen for the study.

Based on Hull cell experimental results the best composition and operating conditions were formulated and are summarized in Table 2.

2.2. Alloy film characterization

2.2.1. Influence of deposition time

After optimizing the bath composition and operating condition, samples were prepared at different duration of time. The influence of deposition time on the optical properties of the black Cu–Ni deposit is given in Table 3 (Fig. 7). The solar absorptance increases from 0.90 to 0.96 on increasing the deposition time from 15 to 120 s. Whereas the solar emittance value remains less than 0.14 for deposition time up to 60 s. The black deposits with optimum combination of optical properties $\alpha = 0.94$ and $\varepsilon = 0.08$ were obtained at a deposition time of 30 s. The coating thickness was found to be critical for high solar absorption with a high selectivity factor (α/ε).

2.2.2. Dependence of optical properties on the composition of the coatings

To understand the effect of composition of black Cu–Ni coatings on the optical properties, the samples were prepared to a constant thickness from the bath solution containing varying copper content. It is observed that, increase in Cu content in the bath solution increases the Cu content in the deposit. It is led to an increase in the solar absorptivity and emissivity of the deposit (Table 4 and Fig. 8).

2.2.3. Thermal stability

Several samples prepared using optimized bath solution on Cu-substrate was subjected to thermal annealing in air inside a tube furnace and the temperature was controlled ± 5 °C around 100, 200 and 300 °C. Fig. 9 depicts the behavior of deposit absorptivity and emissivity, respectively, as a function of time and for different levels of temperature. It shows that the material poses good thermal stability and retains its optical properties (α and ε) with a slight variation under 250 °C. However, above this temperature the optical properties begin to change abruptly indicating the instability of the deposited material.

2.2.4. Surface morphology and microstructure

The coating obtained under fixed experimental condition was subjected to energy dispersive X-ray diffraction analysis (EDAX), which confirmed the presence of both

Fig. 11. Scanning electron microphotograph of Cu–Ni alloys (a) deposited at lower cd; (b) deposited at higher cd; (c) EDAX dot mapping of Cu and (d) EDAX dot mapping of Ni.

Cu and Ni in the coating (Fig. 10). SEM patterns of Cu–Ni alloy films at lower and higher current densities are shown in Figs. 11(a) and (b), respectively. Dot mapping of the coatings (Figs. 11(c) and (d)) shows the uniform distribution of Cu and Ni in the alloy, respectively.

3. Conclusion

Simple bath solution and plating conditions are developed to deposit Cu–Ni alloys which exhibit as black coatings for solar selective application. These coatings were deposited by electrodeposition technique with the use of Hull cell. The black deposits with optimum combination of optical properties ($\alpha = 0.94$ and $\varepsilon = 0.08$) were obtained at a deposition time of 30 s at normal working temperature.

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