

A COMPARATIVE STUDY OF NICKEL UNDERCOATS FOR SOLAR COLLECTORS OPERATING AT HIGH TEMPERATURES

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ABSTRACT

Nickel electrodeposited from electrolytes containing magnesium, manganese, cobalt and sulphur were heat treated at 600°C for 30 hours to find out a suitable undercoat for solar collectors operating at high temperatures ($> 400^{\circ}\text{C}$). Optical properties were measured and microscopic observation was made for the appearance of blisters, cracks and damage. It was found that excepting Watt's nickel other solutions containing magnesium, cobalt and manganese were found suitable for operation at high temperatures.

Key Words: Nickel plating, solar collectors, high temperatures, additives

INTRODUCTION

There is hardly any need to emphasize the utility of solar energy as a possible remedy for the energy crisis. It is freely available, nonpolluting, inexhaustible but is intermittent. For India this source of energy is all the more important as it is available to the tune of 17.7×10^{21} kcal. of solar radiation per year. Efficient conversion of solar energy requires collector panels which strongly absorb in the visible range (0.2-3.0 μm) while emitting poorly in the infrared region ($> 3 \mu\text{m}$). In addition, coatings for solar collectors must meet the following requirements:

1. Sharp spectral transition
2. Long term stability at the desired temperature
3. Stability to/or recovery from short term overheating due to failure to extract energy from the collector
4. Stability against atmospheric corrosion

For low temperature applications such as hot water, hot air, etc various selective coatings such as black chrome, black nickel, black copper, black aluminium and black alloy coatings are used [1-6]. The most popular solar absorber surface in commercial production is that based on electroplating of black chrome [7-9] but not suitable for high temperature applications. If electroplating of selective surface is done on bare collector surfaces, the thinness of the selective coating (1000-3000 \AA) leads to corrosion, resulting in the degradation of optical properties. In order to improve the durability and corrosion resistance of the solar collectors, normally nickel is given as an undercoat. The purpose of this undercoat is twofold. Firstly, it provides adequate corrosion resistance and secondly, it helps in reducing the emittance of the coating.

For plating nickel on collector panels, various baths are available such as Watts nickel, sulphamate, low concentration electrolytes [10] etc. For low temperature applications of plating solar collectors (up to 200°C), plating from any type of bath is possible whereas for high temperature ($> 400^{\circ}\text{C}$) applications, the undercoat undergoes changes, and the optical properties of the coating no longer remain constant. A survey of literature [11-15] indicates that electrodeposited nickel undergoes change in ductility and hardness, and tends to crack owing to sulfur incorporation from the addition agents employed in plating baths, and other residual gases present in the deposit. In commercial nickel, brittleness is

usually eliminated by addition of manganese or magnesium to the molten nickel [16,17] just prior to casting. These elements preferentially combine with the sulfur and prevent the formation of the brittle nickel sulfide. Manganese sulfide forms a high melting point (1325°) eutectic which is precipitated as globules along the grain boundaries. Magnesium sulfide is insoluble in nickel and forms particles which are entrapped within the grains during solidification. In electroplating of nickel from manganese - containing solutions also, the incorporation of manganese prevents catastrophic embrittlement on exposure to elevated temperatures [18]. The nature and cause of grain boundary as bubbles which are formed during the annealing of low current density (21.5 A/m²) Watts nickel electrodeposits [19] are such that the higher concentrations of carbon and oxygen at low c.d. material favour the formation of high densities of gas-filled pores and thus produce the embrittlement.

Premature failures of the nickel electroforms were also reported as due to the inclusion of sulfur arising from the stress relievers incorporated in the electroforming solutions. Addition of 5% cobalt [20] has been found to solve the above problem and hence electroforming industry has switched over to Ni-Co electroforms for the production of moulds and dies for casting glass or zinc where operating temperature is above 400°C.

The present authors have chosen four different nickel electrolytes containing sulfur, manganese, cobalt and magnesium and studied the effect of heat treatment on optical properties before and after heat treatment and made observations of the coatings for blistering for use in high temperature solar applications like concentrators.

EXPERIMENTAL

Nickel plating electrolytes were prepared as per the composition mentioned in Table 1 using laboratory grade reagents. Deionised water was used for solution preparation. The solutions were treated with activated charcoal at a pH of 5.5 to remove any organic contaminants and to precipitate iron and then filtered. Other metal ions were removed by dummy electrolysis at 0.5 A/dm² for 24 hours. Saccharin was added as a stress reliever in Watts nickel bath. Hull cell studies were initially made to fix up operating current density range. Air agitation was employed during deposition.

Table I : Composition and operating conditions for various nickel plating electrolytes

Ingredients in gpl	Watt's Nickel	Nickel-Manganese	Nickel-Cobalt	Nickel-Magnesium
NiSO ₄ .6H ₂ O	300	300	300	300
NiCl ₂ .6H ₂ O	25	25	30	25
H ₃ BO ₃	30	30	30	25
Saccharin	1.0	1.0	-	1.0
MnSO ₄	-	5	-	-
MgSO ₄	-	-	-	10
CoSO ₄ .6H ₂ O	-	-	1-50	-
pH	4.0	4.0	4.0	4.0
Temp°C	55	55	55	55
C.D. A/dm ²	4	4	4	4

Copper panels of size 100 × 75 mm were polished, degreased with trichloroethylene, electrocleaned and etched in 5% v/v sulfuric acid. The panels were plated with 10 μm nickel from the above mentioned solutions.

Emissance of the coating was measured using an Emissometer. The panels were placed in an electric oven kept at a temperature of 600°C for 30 hours and cooled in the furnace itself. Emissance value was measured after heating and visual observations were made to find any blisters, cracks or damage for the coatings using a microscope at a magnification of × 100.

RESULTS AND DISCUSSION

Table II shows the initial and final emissance values for the various deposits.

Table II: Effect of heat treatment at 600°C for 30 hrs on emissance and appearance of nickel deposits

Electrolyte	Emissance		Appearance
	Initial value	After heating	
Watts nickel	0.04	0.10	Blistered
Nickel-manganese	0.04	0.04	No blistering
Nickel-cobalt	0.07	0.09	-do-
Nickel-magnesium	0.03	0.07	-do-

Nickel deposits obtained from electrolyte containing manganese was semibright in appearance. There is no change in emissance after heating. After the treatment, the panels showed discolouration and no cracks were observed. Manganese may preferentially combine with sulfur on heat treatment and prevent the formation of brittle grain boundary films of nickel sulfide.

The deposit obtained from the nickel plating solution containing magnesium was semibright in appearance and the finish is retained after heat treatment. But there is a slight increase in the value of emissance after heat treatment. Here again no crack was observed on microscopic and visual observation. It is reported that magnesium may form magnesium sulfide which is insoluble in the nickel and forms particles which are entrapped within the grains.

Nickel codeposited with cobalt was dull in appearance and developed a light blue colour on heat treatment. There is a small increase in emissance values i.e. from 0.07 to 0.09 after heat treatment. The change in emissance may be due to the change in surface colour. Further as in previous

cases the deposit was crack-and blister-free. In this coating cobalt produces hardening effect for the nickel deposits and eliminates the formation of blisters.

Nickel deposit obtained from Watt's nickel electrolyte containing saccharin showed lots of blistering upon heat treatment. This is in accordance with the earlier observation by others [14,15,19] for decorative and engineering applications of nickel deposits. Hence for high temperature applications Watts nickel containing sulfur imparting addition agents are not recommended.

CONCLUSION

Nickel electrodeposited from Watt's electrolyte undergoes, blistering at high temperatures (600°C) and is not suitable as an undercoat for solar collectors for use in high temperature applications such as concentrators. Addition of magnesium, manganese and cobalt salts to the nickel plating baths produces deposits which are stable at high temperatures and are thus recommended for high temperature applications.

REFERENCES

1. M. Selvam, S. John, N V Shanmugam, K N Srinivasan and B A Shenoi, *Metal Finish* **81-6** (1983) 37
2. M. Selvam, K N Srinivasan, N V Shanmugam, S John and B A Shenoi, *Metal Finish* **80-5** (1982) 107
3. K J Cathro, *Metal Finish*, **76-10** (1978) 57
4. G Mc Donald, *Solar Energy*, **17** (1975) 119
5. N V Shanmugam, S John, M Selvam, K N Srinivasan and B A Shenoi, *Proc Natl Solar Energy Convention*, Jyothi Ltd., Baroda, Allied Publishers, New Delhi, Dec 1983
6. N V Shanmugam, K N Srinivasan, M Selvam, S John and B A Shenoi, *The Indian and Easter Engineer*, **123-7** (1981) 309
7. R R Sowell and R B Pettit, *Proc. D.O.E. DST, Thermal Power Systems workshop on solar absorber coatings*, Solar Energy Research Institute, Golden Colorado 6-8 Dec 1977, pp 183
8. G Mohan Rao, S Mohan, T Balachandra, K I Vasu, and M Ramakrishna Rao, *Proc. Natl. Solar Energy Convention*, Solar India, 82, Allied Publishers, New Delhi, pp 8-028
9. I T Ritchie, S K Sharma, J Valighat and J Spitt, *Solar Energy Materials*, **2** (1979) 167
10. N V Shanmugam, S John, K N Srinivasan, M Selvam and B A Shenoi, *Proc. Second International Symposium, Industrial and Oriented Basic Electrochemistry*, SAEST at Madras, 1980, p 6.1
11. K C Bett, J A Crossky and S A Watson, *Trans Inst Metal Finish*, **48** (1970) 133
12. S J Harris and P M Braddick, *Trans Inst Metal Finish*, **51** (1973) 165
13. J N Dini and H R Johnson, *Plat Sur Finish*, **64-8** (1977) 44
14. J W Dini, H R Johnson and L A West, *Plat Sur Finish*, **65-2** (1978) 36
15. J W Dini, H R Johnson and H J Saxton, *Electrodepos Surface Treat*, **2** (1973/74) 165
16. K M Olsew C F Larkin and P H Schmitt, *Trans A.S.M.*, **53**, (1961) 349
17. A M Hall, *Trans AIME*, **152** (1943) 278
18. W R Wearmouth and K C Bett, *Plat Sur Finish*, **66-10** (1979) 53
19. D M Braddick and S J Harris, *Electrodepos Surface Treat*, **2** (1973/74) 123
20. *Proc INCO Electroforming course*, International Nickel Services Ltd., Bombay, 8-9 March 1979, Session 6