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Development of Black Cobalt Selective Absorber on Copper for Solar Collectors

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An electrolyte is proposed for the deposition of black cobalt selective absorber coating on copper plate. The influence of the electrolyte composition and operating parameters on the properties of black cobalt coatings including optical properties were studied. The optimum conditions to obtain a high absorptance/emittance ratio are described.

Key words: Black cobalt electrodeposition, solar absorber coatings.

Introduction

Electrochemically deposited thin films of black chromium or black nickel are widely used for efficient conversion of solar thermal energy. These films can provide absorber-reflector tandems with good selective properties [1-5]. Absorber-reflector tandem coating systems make use of a highly infrared-reflecting metal substrate under a coating having high absorbance at solar wavelengths (i.e. black), but which is transparent to long-wavelength "black body" radiation. Thus, the tandem has the high solar absorbance of the black exterior deposit and the low thermal emittance of the metallic reflector substrate. The low thermal emittance underlayer surface is generally a metal such as copper, nickel, aluminium or stainless steel. It is well established that the optical performance can be significantly determined by both the metal content and microstructure of the absorber film [6]. The absorber coating should absorb almost all of the solar radiation without losing its thermal energy through re-radiation from the heated surface. An ideal selective coating would completely absorb wavelengths less than about 2 μm and completely reflect wavelengths greater than 2 μm .

The electrochemical deposition method, through the influence of potential, temperature, pH and composition of reactants, offers excellent control over the properties of the film. The purpose of this study was to further evaluate the use of black cobalt as a selective absorber coating through direct electrodeposition. Several researchers [7-14] have studied the electrodeposition of cobalt from various plating baths. Three

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specific types of black cobalt coatings were reported. Greyish-black deposits of CoS plus some metal were reported from a cobalt chloride bath plus potassium thiocyanate (15). Some research was done on the anodic formation of cobalt oxides (12-17). The other possibility was the oxidation of the metallic cobalt in air at 400 °C (12).

In this study, we attempted to plate the cobalt oxides or hydroxides using oxidising agents. In the literature, unsatisfactory results were obtained using oxidising agents, possibly because of the complexity of the bath (12). This paper describes the development of the black cobalt plating system correlating the deposit characteristics, such as optical properties with the operating conditions, oxidant concentration, current density and bath composition.

Experimental

Electrochemical deposition was achieved using a classical double wall thermostated three-electrode cell by the chronopotentiometric method. All experiments were performed with a glassy carbon electrode as the counter and a calomel electrode as the reference. For cobalt deposition a copper sheet (geometric area=4 cm²) was used as the working electrode and Co was cathodically deposited from a solution of CoSO₄, CoCl₂, boric acid and an oxidant (HNO₃ or H₂O₂). The electrolytic solutions were prepared from ultrapure water (Millipore Milli Q system) and Merck reagents. Other experimental details have been given elsewhere [18]. For the cobalt pigmentation of copper substrate, copper was chemically cleaned [19] and nickel plated using a Watts nickel bath of the following composition:

Nickel sulphate 300 g.dm⁻³, nickel chloride 25 g.dm⁻³, boric acid 35 g.dm⁻³, saccharin 0.5 g.dm⁻³, pH=4.0, temperature=50 °C, current density=4 A.dm⁻². After nickel deposition to a thickness of 10 μm the plates were washed in distilled water and black cobalt deposition was carried out. Optical reflection, absorption (α) and emission (ϵ) properties of the samples were characterized using a Jasco V 500 spectrophotometer equipped with an ILN-472 integrated sphere in the UV-Visible range and a Jasco FTIR/700 and RSA-FTIR 6 inch integrating sphere combination. In the IR the reflectance of the samples was recorded using a gold sphere blank as a reference. The solar absorbance was calculated from the integrating sphere measurements using ASTM solar data. The normal emittance at 100 °C was calculated from the infrared spectra data corrected for the emittance of the reference used in the measurements (20). Surface characterisation using XPS measurement details were given elsewhere (4).

Results

The initial plating solution used was the Watts bath with 319 g.dm⁻³ CoSO₄·7H₂O, 45 g.dm⁻³ CoCl₂·6H₂O and 30 g.dm⁻³ boric acid. The cobalt sulphate is the main source of cobalt ions, the cobalt chloride helps improve the conductivity and the boric acid is a levelling agent. The first step was to relate the order of the current density on the appearance of the deposit. During the tests, a black line was observed on the electrolyte-air interface on the sample. The difference between this interface and the bulk solution may be that the interface had an influx of oxygen. Thus, an oxidant (HNO₃ or H₂O₂) was added to the bath to obtain a black deposit on the sample. Further experiments were carried out with the inclusion of nitric acid and H₂O₂ as oxidants.

Influence of oxidant nature:

HNO_3 and H_2O_2 were tried as oxidants. Using HNO_3 , at first a black deposit was obtained at higher current densities, however, a metallic cobalt deposit was obtained at lower current densities if the concentration was less than 0.1 M. When the nitric acid concentration was increased, a black deposit was obtained at lower current densities. H_2O_2 was also tried. But, using dilute hydrogen peroxide (0.1 M) a different range of green deposits were obtained and the spectral selectivity of these samples are not appropriate with low absorption values.

Influence of current density

The influence of current density was studied keeping a concentration of 319 g.dm^{-3} , $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, 45 g.dm^{-3} $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 24.8 g.dm^{-3} boric acid at $20\text{-}22^\circ\text{C}$. It is preferable to keep the current density below 0.5 A.cm^{-2} for application in commercial processes. It is observed that current densities vary as a function of boric acid and nitric acid concentrations. Thus, the conditions were optimised relating to these components. Results are given in Table 1.

Table 1. The variation of α and ϵ values as functions of HNO_3 concentration, current density and plating time.

HNO_3	I/mA.cm^{-2}	Time (s)	α	ϵ
0.035	220	8	0.92	0.4
0.05	100	8	0.93	0.06
0.075	60	18	0.92	0.04
0.1	125	12	0.9	0.12

Effect of boric acid concentration

Tests were run with 0.05M nitric acid at boric acid concentrations of 0.25 M, 0.35 M, 0.5 M and 0.7 M. Fig. 1 shows the current density variation as a function of boric acid concentration. The optimum boric acid concentration was 0.35 M, based on the minimum current density necessary to produce a black deposit.

Influence of nitric acid concentration

The boric acid concentration was 0.35 M. The bath consists of 319 g.dm^{-3} $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, 45 g.dm^{-3} $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 24.8 g.dm^{-3} boric acid at $20\text{-}22^\circ\text{C}$. The variations of spectral properties (absorption and emission values) of surfaces prepared at different HNO_3 concentrations are given in Table 1. However, when the nitric acid concentration was greater than 0.2 M., the film dissolved quickly after the power was shut off.

Influence of temperature

The electrolyte temperature also affects the formation of the black deposit as it affects the nature of the constituents present in the deposit. The same electrolyte was used with 0.05M HNO_3 . The temperature of the electrolyte was varied from 20 to 50°C . At higher temperatures the black coating current density was higher than 600 mA.cm^{-2} and the coating was predominantly greyish. Hence the optimum electrolyte temperature was chosen as $20\text{-}30^\circ\text{C}$.

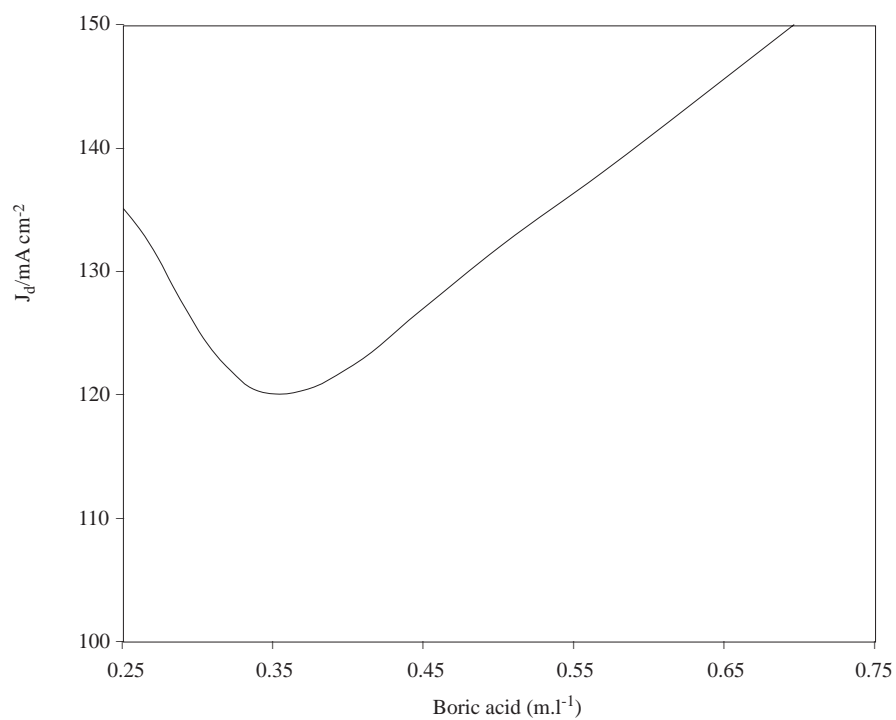


Figure 1. Effect of boric acid on current density necessary to produce a black deposit.

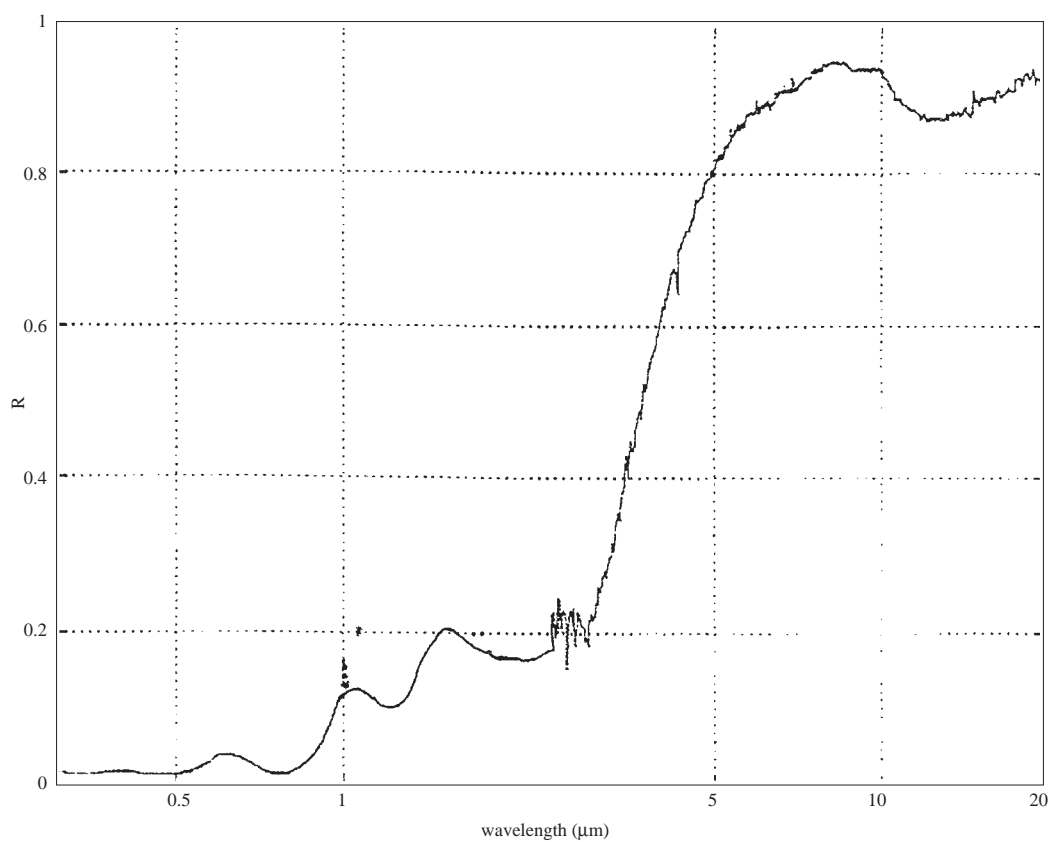


Figure 2. The spectral reflectance curve of Co pigmented Cu sample ($\alpha=0.96$ and $\epsilon=0.1$)

Influence of plating time on optical properties

The selective properties of the surface can also change by varying the film thickness. Absorption (α) and emission (ϵ) values were evaluated and are given in Table 1, for optimal values, obtained as a function of nitric acid concentration, current density and plating time. A spectral reflectance curve of the best coating ($\alpha=0.92$, $\epsilon=0.04$) is shown in Fig. 1

XPS studies

X-ray photoelectron spectroscopies of the cobalt pigmented copper samples have shown that cobalt is present on the surface with an oxidation state of $\geq +2$ [21]. Carbon was always present on the surface due to hydrocarbon deposits and the presence of chlorine was due to the salts used for pigmentation. The measured binding energy for Co 2p_{3/2} was very close to that for Co(OH)₂ (Fig. 3).

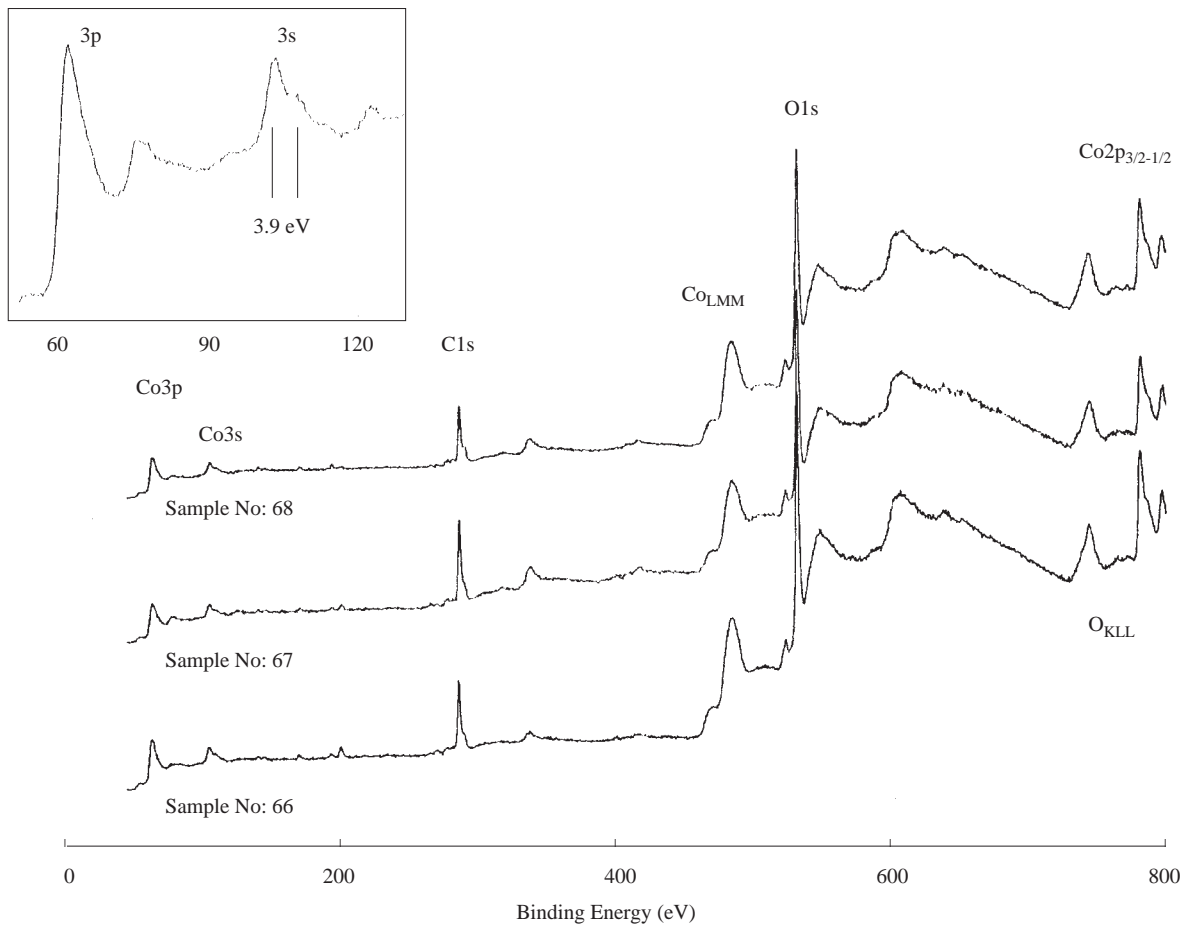


Figure 3. XPS spectra of Co pigmented copper plates. Shown in detail are the 2p and 3p-3s regions and the 3s multiplet splitting.

Thermal stability test

Optical properties (α , ϵ) were evaluated at various time intervals after thermal cycling at 300°C and the changes in α , ϵ are shown in Table 2. After annealing, the emittance drops, and the adsorptance of the

deposited material also decreases slightly. While the emittance drops to 0.07, absorptance decreases to 0.92 for a selective coating with initial solar absorptance of 0.96 and thermal emittance of 0.1. the decrease in emissivity may be due to the recrystallisation and grain growth of the coating at elevated temperatures. A transformation from Co(OH)_2 to CoO or other cobalt oxides is also possible. However, the annealing steps are also accompanied by changes in the porous structure of the coating (Fig. 4). The selectivity of the surface loosens when heated above temperatures of 400° .

Table 2. The variation of α and ϵ values as function of thermal exposure time at 300°C .

Exposure time (s)	α	ϵ
0	92	16
10	91.7	15
20	90	15
30	89.2	14.2
40	88.5	13.5

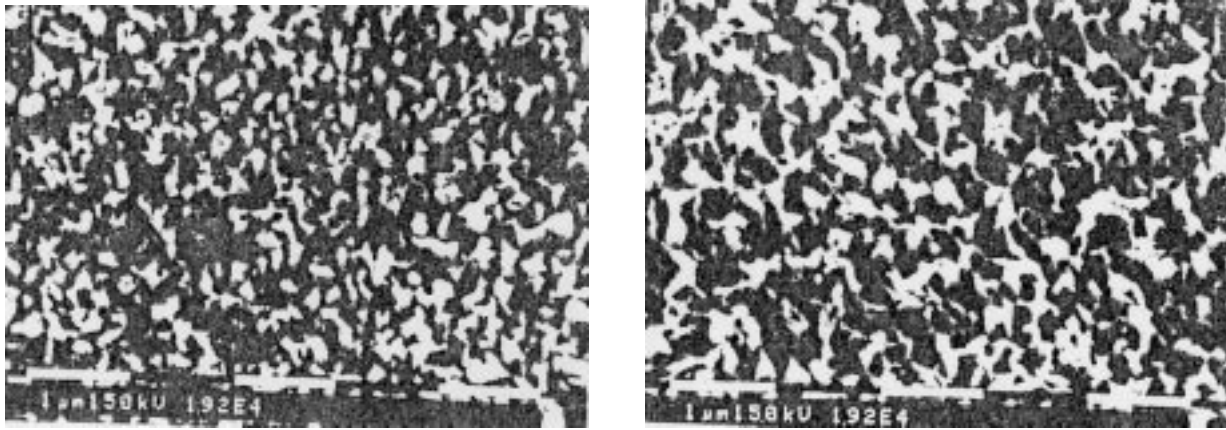


Figure 4. SEM micrographs of black cobalt coating before and after annealing.

a) As-prepared sample b) 30 h annealed at 300°C

Conclusion

It is observed that at low current densities a metallic cobalt deposit is obtained due to the much greater concentration of cobaltous ions than nitrate ions. When the current density is increased, the reduction of nitrate ions increases allowing the flux of nitrate ions to the surface and a totally black deposit is obtained in which no cobaltous ions are reduced. The presence of cobalt oxide alone on the surface is illustrated by XPS measurement [21]. As the current density is increased further, the limiting current for the reduction of nitrate ions may be exceeded. The formation of nitric or nitrous oxides might also explain the formation of the loose sooty deposits at higher current densities. The emittance and absorptance increase with increasing deposition time or thickness. Under heat treatment in air, the conversion of CoO is followed by the formation of grey black Co_3O_4 . Together with the successive oxidation of the copper reflector, the selectivity will be lost. An optimum coating should not only have a high solar absorptance and a low thermal emittance, but also a good adherence, good integrity, stability at high temperatures and reproducibility. Another important point of the selective coatings from the commercial application point of view, is the current density order. It

is preferable to keep the current density below 0.5 A.cm^{-2} . Good adherence was obtained for a low oxidant concentration ($0.03\text{-}0.1\text{M HNO}_3$) and a current density range of $100\text{-}300 \text{ mA.cm}^{-2}$.

Black cobalt is a good candidate as a high temperature selective absorber coating. Electrodeposition provides an economic advantage relative to in-situ annealing because of the direct production of the black cobalt surfaces.

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