Electrodeposition of Black Chromium-Cobalt Alloys From Trivalent Chromium Baths

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Akira Ishihama* and Tadao Hayashi**

The black Cr-Co alloy having a solar absorptance 0.92–0.93 and a thermal emittance 0.12 was electrodeposited at 20–100 A/dm² in the formate bath containing chromium chloride, cobalt chloride, glycine and boric acid when pH and temperature of the bath were adjusted to 2.8 and 50°C. The influence of changes in bath composition, current density, temperature, pH and plating time on the composition of alloys, the solar absorptance, the thermal emittance and appearances of the alloy deposits is described in this report.

1. Introduction

A variety of techniques has been employed to achieve spectrally selective sbsorption of solar energy. In selective absorber coatings, a maximum solar thermal gain is realized by maximizing radiation losses by blackbody emission. In terms of the radiation spectrum, this means that the coating layers, in total, must posses maximum absorptance, intergrated across the solar spectrum, nominally from 0.3–2.5 μm. Assuming no transmission in the solar wavelength range, 100 % integrated absorptance is equivalent to 0 % integrated reflectance as shown in Fig. 1. Since most infrared-transmitting materials
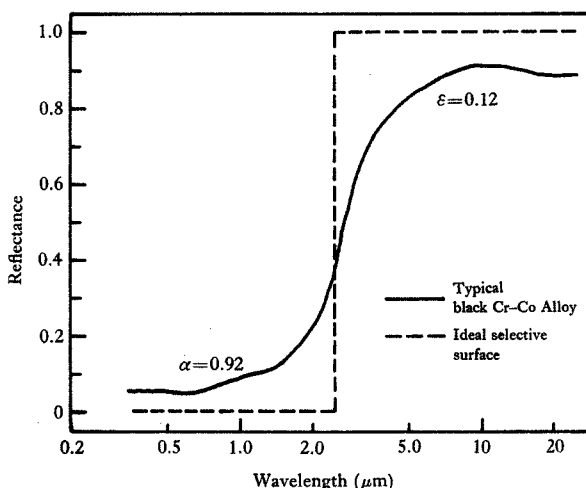

Fig. 1. Spectral reflectance of a typical black Cr-Co alloy

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are not completely transparent to the infrared, the emittance is proportional to the coating thickness.[1),2)]

Selective surfaces of metal oxide on prepared metal substrates are extremely promising. Selective metal or metal oxide systems which have received the greatest attention are electroplated black nickel[3)] and electroplated black chromium[4),5),6)]. However, the black nickel was found to lack the necessary stability. The black chromium are generally obtained from the hexavalent chromium baths.

In an attempt to develop new black Cr-Co alloy coatings for the selective solar collectors, factors affecting the solar properties of the black Cr-Co alloy deposits and the quality of the alloy deposits obtained from a trivalent chromium bath are detailed in this paper.

2. Experimental

2-1. Bath composition and operation condition

Table 1 shows the composition of the plating baths for the formation of balck Cr-Co alloys. These baths consist of 0.2–0.4 M $CrCl_3$, 1 M HCOONa, 0.33 M NH_2CH_2-COOH, 0–10 g/l $CoCl_2 \cdot 6H_2O$ and addition agents.

Table 1. Composition of black Cr-Co alloy baths

Bath	$CrCl_3$ (M)	$CoCl_2 \cdot 6H_2O$ (g/l)
A	0.2	0–10
B	0.3	0–10
C	0.4	0–10
A–1	0.2	1.0
B–2	0.3	2.0
C–3	0.4	2.0

All solutions contained: 1 M HCOONa, 0.33 M NH_2CH_2COOH,
0.1 M NH_4Br, 2 M NH_4Cl, 0.4 M H_3BO_3

A small rectanglar cell was constructed from acrylic acid resin plates, such that the cathode areas filled its cross section, thus ensuring uniform current distribution. A copper sheet electrode was used as a substrate for the electrodeposition of the Cr-Co alloys. In this case, one side of the copper sheet was coated with an insulating resin and the other side was received buffing and nickel palting. An insoluble graphite anode was used.

Nickel plating was most frequently done using a sulfamate bath. However, Watts

Table 2. Composition of nickel baths and operation conditions

Nickel type	$NiSO_4 \cdot 6H_2O$ (g/l)	$NiCl_2 \cdot 6H_2O$ (g/l)	$Ni(NH_2SO_3)_2 \cdot 4H_2O$ (g/l)	H_3BO_3 (g/l)	2-Butyne 1,4-diol (g/l)	1, 5-Naphthalene disulfonic acid disodium salt (g/l)
Sulfamate		7.5	330	35	—	—
Watts	240	45.0	—	30	—	—
Bright	240	45.0	—	30	0.2	7.5

pH 4.0, Bath temperature 45°C, Current density 4.0 A/dm²

nickel plating baths with or without brighteners were used to compare the properties of the underlayer nickel deposits for the solar absorptance and thermal emittance measurement, as shown in Table 2.

2-2. Composition of alloy deposits and cathodic polarization measurement

A wire platinum cathode (1 mmϕ) and insoluble graphite anodes were used. The contents of chromium and cobalt in the alloy deposits were determined by chemical analysis using atomic absorption spectroscopy. Cathode current efficiency was determined from the weight of the alloy deposits and the amount of electricity required for the electrolysis, assuming reduction of Cr^{3+} and Co^{2+}. Cathode potential of the test electrode during electrolysis was measured against a saturated calomel electrode (SCE). Each experiment was carried out by using aged electrolytes (2 days).

2-3. Calculation of the solar absorptance and thermal emittance

The typical optical properties of the selective solar coating prepared in this study are shown in Fig. 1.

The solar absorptance α is determined by the following equation (1).

$$\alpha = \frac{\int_{0.34}^{2.5} AM2(1-r_{VIS})d\lambda}{\int_{0.34}^{2.5} AM2\,d\lambda} \qquad (1)$$

The thermal emittance ε at 100°C can be calculated using the following equation (2)

$$\varepsilon = \frac{\int_{2.5}^{25} BB_{100}(1-r_{IR})d\lambda}{\int_{2.5}^{25} BB_{100}\,d\lambda} \qquad (2)$$

where, $AM\,2 =$ air mass 2 solar curve
$BB_{100} =$ 100°C blackbody curve
$r_{VIS}, r_{IR} =$ monochromatic reflectances in visible and infrared regions, respectively

The monochromatic reflectance r_{VIS} was measured by using Hitachi EPS-3T spectrophotometer with an integrating sphere attachment. Smoked MgO was used as a reflectance standard. The infrared reflectance r_{IR} was measured by using Hitachi 285 infrared reflectometer with a powder reflection attachment. An electropolished copper sheet was used as a reflectance standard. BB_{100} was calculated from Planck's law of radiation.

3. Results and discussion

3-1 Effect of cobalt content in the baths

Fig. 2 shows the effect of the cobalt content in the baths on the solar absorptance of the deposits. Plating conditions were kept constant (pH 2.8, 50°C, 50 A/dm², plating
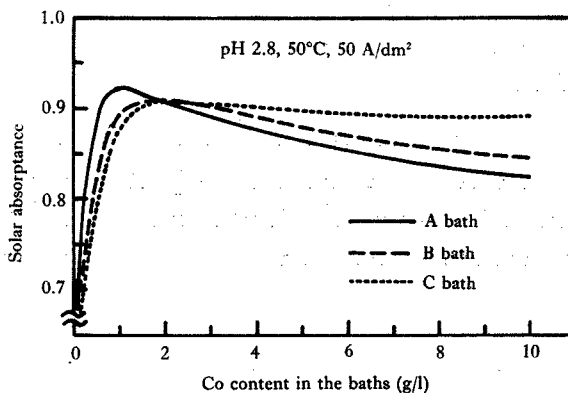
Fig. 2.   Effect of Co content in the baths on solar absorptance
of black Cr-Co alloy deposits

time 2 min).   The concentration of $CrCl_3$ in the baths A, B and C was controlled to be
0.2, 0.3 and 0.4 M, respectively.   The deposits from either chromium bath (0.2–0.4 M
$CrCl_3$) or cobalt bath (1–10 g/l $CoCl_2 \cdot 6H_2O$) exhibited a gray metallic luster so that the
solar absorptance indicated the value in the range of 0.5–0.7.   With an addition of a
small amount of $CoCl_2$ to the chromium baths, the deposits become black, and the solar
absorptance of the Cr-Co alloy deposits increased remarkably.   When the cobalt con-
tent in the baths was 1–2 g/l, the solar absorptance reached the maximum value (0.92–
0.93).   As the cobalt content in the baths increased beyond 2 g/l, the solar absorptance
decreased slightly.   Appearance of the alloy deposits from the A bath was most uniform.
However, the deposits from the B and C baths had streaky appearances which would
be caused by a mass transfer involved in the hydrogen evolution reaction on the cathode.
The appearance of the alloy deposits seemed to become streaky with an increase of the
chromium content in the baths.

3-2.   Effect of current density

The effects of current density on the composition of the alloy deposits and also on
the solar absorptance are shown in Fig. 3 (pH 2.8, 50°C, plating time 2 min).   The solar
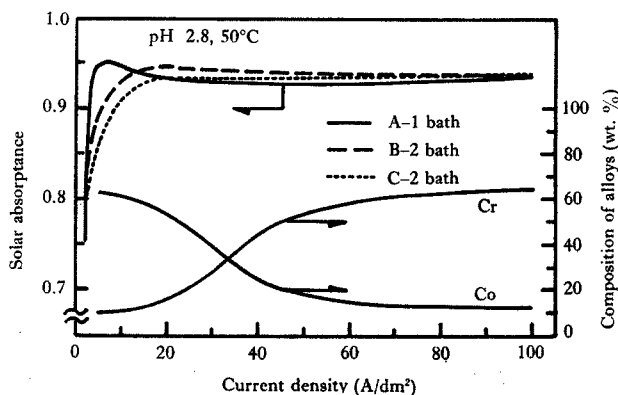

Fig. 3.   Effect of current density on the composition and solar
absorptance of Cr-Co alloy deposits

absorptance of the Cr-Co alloys increased with an increase in current density, and indicated an almost constant value in the range of 20–100 A/dm^2. The uniform deposits were obtained at the current density in the range of 20–100 A/dm^2 in A–1 bath, and 50–100 A/dm^2 in B–2 and C–2 baths. With an increase in current density, the chromium content in the alloy deposits was found to become relatively high compared with that of the noble metal, cobalt. The composition of the typical alloy electrodeposited from the A–1 bath at 50 A/dm^2 was 58 %Cr and 18 %Co.

3–3. Effects of pH and temperature of the bath

Fig. 4 shows the effect of pH of the bath on the solar absorptance of the Cr-Co alloy deposits from the A-1 bath at a current density of 25, 50 and 75 A/dm^2 (50°C). At pH 3 the solar absorptance of the alloy deposits reached the maximum value which was slightly influenced by the current density. with a decrease in pH of the bath, the amount of hydrogen evolved increased, therefore, the entire surface of the alloy deposits became streaky. The solar absorptance of the deposits obtained at pH 1–2 was lower than that obtained at pH 3. Above pH 3, even if the pH value increased, the solar absorptance hardly decreased. In the pH range above 4, a precipitate was observed in the bath within a few weeks. Therefore, the most suitable pH value for the Cr-Co alloy bath seemed to be 2–3.
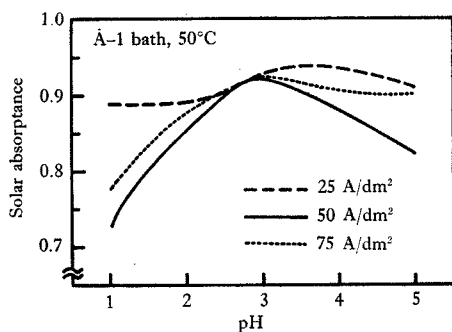

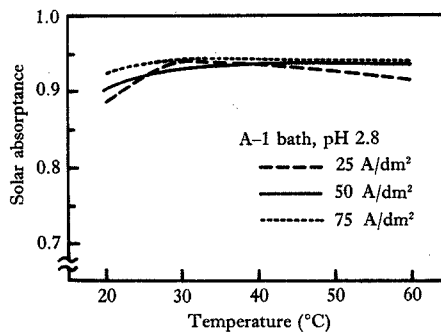Fig. 4.   Effect of pH on solar absorptance

Fig. 5.   Effect of bath temperature on solar absorptance

The bath temperature hardly influenced the solar absorptance of the Cr-Co alloy deposits as seen in Fig. 5. The uniform deposits were obtained at a temperature in the range of 30–60°C.

3–4. Effect of the nickel underalyer on the solar absorptance

The solar absorptance of the nickel-black Cr-Co alloy system has been measured by using different types of nickel underlayer. The black Cr-Co alloys were deposited on the nickel coatings (12.5 μm) plated on the copper substrate. The solar absorptance of the nickel-Cr-Co alloy systems is summarized in Table 3. A black Cr-Co alloy coating was deposited from the A-1 bath at a current density of 50 A/dm^2 for 2 min (pH 2.8, 50°C). The solar absorptance of the black Cr-Co alloys deposited on the nickel under-

layers was found to be almost independent of the type of the nickel underlayer as far as the surface appearance of the nickel deposits was concerned.

3-5. Effects of plating time on the solar absorptance and the thermal emittance

Fig. 6 shows the solar absorptance and the thermal emittance of the black Cr-Co alloy deposits as a function of the plating time (A-1 bath, pH 2.8, 50°C, 50 A/dm²). In the initial stage of electrolysis, a light brown deposit was formed. As deposition proceeded, a blackening threshold was reached. In passing through this point, the solar absorptance increased rapidly, levelling

Table 3. Effect of nickel underlayers on solar absorptance

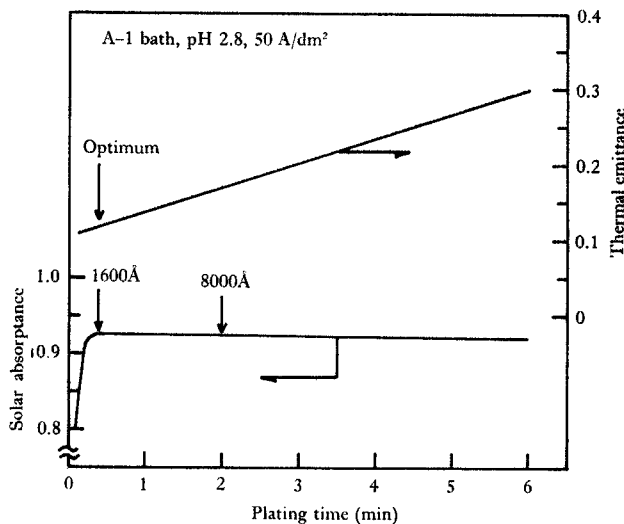| Nickel	Solar absorptance
Watts	0.37
Sulfamate	0.35
Bright	0.28
Nickel+Black Cr—Co alloy (A-1 bath)	
Watts	0.89
Sulfamate	0.92
Bright	0.95

Fig. 6. Solar absorptance and thermal emittance of black Cr-Co alloy deposits as a function of plating time

at a maximum value. The thermal emittance, on the other hand, increased rapidly beyond this point to undesirably high values, possibly because of the loss of transparency in the infrared region. The optimum plating time for a maximum solar absorptance and a low thermal emittance was found to be approximately 0.4 min at 50 A/dm². Calculating from the weight of the deposit and the densities of the metals, the thickness at which the optimum solar properties obtained is 1600 Å.

3-6. Cathodic ploarizations in alloy deposition

The cathode polarization curves and partial currents for chromium and cobalt estimated from the current efficiency in the Cr-Co alloy plating bath are shown in Fig. 7. At a potential of - 1.3 V, the partial current for the electrodeposition of chromium in a chromium bath (0.2 M $CrCl_3$) increased. On the other hand, the partial current for
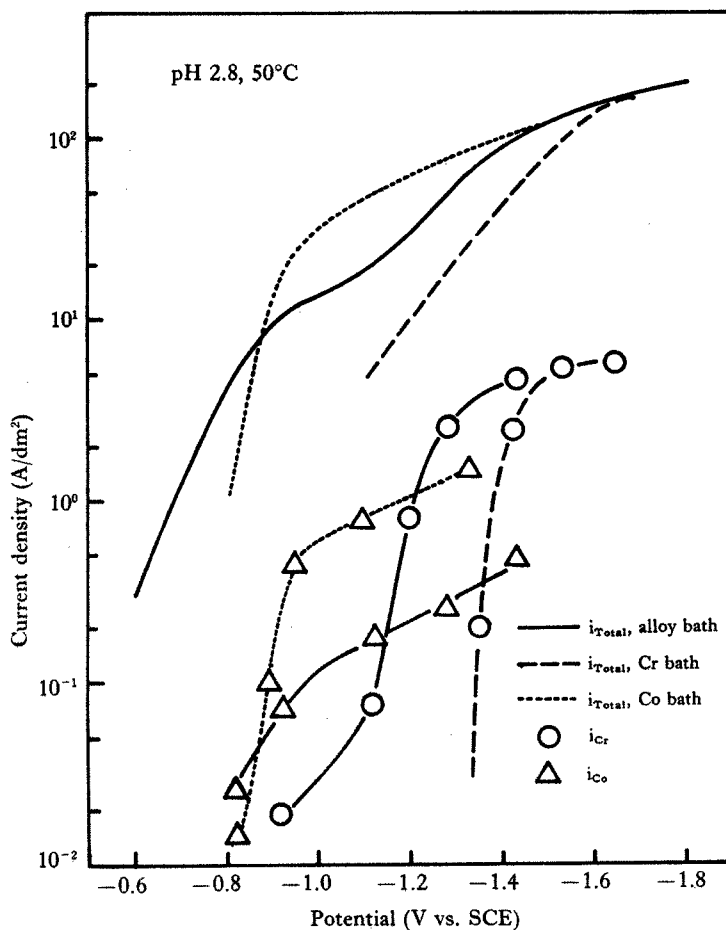
Fig. 7.   Cathodic polarization curves
i_{Total}: Total current
i_{Cr} or i_{Co}: Partial current for the deposition of Cr or Co

the deposition of chromium in the black Cr-Co alloy bath (A-1 bath) increased at - 1.1 V. It seemed that chromium was more depositable in the black Cr-Co alloy bath.   The partial current for the electrodeposition of cobalt in the alloy bath and also in a cobalt bath (1 g/l $CoCl_2 \cdot 6H_2O$) increased at a potential of -0.8 V.   However, the limitting current density for the cobalt deposition in the cobalt bath was found to be about ten times as much as that in the Cr-Co alloy bath as a result of the difference in the ionic strength in both baths.   The cathodic polarization curve of the Cr-Co alloy deposition was located between the curves of the parent metals.   An increase in the partial current for chromium deposition at -1.1 V resulted in a significant increase in the total current for the electrode position of the Cr-Co alloy.   The black Cr-Co alloy deposits were obtained in the potential range more negative than -0.9 V.   The uniform black Cr-Co alloy deposited in the potential range of -1.2 to -1.6 V, where the partial current for the chromium deposition was much greater than that for the cobalt deposition in the

alloy bath.

4. Conclusion

The black Cr-Co alloy deposited at 20–100 A/dm², in a formate bath (pH 2–3, 50°C) containing 0.2 M $CrCl_3$ and 1 g/l $CoCl_2 \cdot 6H_2O$ had the solar absorptance 0.92–0.93 and the thermal emittance 0.12. The solar absorptance of the alloy deposits increased with the increase in current density, the cobalt content in the bath and pH. The bath temperature or the type of the nickel underlayer hardly affected the solar absorptance of the deposits. The optimum plating time for the formation of the black Cr-Co alloy deposits suitable for the solar selective coatings was approximately 0.4 min at a current density of 50 A/dm².

Reference

1) "Taiyo Enerugi no Kiso to Oyo", ed. by Nihon Taiyo Enerugi Gakkai, p. 59, Ohmsha (1978)
2) I. Tanishita, J. Metal Finishing Soc., Japan, 27, 632 (1976)
3) J.T. Borzoni, AES Coating for Collectors Symposium, p. 89 (1976)
4) R.R. Sowell, D.M. Mattox, Plating and Surface Finishing, 65 (1), 50 (1978)
5) R.R. Sowell, R.B. Pettit, ibid, 65 (10), 42(1978)
6) K.J. Cathro, Metal Finishing, 76(10), 57 (1978)