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XPS characterization of Co and Cr pigmented copper solar absorbers

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Abstract

XPS is used to characterize the chemical state of Co and Cr on the surfaces of electrochemically pigmented copper plates. Using both the measured 2p binding energies and the magnitude of the 3s multiplet splitting chemical states of 2+ and 3+ are assigned to Co and Cr, respectively. FTIR reflectance analyses reveal that the surfaces of the pigmented samples contain hydrogen bonded OH groups. Optimum solar absorbance and thermal emittance values obtained are $\alpha = 0.92$ and $\varepsilon = 0.17$, $\alpha = 0.96$ and $\varepsilon = 0.04$ for the Co and Cr pigmented copper collectors, respectively. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Electrodeposition of metallic films is one of the appropriate techniques for obtaining absorber coatings with selective optical properties for solar collectors. The electrodeposition process can provide coatings for large surfaces without the need for complicated/expensive equipment. Understanding of mechanism(s) of selectivity is very crucial for controlling the factors leading to coatings with high solar absorbances and low thermal emittances. Internal film structures including thickness and porosity of the oxide coatings have strong influences on the optical properties. Equally

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important is the nature and chemical state of the pigments used. Transition metal salts of Cr, Co and Ni are the most common pigments and Al, Cu or stainless steel are used as substrates [1–12].

Characterization of the physical/chemical compositions of these coatings have been a major research activity over the last two decades. Microstructural characterization have usually been carried out using optical and/or electron microscopic techniques but for chemical characterization X-ray photo (XPS) or Auger electron spectroscopy (AES) coupled with depth profiling techniques are the most common ones. In our previous study, we had reported on the spectroscopic analysis of the surfaces of Ni pigmented aluminum selective coatings prepared by using both nickel sulfate and acetate [13]. In this study, we report on similar analysis of Co and Cr pigmented selective coatings on copper.

2. Experimental procedure

Copper samples consisting of 3 × 2 cm flat pieces were subjected to a chemical polishing treatment consisting of acid etchants (H_3PO_4, HNO_3 and CH_3COOH) at 65°C. Electroplating was achieved using a classical double walled three electrode cell coupled to an EG&G 273 Potantiostat–Galvanostat system at constant current density. In the cobalt plating bath $CoSO_4 \cdot 7H_2O$, $CoCl_2 \cdot 6H_2O$, H_3BO_3 and HNO_3 were used as electrolyte at a constant temperature of 20°C [14]. A current density between 100 and 300 mA/cm^2 was applied. Black chrome electrodeposition was achieved using CrO_3, $BaCO_3$ and Na_2SiF_6 salts at a temperature interval of 15–50°C. A wider range of current density (75–800 mA/cm^2) was applied to obtain good selectivity.

Optical reflection/emission properties of the samples were characterized using a Jasco V500 spectrophotometer equipped with an ILN-472 integrating sphere in the UV–visible range and a Jasco FTIR/700 and RSA-FTIR 6 in integrating sphere combination in the IR. The reflectance of the samples was recorded using a gold sphere blank as a reference. Surface characterization using XPS measurement was performed on samples cut to 4 × 10 mm dimensions using a Kratos ES300 spectrometer with Mg K_α X-rays (1253.6 eV) equipped with a 1 kV Ar^+ ion gun for etching. Spectrum of $CoCl_2$ is also recorded for comparison. FTIR reflectance analysis were accomplished using a Bomem 102B spectrometer with a Harrick DRA-B03 diffuse reflectance attachment.

3. Results and discussion

In Table 1 we tabulate preparation and measured solar–optical parameters for few representative Co and Cr pigmented samples. The solar absorbance, α, is calculated from the reflectance between 300 and 4000 nm, and the thermal emittance, ε, between the limits 2000 and 20000 nm [11]. Solar absorbance and emittance values are

Table 1
Solar absorbance (α) and thermal emittance (ε) values together with deposition time and temperature

	Dep. Time (s)	Dep. T (°C)	Current density (mA/cm^2)	α	ε
Co-I	5	20	100–140	0.92	0.17
Co-II	15	20	100–140	0.95	0.40
Co-III	20	20	100–140	0.94	0.57
Co-IV	25	20	100–140	0.96	0.71
Cr-I	60	18	100–140	0.85	0.12
Cr-II	90	18	200–250	0.93	0.19
Cr-III	90	30	200–250	0.94	0.46
Cr-IV	10	18	250–800	0.96	0.04

optimized both for Co and Cr pigmented copper plate and reached:
$\alpha = 0.92$ and $\varepsilon = 0.17$ for Co pigmentation [14],
$\alpha = 0.96$ and $\varepsilon = 0.04$ for Cr pigmentation [15].

Fig. 1 depicts the X-ray photoelectron spectra of the Co and Cr samples which have the optimum absorbance/emittance values. Both spectra are dominated by Co (or Cr) photo and Auger electron features together with C-1s, Cl-2p, O-1s and O-KLL Auger peaks. Carbon is always present on the surface due to hydrocarbon deposits and the presence of chlorine is due to the salts used for pigmentation. No features belonging to Cu could be identified. This is quite different from the Ni-pigmented aluminum oxide selective absorbers where it was reported that the surface atomic ratio of Ni/Al was 0.04 determined by XPS which was 15 times lower when compared with the bulk ratio [13]. Filling of the pores of the aluminum oxide by the Ni-pigmentation is obviously not the case for the black cobalt or chromium and copper tandem stacks [16]. Thus, the tandem has the high solar absorbance of the black exterior deposit and the low thermal emittance of the metallic copper reflector substrate.

Assigning the chemical state of the species observed in XPS have always been one of the major source of discrepancy among the researchers in this field and the most common practice is to use the C-1s peak as a reference at 285.0 eV arising from hydrocarbon deposits. Even in this method referencing errors up to about 1 eV is not uncommon. Considering the fact that most chemical shifts between different cationic charges are about 1–2 eV and can also vary again from 1–2 eV with respect to the counterion, serious errors in chemical state assignments can occur. For example the tabulated values for the Co-$2p_{3/2}$ peak in CoO and $Co(OH)_2$ are 780.4 and 781.3 eV [17] and our measurement gives 781.8 eV for $CoCl_2$. Our measured binding energy for Co-$2p_{3/2}$, 781.2 eV, is very close to $Co(OH)_2$ and suggest $2+$ for the chemical state of Co on the surface of pigmented copper. The tabulated values for Cr^{3+} have even larger variations; for Cr $2p_{3/2}$ in Cr_2O_3, $CrCl_3$ and CrF_3 the tabulated binding energies are 576.6, 577.8 and 579.4 eV, respectively (see Table 2) [18] and there is no tabulated value for $Cr(OH)_3$. Extrapolating from the Cr values one would estimate an approximate 0.8 eV up-shift from the Cr_2O_3 to yield 577.4 eV for the Cr-$2p_{3/2}$ binding energy in the hydroxide which is very close to our measured binding value, hence,

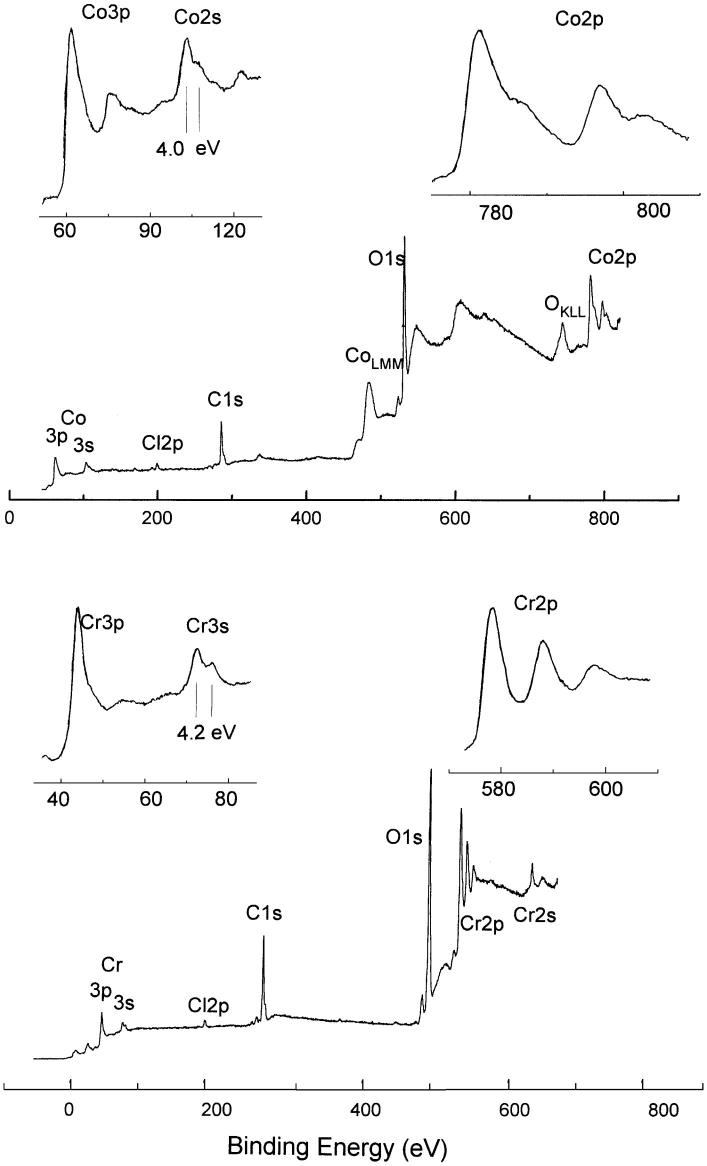

Fig. 1. XPS spectra of Co and Cr pigmented copper plates. Shown in detail are the 2p and 3p–3s regions and the 3s multiplet splitting.

a 3 + chemical state can be assigned to the Cr on the surface of our pigmented samples. Both surfaces also contain hydroxides which is further evidenced by the presence of strong and broad absorption band between 3000 and 3500 cm^{-1} in the IR reflectance spectra of these samples recorded by using an FTIR spectrometer equipped with a diffuse reflectance attachment.

Table 2
Measured and tabulated 2p binding energies and 3s splittings of Co and Cr

	$2p_{3/2}$ (eV)		$\Delta E3s$ (eV)
Co (pig)	781.2	–	4.0
Co (pig) [Ar^+etch]	781.1	779.0	
CoO	780.4[a]	–	
$Co(OH)_2$	781.3[a]	–	
$CoCl_2$	781.8	–	
$CoCl_2$ [Ar^+etch]	781.7	779.6	
CoF_2			4.9[b]
CoF_3			5.3[b]
Cr (Pig)	577.5		4.2
Cr_2O_3	576.6[a]		4.1[b]
$CrCl_3$	577.8[a]		3.9[b]
CrF_3	579.4[a]		4.2[b]

[a] Ref. [16].
[b] Ref. [18].

When paramagnetic atoms or ions are present there are additional features in the XPS spectra due to paramagnetic splitting which could also be used to reinforce chemical state assignment. For example, the 3s peaks in Co and Cr are split into two as a result of the coupling of the remaining 3s electron in parallel or antiparallel spin state to the spin of the unpaired 3d electrons of the element. The observed multiplet splitting is approximately 4.1 eV for Co^{2+} ($3d^6$) but is around 5.3 eV for Co^{3+} ($3d^5$) [18,19]. Our measured value of 4.0 eV multiplet splitting in Co pigmented samples also corroborates our assignment as Co^{2+}. Similarly for Cr^{3+} the previously tabulated 3s multiplet splitting of 4.2 eV matches the 4.2 eV splitting measured for our samples.

With respect to Ar^+ ion etching, to investigate the changes in the chemical state of certain species as a function of depth, one has to exercise even more care since it is well-established that energetic Ar^+ ions (as well as X-rays and electrons) can cause severe chemical alterations [20]. Fig. 2 demonstrates one of these alterations under typical etching conditions. The top two spectra display the Co-2p XPS spectra of our pigmented sample before and after 30 min of 1 kV Ar^+ ion-etching. As can be seen additional features which can be assigned to zero-valence Co show up in the spectrum. Exactly the same type of reduction under Ar^+ bombardment is also observed for $CoCl_2$ powders as shown at the bottom of the figure. As a result we did not continue to determine either the variation in the chemical state or the composition as a function of depth of our pigmented samples.

4. Conclusions

Determination of the chemical state of the pigments in the absorber layer is very crucial for predicting their behavior against atmospheric and/or overcoating

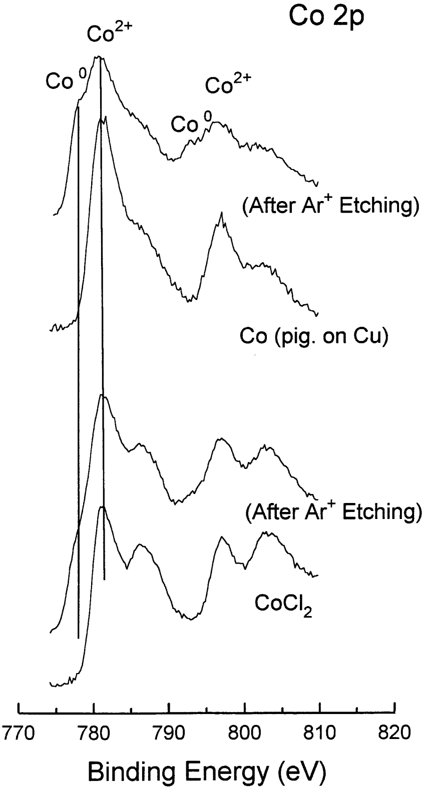

Fig. 2. Co-2p XPS spectra of Co pigmented copper and $CoCl_2$ before and after 30 min 1 kV Ar^{+} ion etching.

preparation conditions. Our results reveal that only oxidized or oxy-hydrated forms of cobalt or chromium are present on the selective surfaces as opposed to the previously reported observation of metallic Co and Cr as the electrochemically deposited composites of Co_xO_y and Cr_xO_y [5,6,21]. From the thermodynamic point of view the presence of metallic cobalt is possible since it is a slightly noble metal and can electrochemically be obtained in the metallic state by the action of hydrogen at low potential values [22]. However, we have to mention that the Pourbaix diagram represents a simple Co–O–H system and is not truly representative of the complex electrolyte system involved in our work which includes nitrate ions as oxidant. Thus, use of an oxidant and the application of a relatively high current density (100–300 mA/cm^2) resulted in the formation of only the oxidized form of cobalt on the surface. Other studies have also shown that cobalt oxide absorber layers on noble metal substrate are stable to air exposures of 1000 h at 500°C [23]. It appears that surfaces containing cobalt oxide not only possess favorable selective optical properties but also, in combination with a passivated substrate, can be considered as worthy components of a viable high-temperature selective solar coatings. Similarly, the high current density applied might be the cause for the observation of only the oxidized form of chromium on the surface. We cannot, however, ascertain whether or not cobalt or chromium are present in the metallic state away from the surface of our samples since we cannot satisfactorily discriminate against Ar^+ ion-induced reduction.

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