



# The use of trivalent chromium bath to obtain a solar selective black chromium coating



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## ABSTRACT

Black chromium coatings were electrodeposited from a trivalent chromium bath using a ZnO additive as a second main component. Black chromium was electrodeposited on steel and copper plates and substrates plated with bright nickel prior to black chromium electrodeposition. The black chromium coatings were characterized by XRD and SEM. The XRD data suggest that the phase structure of black chromium may be defined as a zinc solid solution in chromium or a chromium solid solution in zinc depending on the chromium/zinc ratio in the deposit. The role of substrate finish was evaluated through the corrosion resistance and reflectance of black chromium. According to corrosion tests the samples plated with bright nickel prior to black chromium deposition have shown the highest corrosion resistance. The electrodeposited black chromium possesses good optical properties for the absorption of solar energy. The absorption coefficient of black chromium was found to be over 0.99 for the samples obtained without the Ni undercoat and below 0.99 for those obtained with the use of Ni undercoat. However, the use of nickel undercoat before black chromium plating is recommended because it remarkably improves the corrosion resistance of samples.

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## 1. Introduction

Solar selective coatings absorb solar radiation and convert it into thermal energy. Black deposits containing chromium are used as commercial finishes under the name “black chromium”. Black chromium is widely used in solar collectors due to its high absorptance, good stability and high thermal resistance. Traditionally, the solar selective coatings are deposited on metallic substrates (Ni, Cu, steel) from a hexavalent chromium bath using pulse current electrolysis to improve the optical properties of the coatings [1]. The data on electrodeposition of selective black chromium coatings, their microstructures, optical properties and degradation as absorbers have been published in several works [2–9]. As for composition of black chromium, there is no general agreement among authors. One view holds that as-deposited black chromium consists of chromium hydroxide and metallic Cr, both of which convert into oxides during thermal annealing at temperatures about 400 °C [7,8], whereas, no evidence for metallic chromium was found in other works [10,11]. The earlier sources [12,13], which were

devoted to the research in the field of black coatings electrodeposition, suppose that metal was incorporated into the oxide film as fine separate grains that formed light absorption centres. In the case when the metal content in the deposit is low, the optical constants are such as to give low reflectance at a sufficiently large thickness. The appearance of black deposits arises from a decrease in reflectance. The authors suggest that appreciably thick layers of a dielectric containing metal in the form of dispersed particles smaller than the wave-length of light may look black even though the metal content is not too high [13]. It was found [6] that the solar absorptance of black chromium is dependent on the volume ratio of Cr to Cr+Cr<sub>2</sub>O<sub>3</sub> in the deposit and the coating thickness. The substrate influences the solar absorption as well. The best suited thickness of black chromium was found to be about 1.0 μm for the copper substrate and about 0.7 μm for the nickel one [14]. The substrate morphology influences the structure and thermal stability of black chromium [10,15]. The black chromium coatings are stable at temperatures under 350 °C; however, a stainless steel/black chromium system is stable up to 450 °C [16]. Various substrate treatments, which are used prior to plating, affect the structure, morphology, chemical composition and selective characteristics of black chromium [17]. It was found that electropolishing of the substrate allows obtaining coatings with

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more metallic chromium, whereas, mechanical polishing results in a coating with more oxides of chromium. This suggests that the use of electropolishing after mechanical polishing of the substrate makes it possible to improve selectivity of black chromium.

It is known [18], that monodispersed spherical particles of  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub>, which are synthesized from a diluted solution of KCr(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O using the aqueous chemical growth (ACG) technique, may be used for solar absorber applications. The structural, morphological and chemical characteristics of the black Cr-Cr<sub>2</sub>O<sub>3</sub> coatings deposited on the tantalum substrate using the physical–chemical ACG method and modified by annealing to Cr/ $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> were discussed in [19]. The black Cr-Cr<sub>2</sub>O<sub>3</sub> coating, which consists of metallic Cr, Cr<sub>2</sub>O<sub>3</sub>, hydrated oxides and hydroxides of Cr, are transformed during annealing into the polycrystalline Cr/ $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> of high absorptivity. It should be noted that the hydrated Cr<sub>2</sub>O<sub>3</sub> *n*H<sub>2</sub>O is amorphous, whereas,  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> is a stable corundum phase. The results of electron spin resonance (ESR) study show that dehydration/rehydration of Cr<sub>2</sub>O<sub>3</sub> *n*H<sub>2</sub>O is possible during the heating-cooling cycles [20]. According to the published data [21], the Cr/ $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> coatings deposited on Cu or stainless steel substrates are good candidates for solar absorbers. The film microstructure, surface composition and morphology affect the optical properties of the black coating.

The solar selective black coatings may be electrodeposited from trivalent chromium baths [22]. It is known [23], that ions of metals of high density such as Ni(II), Co(II) or Fe(II) were used as a second main component to improve the efficiency of Cr(III) bath. However, the information on the use of zinc as a second component in a trivalent black chromium bath is lacking. Taking into account that zinc is an anodic metal as compared to nickel, iron or other cathodic metals, it was expected that co-deposition of zinc with chromium will improve the protection of the substrate. As impurities of hydrogen, oxygen and other elements influence the properties of black chromium [24–26]; our interest was to clarify the influence of zinc on the electrodeposition and properties of the black chromium.

The aim of this research was to obtain solar selective black chromium using a trivalent chromium bath and to study the properties of the deposits in order to optimize the bath composition and plating parameters.

## 2. Experimental

Black chromium coatings were electrodeposited on steel containing 99.4% of iron (Steel-3), copper and nickel undercoat (10  $\mu$ m). Before electrodeposition the substrates were mechanically polished with further electropolishing. The Cu substrate was mechanically degreased by grinding with 600-grit SiC paper and then electropolished in a commercial degreasing solution at 20 °C under a current density of 0.05 A cm<sup>-2</sup> for 3 min, using the substrate as an anode. After that, samples were washed with distilled water and immediately placed in the plating bath. The steel substrate was also treated mechanically and electropolished in the commercial solution containing 27.5 g l<sup>-1</sup> sodium carbonate, 17.5 g l<sup>-1</sup> sodium triphosphosphate, 2.5 g l<sup>-1</sup> sodium silicate, 2.5 g l<sup>-1</sup> synthanol DS-10 (CAS No 12679-83-3) and 50 g l<sup>-1</sup> sodium hydrate at a current density of 0.05 A cm<sup>-2</sup> for 5 min at 50 °C, using the substrate as an anode and a Ti plate as a cathode. After that samples were washed with distilled water, soaked in a hot 20 vol.% HCl solution, washed again with distilled water and then immediately placed in the plating bath. A bath of a volume of 1 l with two vertical Pt anodes and a cathode between them was maintained at a constant temperature. The cathode (substrate) and anode were disposed within the bath at a distance of 25 mm. The current density during plating was 0.2–0.4 A cm<sup>-2</sup> and the temperature was 20–35 °C. A current density of 0.4 A cm<sup>-2</sup> and a temperature of 20 °C were selected as a

**Table 1**

The base composition of the black Cr(III) bath.

Component	g l <sup>-1</sup>
CrCl <sub>3</sub> ·6H <sub>2</sub> O	250
NH <sub>2</sub> CH <sub>2</sub> COOH	18.75
H <sub>3</sub> BO <sub>3</sub>	30.0
NaCl	60.0
NaNO <sub>3</sub>	3.0
ZnO	5.0
pH = 1.2	
Temperature 18–20 °C	
<i>i</i> <sub>c</sub> = 0.2–0.4 A cm <sup>-2</sup>	

compromise between efficiency and deposit quality. The electrodeposition rate of black chromium was determined gravimetrically.

Initially, the chemical composition of the plating bath and working conditions were designed taking into account the colour, homogeneity and adhesion of the coating. Inexpensive materials such as chromium chloride, zinc oxide, boric acid, sodium chloride and sodium nitrate were used to prepare the plating bath. All solutions were prepared from analytical grade chemicals (manufacturer AppliChem GMBH) without further purification using distilled water. To improve the optical properties of a black coating the additive materials were selected experimentally. Glycine (NH<sub>2</sub>CH<sub>2</sub>COOH) was found to be the proper complexing agent for Cr(III) and ZnO was used to improve the quality of the black chromium coatings. The final chemical composition of plating bath is presented in Table 1.

The quality of the deposits was assessed visually and by using an optical microscope. A deposit of good appearance and good adhesion was defined as a high quality deposit for further research.

The black chromium coatings were examined for morphology and chemical composition using scanning electron microscopy (SEM) and energy disperse spectroscopy (EDS), respectively. In order to choose a typical picture for each coating, three–four locations (in the central zone) were taken. The phase composition of black chromium was examined by using X-ray diffraction (XRD). The XRD 2 $\theta$  scans of the coatings were measured using an X-ray diffractometer SmartLab (Rigaku) equipped with a 9 kW rotating Cu anode X-ray tube. The grazing incidence (GIXRD) method was used in the 2 $\theta$  range 30–75°. The angle between the parallel beam of X-rays and the specimen surface ( $\omega$  angle) was adjusted to 0.5°.

Reflectance measurements were performed by using a UV VIS spectrophotometer SPECORD® 2500 with variable angle reflectance attachment from analytic Jena (Germany). The Wavelength range in which this Spectrophotometer may be employed is 190–1100 nm. The angle of reflection is variable in the range of 11–60°. Based on our practice, reflection measurements under an incidence of 12° are the most stable compared to those under 8–11°. Therefore, in our experiments the angle of incident light is 12°.

The corrosion resistance of the coatings was tested according to LST EN ISO 9227:2012 standard [27], using a salt-spray chamber “Q-Fog CCT 600-CE”. The samples were submitted to the salt spray test and evaluated according to LST EN ISO 10289:1999 by the time until the emergence of the first corrosion points. The temperature in the testing chamber was maintained at 35 ± 2 °C.

## 3. Results and discussion

It is known that trivalent chromium has a tendency to form various complexes in aqueous solutions [28]. In order to prevent the formation of undesirable complexes, it is essential to use a weak complexing agent. The optimal electrolyte composition and operating conditions of black chromium electrodeposition were determined experimentally. According to experiments, formic acid

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