Characterization of black chrome films prepared by electroplating technique

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Abstract: The surface and optical properties of black chrome films prepared by two different electrochemical baths were characterized. The black chrome films have been deposited on bright nickel substrates by electroplating technique. The surface morphology and phase structure of the films were investigated by using scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. The chemical composition of prepared films was determined by energy-dispersive x-ray analysis (EDS). The spectral reflectance was also measured in the UV-Vis-NIR and IR regions. From the SEM analysis, it was found that prepared films by the first chemical bath is denser with nano size grains and by the second chemical bath they become porous, with micro sized grains. The XRD results show that in both cases chrome is the main chemical component in the films. The films prepared by second chemical bath have better optical properties than the films prepared by first chemical bath.

Keywords: *Black chrome, Electroplating, Solar collector.*

1. Introduction

The growing energy demand through out the world has attached great important to the study of renewable source [1]. The cost and effective utilization of solar energy and conversion of that into thermal energy requires an efficient solar coating as having high solar absorptance (>0.9) in the visible region and very low thermal emittance (<0.1) in the infrared to minimize the radiation heat loss [2, 3]. This property is named selectivity [4]. The higher the selectivity value, the better the thermodynamical efficiency of the solar energy collectors [1]. Other necessary properties of a practical solar selective coating are ease and availability of application, low cost and long-term durability under solar radiation [5]. Black chrome is one of the most commonly used solar selective coatings in solar collector systems for the efficient conversion of solar energy into thermal energy. A variety of deposition techniques such as chemical oxidation, CVD, spray, sputtering and electroplating are available for preparation of solar selective surfaces. Of the above techniques, electroplating is attractive due to its simplicity, low cost and large area involved [2]. Electroplating of metallic films is one the appropriate techniques for obtaining absorber coatings with selective optical properties for solar collectors. Electroplated black chrome is one of the most widely used solar absorber, mainly due to its high absorptance, good stability in a wide rang of oxidizing/reducing environments and high thermal resistance [3]. Coatings used as solar selective surface in solar collectors have low thicknesses, therefore these coatings cannot protect the substrate against atmospheric corrosion and thermal oxidation. For solving this problem bright nickel coating before black chrome deposition is recommended [6]. Nickel under coat before black chrome deposition decreases thermal emissivity and increases thermal resistance of black chrome coatings [3].

2. Experimental method

Electroplating is an electrodeposition process for producing a dense, uniform, and adherent coating, usually of a metal or an alloy, upon a conductive surface by the act of electric current. The core part of the electroplating process is the electrolytic cell (electroplating unit). In the electrolytic cell a current is passed through a bath containing electrolyte, the anode, and the cathode. The workpiece to be plated is the cathode (negative terminal). The anode, however, can be one of the two types: sacrificial anode (dissolvable anode) and permanent anode (inert anode). The sacrificial anodes are made of the metal that is to be deposited. The permanent anodes can only complete the electrical circuit, but cannot provide a source of fresh metal to replace what has been removed from the solution by deposition at the cathode. Electrolyte is the electrical conductor in which current is carried by ions rather than by free electrons (as in a m etal). Electrolyte completes an electric circuit between two electrodes. Upon application of electric current, the positive ions in the electrolyte will move toward the cathode and negatively charged ions toward the anode. This migration of ions through the electrolyte constitutes the electric current in that part of the circuit. The migration of electrons into the anode through the wiring and an electric generator and then back to the cathode constitutes the current in the external circuit. The metallic ions of the salt in the electrolyte carry a positive charge and are thus attracted to the cathode. When they reach the negatively charged workpiece, it provides electrons to reduce those positively charged ions to metallic form, and then the metal atoms will be deposited onto the surface of negatively charged workpiece [7].

Black chrome electroplates are obtained by replacing the sulphate ion in conventional chrome plating baths by fluoride, silicofluoride, acetate, borate, nitrate or sulphamate ions. Care should be taken to ensure complete removal of the sulphate ions; these are deleterious to the bath. The substances introduced in to the bath as catalysts can be divided into three groups, acetate baths, floride-catalysed baths and nitrates and other catalysts. In the fluoride or mixed catalyst plating baths a higher plating efficiency, a harder, more corrosion and wear-resistance deposit is obtained. The fluoride is commonly added as the SiF_6^{2-} ion in amount of 2-3g/l. this chemistry provides better substrate activation for plating on bright nickel [8].

The deposition of black chrome was carried out on bright nickel plated brass substrates in an electrochemical bath by electroplating technique. The brass substrates of 0.1 mm thickness were cut in strips of 5.5 cm × 6.5 cm for electroplating of bright nickel. The brass substrates were pretreated by different cleaning procedure. Mechanical polishing was done with a grinding paper No.2000, followed by rinsing in distilled water. Then substrates were cleaned in a hot commercial alkaline cleaner, followed by rinsing in distilled water and activated in an aqueous 10 vol% H_2SO_4 solution, followed by rinsing in distilled water. Then bright nickel deposited on pr epared brass substrates by electroplating technique. The chemical bath for bright nickel deposition consists of nickel sulphate ($NiSO_4$), nickel chloride ($NiCL_2$) and boric acid (H_3BO_3). The bright nickel deposition carried out in 0.5A/dm^2 current density for 5 min in 50 °C-60 °C temperatures. Nickel metal with 99.9% purity used as anode for bright nickel deposition and brass substrate was used as cathode. Prior to the deposition of black chrome, the prepared bright nickel substrates were cleaned in a hot commercial alkaline cleaner, followed by rinsing in distilled water and activated in an aqueous 10 vol% H_2SO_4 solution. Following activation the plates were thoroughly rinsed in distilled water to remove all trace sulphate. Then black chrome was deposited on br ight nickel substrates. The deposition conditions to get black chrome were optimized by varying the chemical bath composition, current density and plating time. In this paper, two chemical baths were used for electroplating to comparison of surface and optical properties of these surfaces and selecting the better films.

The first bath for black chrome deposition consists of chromic acid, acetic acid and barium acetate (acetate bath). Electrodeposition carried out in 3A/dm^2 current density for 180 seconds in 50 °C temperature. The second bath for black chrome deposition consists of chromic acid, fluorosilicic acid and barium carbonate (floride-catalysed bath). Deposition carried out in 6A/dm2 current density for 120 seconds in 25 °C temperature. Several experiments were done to prove the reproducibility of the samples.

Details of the optimized plating processes used in this study are given in table 1.

Table 1. Experimental electrodeposition parameters.

Bath	Composition	Temperature (°C)	Current density (A/dm^2)	Plating time (s)
First	Chromic acid (CrO_3) Acetic acid (CH_3COOH) Barium acetate ($Ba(CH_3COO)_2$)	50	3	180
Second	Chromic acid (CrO_3) Fluorosilicic acid (H_2SiF_6) Barium carbonate ($BaCO_3$)	25	6	120

Barium compounds such as the carbonate, acetate or hydroxide are usually added to black chrome plating solutions. Their role is to precipitate any sulphate ions from solution, and apart from possible complexation of the carbonate ion with Cr (III), they are not expected to significantly affect black chrome electrochemistry [9].
For the black chrome deposition Pb-Sb alloy, which contains only 2-5% Sb, was used as the anode(the permanent anode) and bright nickel substrate used as cathode. After deposition the samples were cleaned in distilled water and air dried at room temperature. Surface morphology of the coatings was characterized with scanning electron microscopy (SEM), manufactured by Philips, XL30 model. The X-ray diffraction (XRD) analysis was done using a PW1840 diffractometer. The normal spectral reflectance of the electrodeposited black chrome coating in UV-Vis-NIR and IR regions was recorded using a Cary 500 Scan UV-Vis-NIR spectrophotometer and FTIR Jasco, respectively.

3. Results and discussion

3.1. SEM analysis

Fig. 1 gives the scanning electron microscopy (SEM) of magnification 15000× for black chrome films prepared from two different baths. Figure 1 shows that the surface morphology of films deposited from different bath composition are different. From the SEM analysis it was found that the black chrome films achieved from the first bath is denser with nano size grains but films deposited from the second bath they become porous, with micro sized grains.

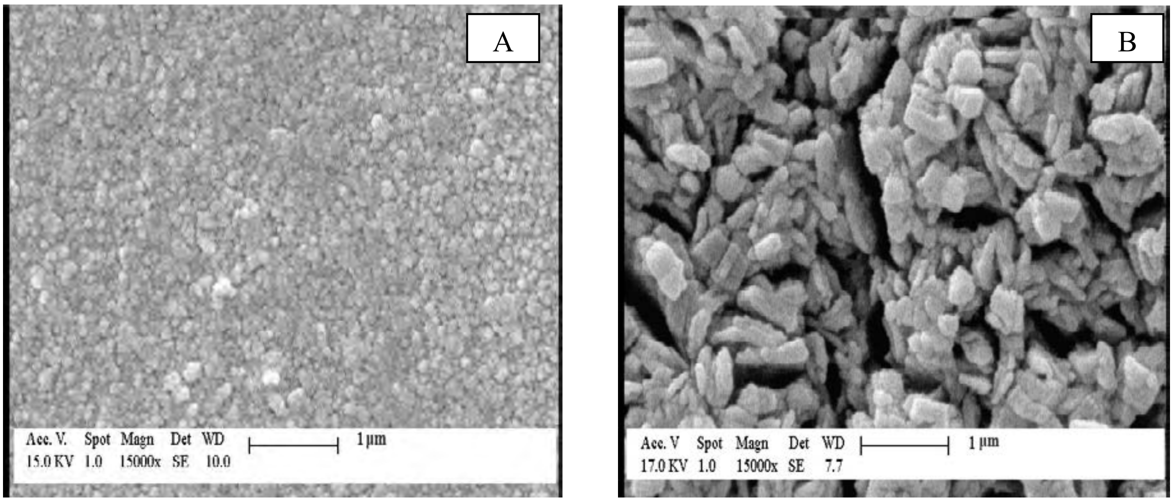

Fig. 1. The SEM images of black chrome films deposited on bright nickel substrates from two different baths. A: first bath, B: second bath.

3.2. EDS analysis

Fig. 2 and Table 2 show the chemical composition of black chrome deposited from two different baths. The data indicate that films prepared from both baths have contained chrome in their composition. Wight percentage of chrome in films prepared from the second bath is more than of the films prepared from the first bath.

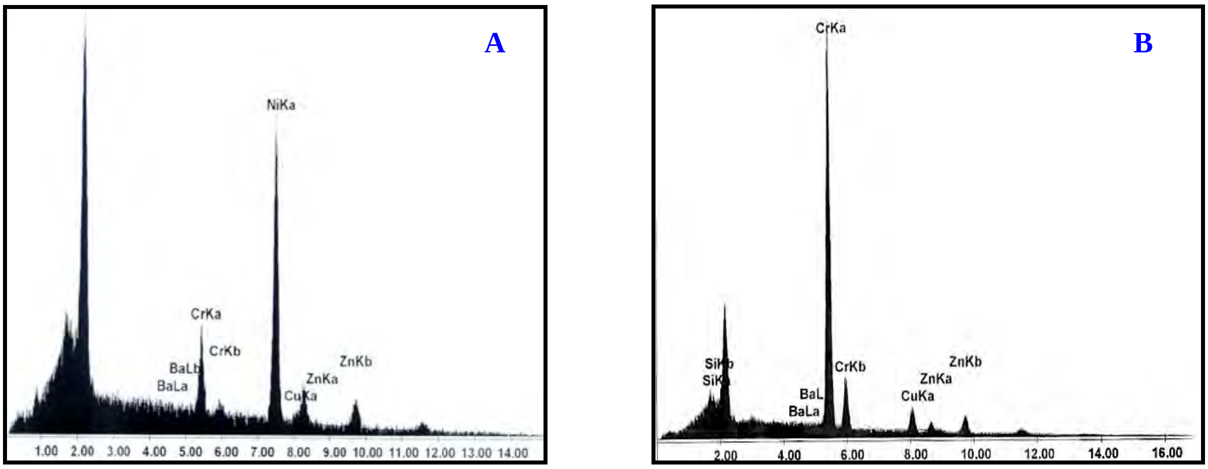

Fig. 2. The EDS spectrum for black chrome films deposited d on bright nickel substrate from two different baths. A: First bath, B: Second bath.

Table 2. The EDS analysis of black chrome deposited from two different baths.

Elements	Wt.% first bathe	Wt.% second bath
Cr	8.38	62.62
Ni	84.23	12.50
Cu	4.58	12.80
Zn	1.65	8.53
Si	-	1.92
Ba	1.16	1.63

3.3. XRD analysis

In order to identify the predominant chrome phase in the deposited films, it is necessary to investigate the coatings using X-ray diffractometer. Fig. 3 shows the XRD patterns for the bright nickel substrate coated with black chrome films. It is possible to detect that the bulk structure of the black chrome films were mainly consist of metallic chrome with the crystallographic plane (110) perpendicular to the substrate [6, 7]. As can be seen from Fig. 3, the different compositions of chrome are obtained in these two films prepared from two different baths.

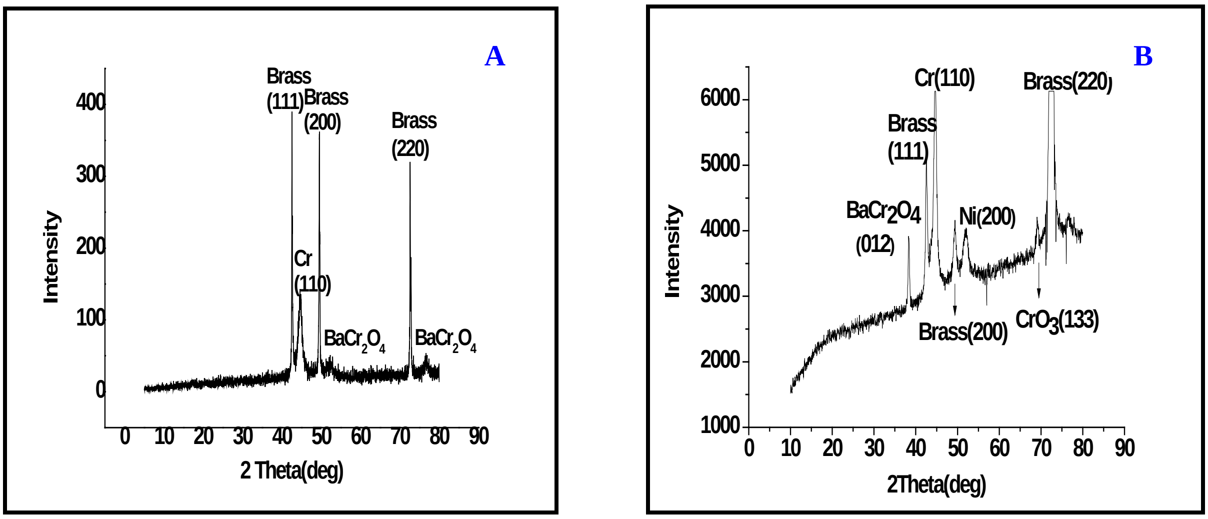

Fig. 3. The XRD patterns for black chrome films deposited on bright nickel substrate from two different baths. A: First bath, B: Second bath.

3.4. Spectral reflectance

The influence of two different electrochemical baths on the selective absorber properties of black chrome films are given in Figs. 4 and 5. Figs. 4 and 5 shows the spectral reflectance in the UV-Vis-NIR and IR regions for black chrome deposited on b right nickel substrates prepared from two different baths respectively. From figure 4 it is evident that the spectral reflectance in UV-Vis-NIR region is below 12% for black chrome films deposited on bright nickel prepared from both baths, indicating that in this spectral region the solar absorptance is quite high [2]. Spectral reflectance for black chrome films prepared from the second bath is less than of films prepared from the first bath, hence, its absorption is higher. This difference is probably due to the rougher surface and chemical composition of these samples which enhances the absorption of the radiation and can explain the high absorptance level of this material. Hence, using of second bath is recommended to get good solar selective black chrome coating in the UV-Vis-NIR region. Fig. 5 indicates that the spectral reflectance of black chrome films in the IR (2.5µm-20µm) region, and hence the emissivity of them. From Fig. 5 it is evident that films prepared from the second bath have lower thermal emittance. It can be seen in the figure 5 that by using of the first bath spectral reflectance is reduced and hence increases the thermal emittance of films will increase.

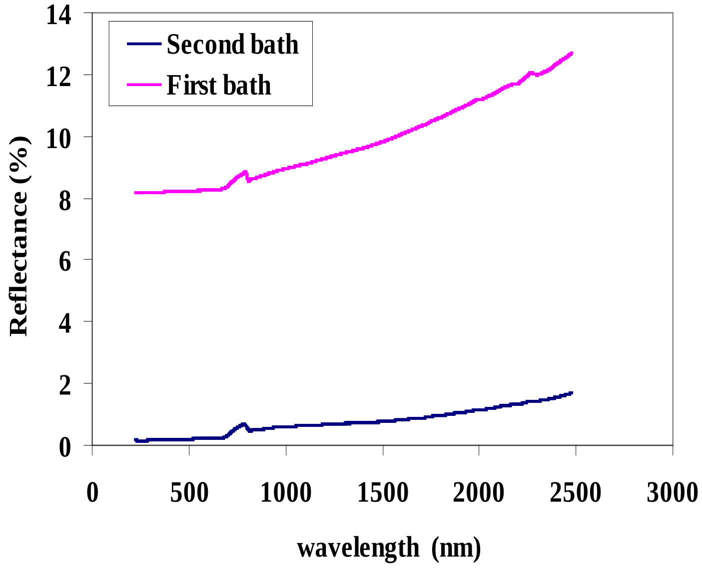

Fig. 4. The Spectral reflectance in the UV-Vis-NIR region for black chrome films deposited on bright nickel substrates from two different baths.

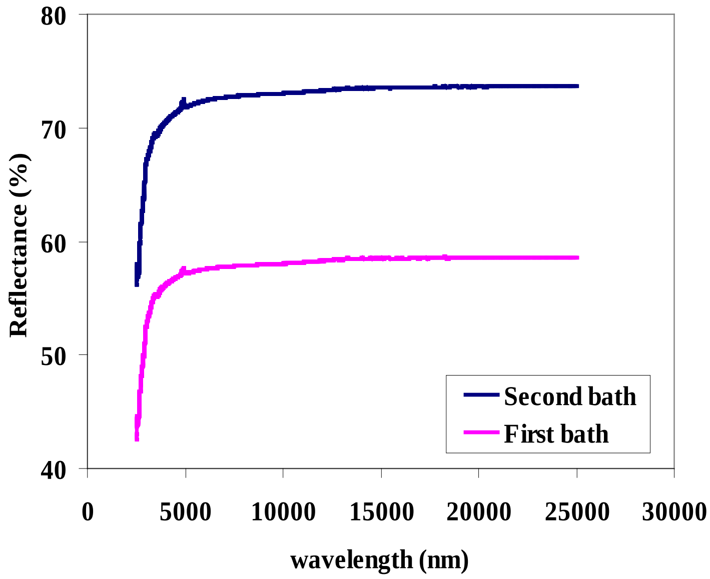

Fig. 5. The Spectral reflectance in the IR region for black chrome films deposited on bright nickel substrates from two different baths.

4. Conclusion

The black chrome films were prepared by electroplating technique from two different baths on bright nickel substrates. SEM analysis shows that films prepared from first bath is denser with nano size grains while films prepared from the second bath become porous, with micro sized grains. The EDS analysis results indicate the presence of chrome on films prepared from both baths. The chrome amount in the films prepared from second bath is higher than one. XRD analysis shows that structure of black chrome films from both baths were mainly consist of metallic chrome with (110) orientation. Black chrome films have good optical properties for solar energy absorption. The spectral reflectance in the UV-Vis-NIR and IR regions shows that films prepared from the second bath have higher absorption and lower emittance, Hence these films are better for using in solar collectors.

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