

Selective Solar Surface Solar Based on Black Chromium: Influence of Electrodeposition Parameters in the Absorption of Surfaces

Ithyara Dheylle Machado Medeiros^{a,*}, Kelly Cristiane Gomes^{a,b} 

Ronny Peterson da Nobrega Gonçalves^a, Gabriela Oliveira Galvão^b

^aPrograma de Pós-Graduação em Engenharia Mecânica, Universidade Federal da Paraíba - UFPB, João Pessoa, PB, Brasil

^bDepartamento de Engenharia de Energias Renováveis, Universidade Federal da Paraíba - UFPB, João Pessoa, PB, Brasil

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The search for the reduction of costs for the implementation of renewable energies implies in the optimization of the parameters of the manufacturing processes of consolidated technologies. Among these technologies are the solar collectors composed of absorber films characterized by high absorption in the spectrum range corresponding to solar radiation and low emittance in the infrared range, allowing an increase in the collector's operating temperature (300 to 700°C). The present work produced selective surfaces based on black chrome absorber films on stainless steel substrate by electrodeposition. The substrates were immersed in a chromium trioxide bath with hexafluorosilicic acid using a Pb-Sn electrode. In the project some parameters of deposition were evaluated (time, distance and voltage) and their influence on the surface roughness of the coatings obtained by correlating them with the absorptions of the produced surfaces. For this, the surfaces produced were characterized by UV-Vis-NIR, profilometry and SEM. The results indicate that the working distance directly influenced the increase of the films absorption and that the influence of the surface roughness on the film absorption is related to the electrodeposition time as the voltage is raised.

Keywords: selective surfaces, black chromium, electrodeposition, solar energy.

1. Introduction

The study of renewable sources of energy has become extremely relevant ahead of the growing world demand for energy¹. Among these sources, solar energy stands out. One of its forms of exploitation is through the use of solar collectors, which promote the conversion of solar energy into thermal energy². This conversion might have its efficiency amplified by the use of special coatings, called selective surfaces, which absorb the maximum possible radiation in the ultraviolet, visible and near infrared (UV-Vis-NIR) range of the electromagnetic spectrum³, while emitting little in the medium and distant infrared region, that is, they have an absorptance above 85% and emittance below 15% in the wavelength ranges mentioned⁴.

In addition to these optical characteristics, it is necessary that the coating does not suffer significant degradations during the lifetime of the collector. As a result, the selection of the most suitable deposition technique is fundamental for a good system performance. However, there are several techniques for obtaining selective solar coatings, such as: Electrodeposition, Chemical Vapor Deposition, Sputtering, Chemical Oxidation and Sol-Gel⁵.

Among these, the electrodeposition technique excels for its simplicity, low cost and possibility of large-scale

production³, apart from making films with great hardness and mechanical resistance in addition to excellent optical and thermal properties⁶. Regarding the type of material, black chromium is one of the most used coatings for the efficient conversion of solar energy into thermal energy, that along with the electrodeposition technique compose the set of fundamental characteristics for high performance⁷.

To assemble a reproducible electrochemical process of a black chromium, adhesive and homogeneous film on a metallic substrate with well defined optical and mechanical properties it is necessary to control all the electrochemical parameters involved and to understand their influence⁷. Therefore, the objective of the present study is to determine the set of parameters (voltage, anode-cathode distance and time) that produce selective black coatings electrodeposited on stainless steel substrates with the highest level of absorption in the UV-Vis-NIR region, and to correlate this maximum absorption with the thickness and the roughness of the obtained film.

The absorptance in thin films is the ratio of the amount of radiation absorbed by a solid to the amount of radiation incident on that solid. Therefore, when it is intended to evaluate the absorptance in the radiation range comprising the solar spectrum, it is necessary to verify how much of

*e-mail: gomes@cear.ufpb.br

this radiation is absorbed by the solid. This parameter can be calculated from Equation 1⁸, shown below.

$$\alpha = \frac{\int_{300}^{2500} \alpha_{\lambda} I_{sun} d\lambda}{\int_{300}^{2500} I_{sun} d\lambda} \quad (1)$$

Where α_{λ} is the spectral absorbance of the solid, I_{sun} is the spectral distribution of the solar irradiation and α is the total hemispherical absorbance.

Considering the solid to be opaque, so, there is no radiation transmitted through it, the following equation is obtained:

$$\alpha = \frac{\int_{300}^{2500} (1 - \rho_{\lambda}) I_{sun} d\lambda}{\int_{300}^{2500} I_{sun} d\lambda} \quad (2)$$

Where ρ_{λ} is the spectral reflectance of the solid.

It is therefore observed from Equation 2 that the absorbance of opaque solid materials can be calculated by measuring its spectral reflectance, which can be done from appropriate analytical techniques, such as UV-Vis-NIR spectrophotometry.

2. Experimental Techniques

2.1 Substrate cleaning

The black chrome coatings were electrodeposited on AISI 304 stainless steel substrates with dimensions of 20 mm x 30 mm x 3 mm. Before electrodeposition, the substrates were cleaned in order to eliminate any impurities that would influence the results and to allow a good adhesion between the film and the substrate⁹. They were initially submitted to a degreasing bath. Then, a solution of 0.768 g/ml of citric acid was prepared, which was diluted for 5 min at 50 °C. The substrates were then immersed in this heated solution, where they remained for 30 min. After that time, the samples were removed from the solution and placed in a beaker with isopropyl alcohol, where they were submitted through an ultrasonic bath for 15 min, being subsequently washed in distilled water, dried and stored.

2.2 Electrolytic bath

The black chromium electrodeposition of the present study used a bath composed of 274 g/l of chromium trioxide (CrO_3) and 0.854 g/l of hexafluorosilicic acid (H_2SiF_6). The temperature of the bath varied from 24 to 30°C and the electric current density was in the range of 11 to 54 A/dm². These measurements are due to the applied voltage and the components of the electrochemical bath. However, the determined values are consistent with the literature. Daryabegy and Mahmoodpoor¹⁰, for example, worked with the temperature ranging from 26 to 35°C and current

density of 19 A/dm² using the same components as the bath under analysis.

The variation of temperature and electric current density occurred due to the fact that the voltage source used only allowed the adjustment of the voltage, while the current oscillated as a function of this voltage. The source used was the continuous current one from the brand Agilent, model E3631A. For the electrodeposition, the substrate was connected to the negative pole (cathode) of the power supply, while a Pb-Sb alloy (95-5%) was connected to the positive pole (anode).

2.3 Electrodeposition parameters

During the electrodeposition process, some parameters may affect the morphology and the performance of the obtained film². Moise *et al.*¹¹, for example, cite the chemical composition of the bath, the current density and the temperature at which the electrodeposition occurs as parameters to be taken into account to obtain a reproducible coating.

While Window *et al.*¹² emphasized the interference of time, performing electrodepositions between 20 and 80 seconds. Sheu *et al.*⁹ preferred to evaluate the behavior of the film as a function of the current density variation from 10 to 70 A/dm². In contrast, Spitz *et al.*¹³ adopted the anode-cathode distance variation as one of their electrodeposition variables. From the above, it can be seen that many are the parameters studied in the literature.

As a result, the present study chose to vary three parameters of electrodeposition (voltage, anode-cathode distance and time), since these are the ones that present greater possibilities of modifications allowing a greater range of study. So that eight samples were obtained, so that three specimens were produced for each set of parameters, totaling the production of 24 samples, according to Table 1.

The choices of voltage values (5 and 6 V), anode-cathode distance (5 and 10 cm) and time (5 and 10 min) were based on literature studies. According to Daryabegy and Mahmoodpoor¹⁰ the appropriate time for electrodeposition of black chromium is 0.5 to 5 minutes. In terms of anode-cathode distance, Spitz *et al.*¹³ used 4 and 7 cm, while Lee⁶ adopted 5 cm. Through these works, the time and the distance

Table 1. Samples obtained with the variation of the parameters.

Sample Number	Electrodeposition Parameter		
	Voltage (V)	Distance (cm)	Time (min)
1	5	10	10
2	5	10	5
3	6	10	10
4	6	10	5
5	5	5	10
6	5	5	5
7	6	5	10
8	6	5	5

of 5 min and 5 cm, respectively, were chosen. While 10 min and 10 cm were used in order to investigate if larger times and distances would provide films with higher absorption.

Regarding the voltage, since the equipment used in the present study did not allow the study of the current density, the voltage was chosen to represent this parameter. So, through the works of Sheu *et al.*⁹ and Daryabegy and Mahmoodpoor¹⁰, a mean of tension was determined in which the best results of these works were obtained.

2.4 Characterization of selective films

The main parameter to be evaluated, regarding the optical properties of the selective films, is the ability of these materials to absorb solar radiation. For this purpose, the electrodeposited coatings were subjected to UV-Vis-NIR spectrophotometry. The equipment used was a Spectrophotometer in the region of UV-Vis-NIR, by Shimadzu, model UV-2600 operating in the region of the electromagnetic spectrum from 220 nm to 1400 nm with measurement of reflectance, using the integrating sphere accessory that allows the analysis of films.

This characterization was used to determine the reflectance of the coatings. Knowing that, according to Kirchhoff's law, the sum of the absorptance, transmittance and reflectance of a surface at a particular wavelength is equal to one¹⁴. This law can be written according to Equation 3 below:

$$\alpha + \tau + \rho = 1 \quad (3)$$

Where, α is the absorptance, τ is the transmittance and ρ is the reflectance of the surface.

On opaque surfaces in which the transmittance is zero¹⁵, the equation takes the form below:

$$\alpha + \rho = 1 \rightarrow \alpha = 1 - \rho \quad (4)$$

Thus, to obtain the levels of absorption of the coating produced in the present study, the Equation 4 described above was applied.

The determination of the surface roughness of the electrodeposited films as well as the measurement of the thickness of the surfaces obtained on the steel were identified by the CCI MP non-contact optical profilometer, by Taylor Hobson, connected to a computerized unit containing Talysurf CCI software (Taylor Hobson, United Kingdom) for obtaining and analyzing the data.

For the determination of surface roughness, 14 uniformly spaced readings were obtained along each of the samples. So the value of Ra provided in the results is the average of these readings.

The determination of film thickness was obtained using the "step" method, in which only part of the substrate undergoes deposition. This methodology can be better understood by observing Figure 1, in which it exhibits the substrate before and after the procedure.

After the electrodeposition, the transition region was subjected to profilometry and it was possible to determine the thickness of the film, as can be observed in Figure 2.

The visualization of the morphological characteristics of the coatings was obtained through the use of a Scanning Electron Microscope (SEM) applying the operation principle of secondary electrons with environmental module. The microscope used was the Quanta 450 model, by FEI.

3. Results and Discussion

3.1 Spectrophotometry in the UV-Vis-NIR

The absorptive films produced by electrodeposition of black chromium, through alternation of voltage, anode-cathode distance and residence time in the electrolytic bath, were subjected to radiation with wavelengths in the range of 220 nm to 1400 nm, in order to determine spectral reflectance of these films. After the proper conversions to levels of absorptance, Figure 3 shows the results obtained on the steel substrate.

Through Figure 3, it is noticeable that sample 6 presented the highest levels of absorption and of absorption stability throughout the spectrum under analysis (220 nm to 1400 nm - with a mean of 94.60 %). When considering the standard deviation, sample 6 reached a maximum absorptance of 96%. This means that, regarding the electrodeposition parameters, the 5V and 5 cm distance between anode-cathode and the time of 5 minutes in the electrolytic bath allowed the best conditions in terms of absorption and stability.

The data shown in Figure 3 corroborate with the literature as observed in the work of Bayati *et al.*¹⁶ which determined that the electrodeposition time of 5 min provided and absorption around 91 to 96% in black chromium based absorber films. The smaller anode-cathode working distances are the ones that provide the best results, as was perceived by Spitz *et al.*¹³.

This can be explained by the fact that Newby¹⁷ states that an excellent method for obtaining a uniform deposition thickness is to make the anode-cathode distance the same at all points of a part, which is more likely at smaller distances. Associated with the fact that Mandich¹⁸ reported that the ability of an electrochemical bath to uniformly deposit metal on the surface of the cathode is a measure of its throwing power, the geometrical properties of the system being that is the shape and the distance from the anode to the cathode are factors influencing this power. Hence, the smaller the distance, the greater the deposition capacity of the bath, which possibly increases the absorption of the film.

3.2 Optical profilometry

The results of the measurement of the roughness parameter *Ra* of the coatings obtained on the steel substrate can be seen in Table 2, as well as the thicknesses (maximum, minimum and average).

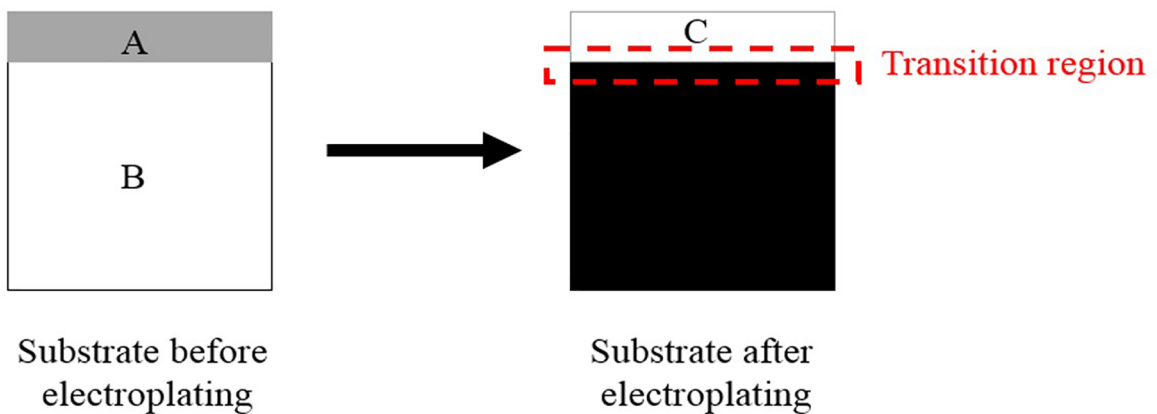


Figure 1. (a) region of the substrate that has been prevented from being deposited, (b) region of the substrate where the deposition will be made, (c) region of the substrate that was not covered during electrodeposition.

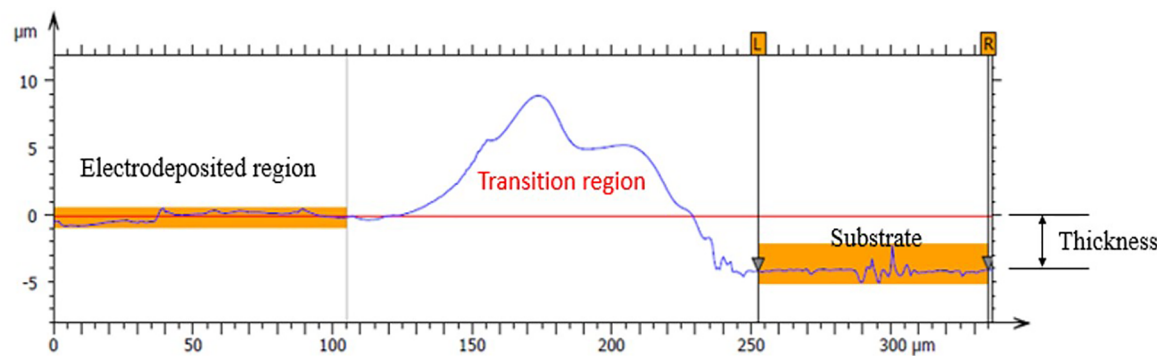


Figure 2. Determination of the thickness in the sample 6.

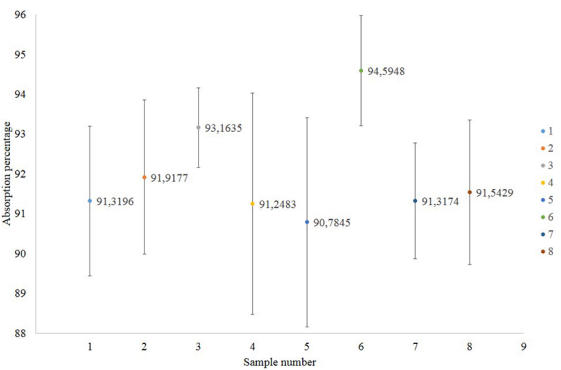


Figure 3. Average and standard deviation of the absorbance for the different absorber films deposited on steel substrates.

Table 2 shows an increase in roughness (parameter Ra) as the voltage was increased. The same was evidenced by Sheu *et al.*⁹ when studying the effects of the current density of the electrodeposition of black chromium coatings. As for the time, it was determined that the longer the electrodeposition time the larger the surface roughness obtained (parameter Ra). When establishing a relation with the absorptance, it was observed that the film that obtained the best response (sample 6) was also the one that presented the lowest level of roughness (Ra = 0.05 μm and average thickness of 3.63 μm).

Table 2. Parameter Ra of the electrodeposited films on the steel substrate and the film thicknesses.

Sample Number	Ra (μm)	Maximum thickness of the film (μm)	Minimum thickness of the film (μm)	Average thickness of the film (μm)
1	0.29	5.68	4.98	5.33
2	0.09	7.00	5.44	6.22
3	0.43	3.28	2.12	2.70
4	0.26	3.13	2.03	2.58
5	0.19	2.66	1.71	2.18
6	0.05	3.88	3.38	3.63
7	0.29	4.69	4.17	4.43
8	0.33	5.05	4.39	4.72

In relation to the working distance, the roughness is smaller at smaller distances due to the power of the bath, which at lower distances produces a greater uniformity of the film produced by the increase^{17,18}.

3.3 Scanning Electron Microscope (SEM)

The SEM analysis allowed the visualization of the surfaces of the films, thus enabling the comprehension of

the solidification processes of the films. Figure 4 shows the surfaces of the coatings.

The Figure 5 shows the surfaces of the coatings that obtained the lowest (sample 5) and highest (sample 6) absorbance.

The micrography of the present study corroborate with the literature, as in the work of Aguilar *et al.*³ which produced thin films of white and black chromium by electrodeposition on steel substrates, so that from the SEM analysis, they verified that black chromium has a lamellar morphology that leads to a strong level of dispersion, indicating a higher roughness coefficient of this film and, therefore, the dark appearance. Surviliené *et al.*¹⁹ made black chromium films electrodeposited on steel substrates and realized through SEM that black chromium coatings have a micro-fissured structure with numerous lamellar crystals.

Protsenko *et al.*²⁰ observed that when the thickness of the coatings is not very high ($\sim 10 \mu\text{m}$), the surface contains a large number of spheroids with different diameters (up to several micrometers), which coincides with that observed in Figure 2, in which the films have thicknesses smaller than $10 \mu\text{m}$ as shown in Table 2.

Thus, through the visualization of Figure 5b, it can be seen that a more uniform surface with the micro-fissured region in prominence, allowed the obtainment of higher levels of absorption.

4. Conclusion

The solar selective coating made of black chromium by the electrodeposition technique that obtained the highest level of absorption, with a mean of 94.6% and maximum of 96%

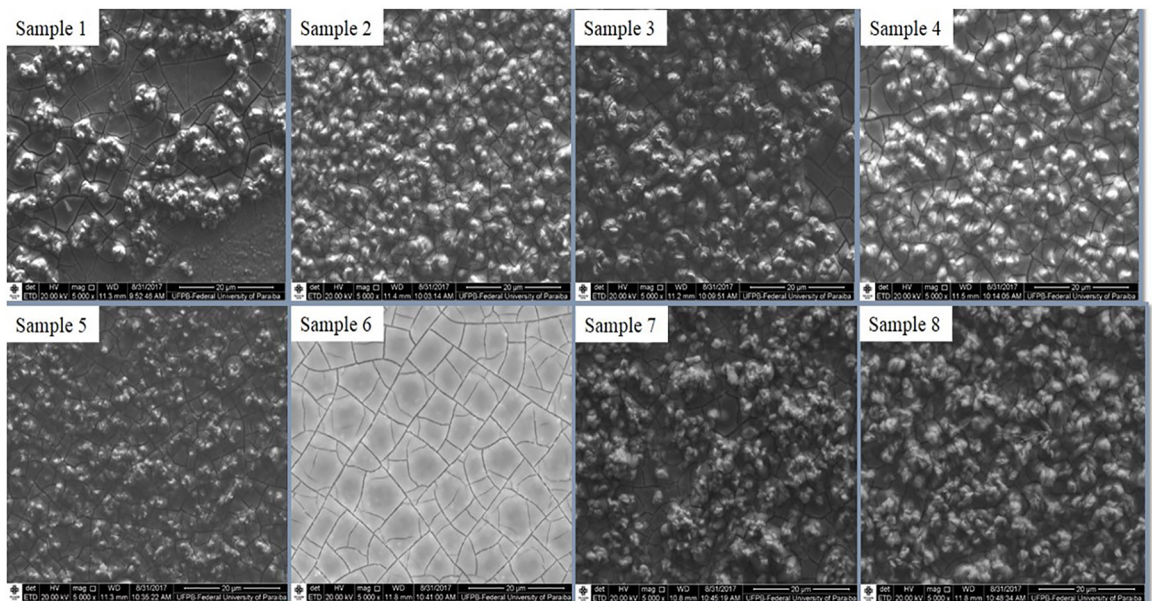


Figure 4. Micrography of films produced (Films 1 to 8).

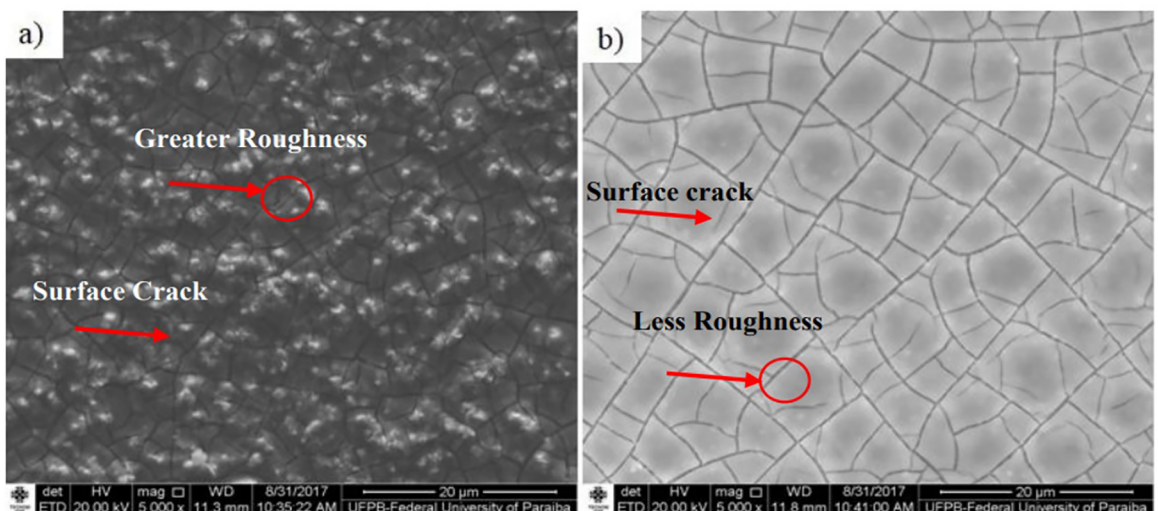


Figure 5. Micrography of (a) sample 5 and (b) sample 6.

in the UV-Vis-NIR range was the one produced with the voltage of 5V, the distance of 5 cm between anode-cathode and the time of 5 min in the electrolytic bath.

This set of parameters allowed the formation of a low roughness surface ($R_a = 0.05 \mu\text{m}$) when compared to the other films obtained, in addition to an average thickness of $3.63 \mu\text{m}$.

This roughness was observed by SEM, in which it was determined that a greater uniformity allowed higher levels of absorption of the film under study.

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