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EVALUATION OF OPTICAL AND MICROSTRUCTURAL CHARACTERISTICS OF CHROME ABSORBING FILMS

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Abstract. *The most commonly used energy sources today are non-renewable energy sources, which contribute to the greenhouse effect. Renewable energies are shown as alternative to conventional sources, among them is solar energy, solar thermal being one of the ways to use this energy, where the radiation is used for the heating of fluids, through technologies of solar concentration or in Solar collector plan to heat water up to medium temperatures. This work had as objective to produce and characterize selective surfaces of black chrome for the application in solar collectors. To perform the present study, the electrodeposition technique was used, varying the residence time in the electrolytic solution. The manufactured coatings were characterized by the techniques of X-ray Diffraction and Spectrophotometry in the region of Ultraviolet-Visible and Near Infrared (UV-Visible-NIR). The microstructural characterization showed the presence of more than one type of chromium oxide in the absorber films, whereas the optical evaluation allowed to determine that the time in the electrodeposition process has a great influence on the films' absorptance, since those with smaller times, except for 30 seconds and 1 minute, had higher absorptance.*

Keywords: *electrodeposition, black chrome, selective surface.*

1. INTRODUCTION

One of the main constituents of modern society is energy. It is necessary to create consumer goods and to provide many of the services that have benefited society. Concerns over the availability of an adequate and reliable supply of energy due to the high standards of living associated with the finite nature of fuels and the pollution generated by burning them have increased in recent years (Hinrichs and Kleinbach, 2003; Braga, 2008).

The current energy revolution has driven the use of renewable energy sources around the world. This is mainly due to three factors: The proximity of the time when the volume of oil produced will be lower than that of the newly discovered reserves, the late awareness that a strict policy to reduce fossil energy consumption in favor of sustainable environment and, finally, peace-threatening problems arising from the dispute over oil, such as those in Iraq.

In this context, it is necessary to search for new alternative sources of energy that allow meeting the increasing demand minimizing the associated environmental impacts. The implementation of renewable energies emerges as an alternative energy to the conventional systems of generators of energy, since they constitute a wide variety of sources of energy that are made available in the nature of cyclical form (Costa and Prates, 2005). Renewable sources can be used to generate electricity, heat or produce liquid fuels for the transport sector. Currently, it is essential that they be included in the countries' energy policies, in view of the benefits provided by these sources, such as: reduction in regional differences regarding access to energy, promote the sustainability and diversification of the energy matrix as well as increase the energy security of countries.

Brazil is one of the countries with the greatest potential for exploration in renewable energies due to its geographical location, territorial extension and climate. According to the National Energy Balance of 2018 with base year 2017, the share of renewable energies was 42.9% in the Brazilian Energy Matrix, thus occupying a prominent position in the world (EPE, 2018).

Renewable energy technologies use solar energy and its direct and indirect effects on earth (solar radiation, wind,

water fall and various plants, biomass), gravitational forces (tides) and heat from the earth's core (geothermal) as resources for energy production. These resources have enormous energy potential, however, they are generally diffuse and not fully accessible, since most of them are intermittent and have distinct regional variabilities. These characteristics give rise to difficult but technically difficult technical and economic challenges (Tian and Zhao, 2013).

Energy from the Sun can be harnessed as a source of heat for heating or for the generation of electricity. One way of harnessing the Sun's energy in electricity generation is through flat-plate solar collectors. In this type of collector, when solar radiation passes through a transparent cover and collides with the blackened, high-absorbent absorbent surface, much of that energy is absorbed by the plate and then transferred to the fluid circulating through the tubing. Absorption plate underside and housing side are well insulated to reduce conduction losses.

Although its use is usually employed for heating water at low temperatures, the use of selective adsorbent films has increased the efficiency of this equipment, allowing a higher operating temperature at the collector outlet, thus expanding a scenario for new applications (Mihelcic et al., 2015). For operations in regions with low insolation or in solar collectors for thermoelectric applications, the absorptive material must have selective reflectivity. This implies that the material must be able to absorb the maximum of the incident solar radiation and minimize the thermal losses caused by the emission of infrared radiation (Martins, 2010). This absorber is called a selective surface and is usually composed of a thin film superimposed on a thermal conductive substrate, which can be preceded by an anti-diffusive or anti-diffusive layer and succeeded by an antireflective layer in contact with the environment (Gomes, 2001).

The selective surface production techniques are the most varied, the present study opted for the electrodeposition, considering that it is simple, requires low cost and allows the large-scale production, associated to the fact of producing films with great hardness and resistance mechanical properties, as well as excellent optical and thermal properties (Medeiros et al., 2019). Thus, the objective of the work was to produce and characterize selective surfaces of black chromium obtained by electrodeposition for the application in solar collectors.

2. MATERIALS AND METHOD

2.1 Metal substrate

A single type of metallic substrate (stainless steel) was used to evaluate exclusively the influence of the electrodeposition time of the chromium on the substrate as a function of the film absorption. The substrates underwent a single cleaning process, the plates were soaked in isopropyl alcohol for 10 minutes. After drying, the substrates would be prepared to begin the electrodeposition process.

2.2 Black chrome

The material used to produce the thin films was black chromium. To perform the electrodeposition of the same in the steel substrate, a chromium electrochemical bath was prepared following the methodology of work of Daryabegy and Mahmoodpoor (2006) being composed by:

- 274 g/l of chromium trioxide (CrO_3);
- 0.854 g/l of hexafluorosilicic acid (H_2SiF_6)

2.3 Voltage source

In order to perform the electrodeposition of the Black Chrome on the stainless-steel substrate, an Agilent brand E3631A source was used. The source used only allows voltage regulation, so the bath temperature and current density have changed during the process.

2.4 Electrodeposition

The electrodes used were the steel substrate, connected to the negative pole of the source, while in the positive pole the Pb-Sb inert electrode was used (95-5%), both remained during the entire process, submerged in the chromium bath (electrolytic solution). The parameters evaluated in the present study are shown in Tab. 1.

Table 1. Electrodeposition parameters adopted.

Sample	Distance	Working Voltage	Time
1	30 mm	5 V	30 seconds
2			1 minute
3			2 minutes
4			5 minutes
5			10 minutes
6			20 minutes
7			40 minutes
8			1 hour
9			2 hours

In order to perform a statistical evaluation of the absorptivity for each time value, samples were prepared in triplicate for each film (1, 2, 3, 4, 5, 6, 7, 8 and 9) with their respective parameters, as observed in Tab. 1. This methodology was used to obtain an average of absorbance for each film with its variation of deposition time, and thus, to verify their respective values of standard deviation.

2.5 X-ray Diffraction

In the X-ray diffraction, a Bruker diffractometer, model D2-Phaser was used, operating with copper $K\alpha$ radiation, whose parameters were voltage and current of 30 mV and 10 mA, respectively, with a scan of 2θ between 10° and 60° , with pitch of 0.02° , time of 1s and slot of 1 mm.

2.6 Spectrophotometry in the Ultraviolet-Visible region (UV-Vis)

The optical properties of the produced films were obtained through tests performed in UV-Visible Spectrophotometer of the brand Shimadzu model UV-2600 with sphere of integration. The analysis wavelength range was between 220 and 1400nm, the material being analyzed for reflectivity in the UV-Vis region and part of the Near Infrared. Because it was an opaque material it was possible to evaluate from the reflectivity, the material's absorptance.

2.7 Activity flowchart

The flowchart of activities developed in the present study can be seen in Figure 1.

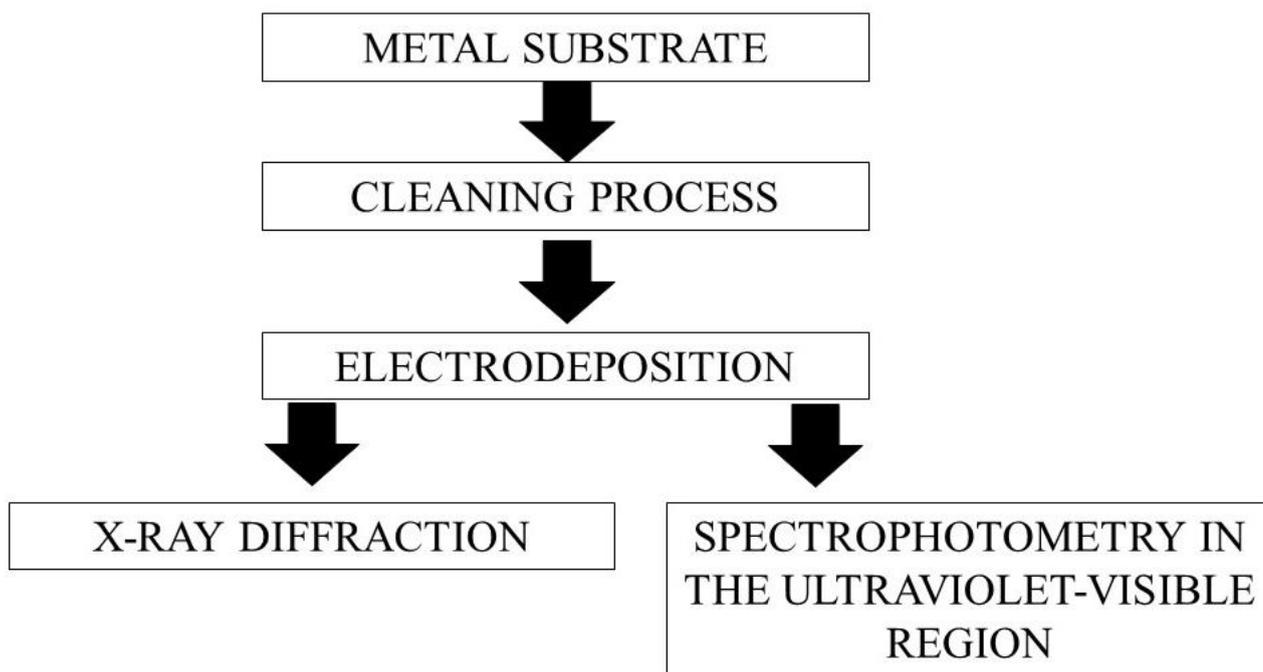


Figure 1. Activity flowchart

3. RESULTS

3.1 X-ray Diffraction

The X-Ray Diffraction analysis had as objective to identify the microstructural behavior in terms of crystallinity of the electrodeposited chromium. Figure 2 shows the behavior of films deposited at different times.

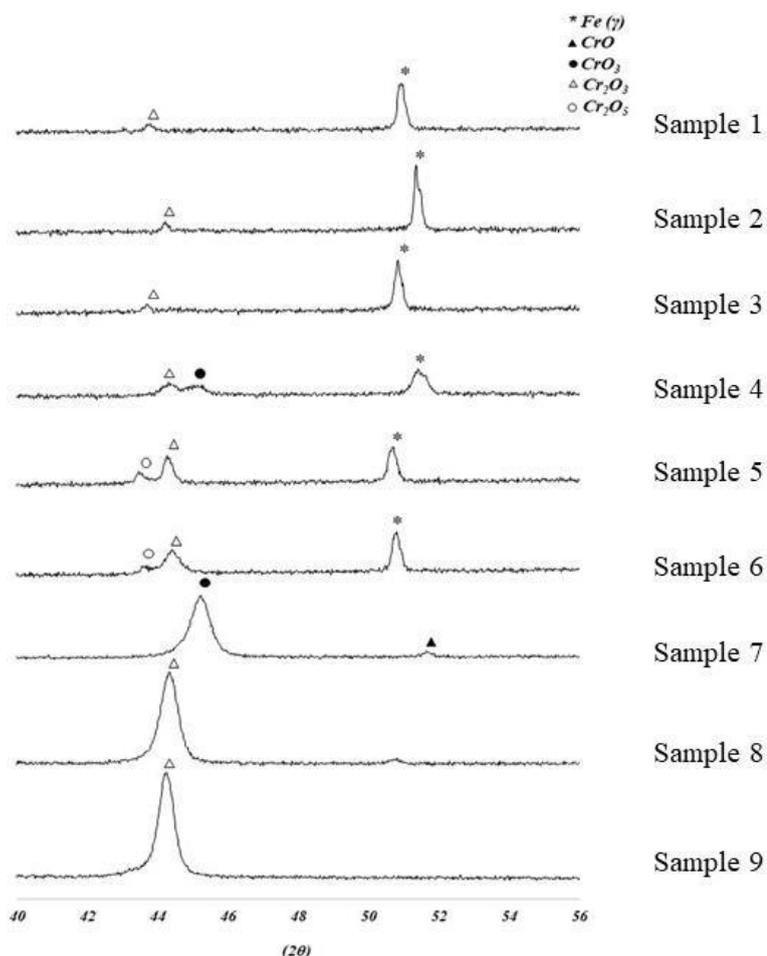


Figure 2. Diffractograms of the films produced.

Figure 2 shows the presence of more than one type of chromium oxide and between the films from 30 seconds to 20 minutes, in the higher intensity peaks the austenite or iron-gamma phase present in the steel substrate stainless. The presence of iron is due to the thickness of the films, where it is observed that the lower the time, the lower the film thickness, thus allowing the radiation to interact with the substrate, thus identifying the ferro-gamma phase.

Peaks of CrO, CrO₃, Cr₂O₃ and Cr₂O₅ were observed. It was observed that the longer the deposition time of chromium, the greater the thickness of the film and thus the greater the presence of Cr₂O₃.

3.2 Spectrophotometry in the Ultraviolet-Visible region (UV-Vis)

Figure 3 illustrates the optical behavior of each sample in the visible ultraviolet region and part of the near infrared.

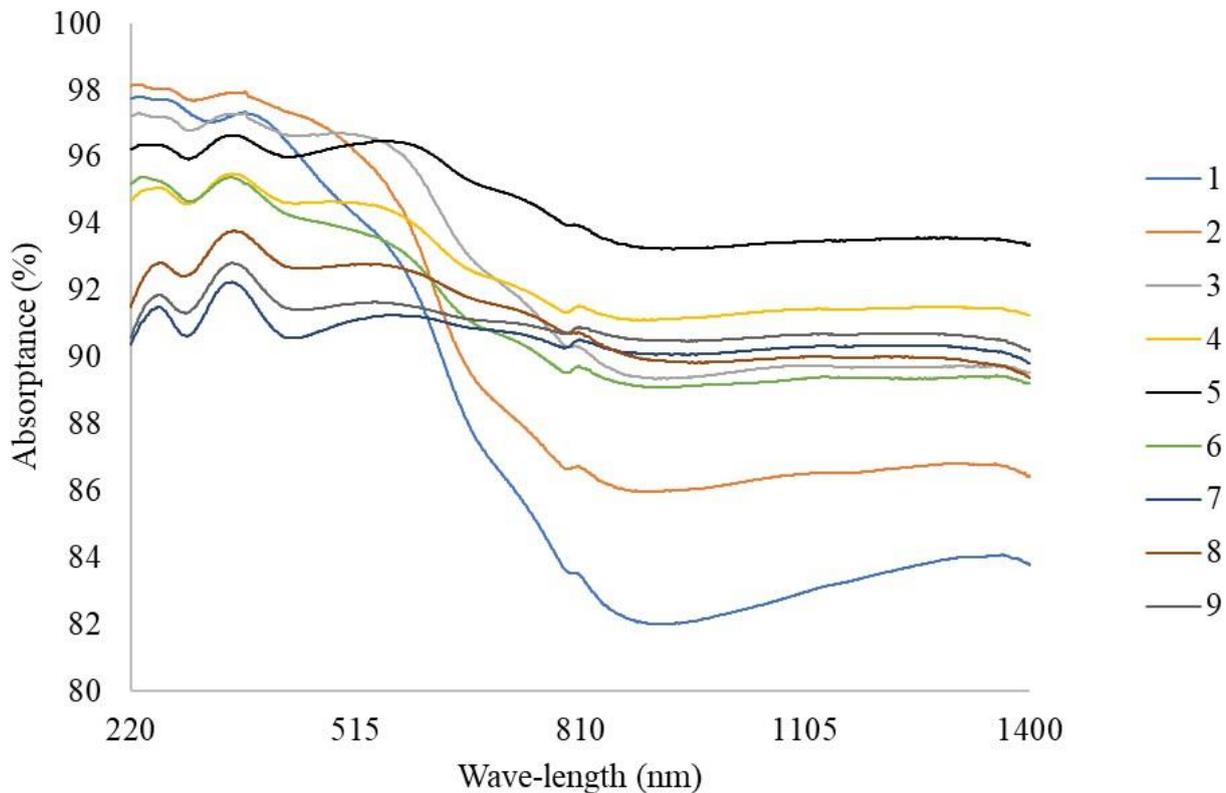


Figure 3. Absorption spectroscopy in the UV-Vis range and near infrared of the films produced.

It can be observed from Fig. 3 that the 10-minute sample demonstrated a greater stability in the absorptivity levels throughout the analyzed spectrum and among the others it was the one that obtained better performance (94.65%) in relation to the entrapment of the radiation, followed by 5 minutes and 2 minutes, respectively 92.64% and 92.44%. The other times of electrodeposition provided films with high levels of absorptance, as according to the literature. According to Jafari and Rozati (2011) and Sheu et al. (2016) it was verified that shorter electrodeposition times produce films with higher absorptivity.

4. CONCLUSIONS

With the present work it can be concluded that it was possible to obtain selective solar surfaces with high levels of absorptivity through the deposition of chromium in stainless steel substrate by the technique of electrodeposition. The time variation as a parameter of the electrodeposition produced absorptive surfaces with varying levels of absorptivity, being the time of 10 minutes in the conditions of the present research (30 mm distance between the electrodes and 5 V of voltage) the time to obtain better performance.

As for the microstructural characterization of the films produced, it was possible to observe the presence of several types of chromium oxides in the films, where the presence of Cr₂O₃ was increased as the deposition time increased.

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