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MICROSTRUCTURAL AND THERMAL BEHAVIOR STUDY OF SOLAR BLACK CHROMIUM ABSORBERS

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Abstract. Energy from the sun can be harnessed as a source of heat for heating or for the generation of electricity. One of the ways of harnessing solar energy is through flat plate solar collectors. Although its use is usually employed for heating water at low temperatures, the use of selective adsorbent films has provided increased efficiency of this equipment, enabling a higher operating temperature (above 400 ° C). As a result of the above, this study had the objective of producing and evaluating black chromium absorber films by the electrodeposition technique to be used as a selective surface for application in medium and high temperature solar collectors. For that, microstructural and thermal analyzes of the films were performed. In this way, it was possible to identify that the films are amorphous in nature, that the electrodeposited coating for 10 minutes presents values of Rp and Rv within the range of interest of the studied wavelength, due to the nucleation that is accentuated in greater times, and it was evidenced that the loss of mass up to 400 ° C was approximately 5%, so it is interesting to use a selective surface of the multilayer type to increase the performance of the absorber film.

Keywords: solar energy, electrodeposition, black chrome.

1. INTRODUCTION

The simplest and most direct way of harnessing solar energy is through its thermal conversion. Solar thermal conversion consists of taking advantage of the heat transmitted by solar radiation. This form of energy is most commonly used in residential water heating and steam generation for industrial processes (Weiss and Rommel, 2008). In both applications, special heat exchangers called solar collectors are used to promote the heating of the fluid of interest. However, although solar thermal conversion is cost-effective (Sani et al., 2012), this use has limitations when heating fluids at a temperature between 100°C and 400°C (medium temperature collectors) or above 400°C (high temperature collectors).

As heat emission by radiation is a surface phenomenon (Incropera and Witt, 1992), Tabor (1961) and others (Kokoropoulos et al., 1959; Shaffer, 1958) proposed that solar collectors be surface coated with materials that were good absorbers of radiation in the spectral range of the solar irradiation and at the same time they emitted little heat in the spectral band associated to the emission of heat by radiation in the temperatures in which those collectors operate. These coatings were called selective absorbing surfaces.

Within thermal radiation there is a range of wavelengths called "light", this term is simply the visible part of the electromagnetic spectrum, which lies between 0.40 and 0.76 μm. The characteristics of light are no different from other electromagnetic radiation, except that it triggers the sensation of sight in the human eye (Incropera and Witt, 1992). Thus, radiation emitted by the main light source on Earth, the Sun, is called solar radiation.

Solar radiation, commonly called the solar radiation spectrum, consists of the range of wavelengths of radiation emitted by the sun and reaching planet Earth. It comprises a range of thermal radiation, being between 0.3-2.5 μm. Thus, solar radiation is formed by part of the ultraviolet region, passing through the entire visible range of radiation and going to the beginning of the infrared region, called near infrared. (Cengel and Ghajar, 2012).

A body that is at a thermodynamic temperature above absolute zero (0 K) is continuously emitting radiation in all

directions over the wide wavelength range, so it is understood that all bodies are also constantly receiving radiation. of nearby objects. The amount of radiation energy emitted from the surface at a given wavelength depends on the body material and the condition and temperature of the surface. Radiation emitted by a body at room temperature is in the infrared region of the spectrum (0.76 to 100 μm). Only from 800 K the bodies begin to emit visible radiation (Cengel and Ghajar, 2012).

Different types of coating have been studied, but in all of them we have sought to improve surface texturization by creating optical traps for incident radiation, thermal stability, good adhesion between the deposited material and the substrate. On the other hand, the technique used in the application of the selective coating on the solar collector also presents as a fundamental variable to the success of good optical properties of the coating. In view of the above, the present study aimed to produce and evaluate black chromium absorber films produced by the electrodeposition technique.

2. MATERIALS AND METHOD

The material used to produce the thin films was black chromium. To perform the electrodeposition of the same on the steel substrate, a chromium electrochemical bath was prepared following the work methodology of Daryabegy and Mahmoodpoor (2006), consisting of 274 g/l of chromium trioxide (CrO_3) and 0.854 g/l of hexafluorosilicic acid (H_2SiF_6). A single type of metallic substrate (stainless steel) was used to evaluate the influence of the electrodeposition time of the chromium on the substrate, while the working distance and tension remained constant, 30 mm and 5 V, respectively. The substrates underwent a cleaning process, in which the plates were soaked in isopropyl alcohol for 10 minutes, followed by drying.

The voltage source used in the process belongs to the Agilent brand model E3631A. This source only allows voltage regulation, so the bath temperature and current density have changed throughout the process.

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 (solution). The parameters evaluated in the present study are shown in Tab. 1.

Table 1. Electrodeposition parameters adopted.

Sample	Time
1	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

For the microstructural characterization of the films, Fourier transform infrared (FTIR) spectroscopy was performed using Shimadzu's IR-Prestibe 21 spectrophotometer with attenuated total reflectance (ATR) spectrometer, in the region between 4000 and 600 cm^{-1}, corresponding to the range of 2500 nm to 16.666 nm, in transmittance and reflectance mode. The Scanning Electron Microscopy was performed in a microscope with a Quanta 450 model of the FEI brand, operating in the Electrosecondary mode, while the Profileometry was obtained through the non-contact profile CCI MP of the Taylor Hobson brand.

The samples were also subjected to thermogravimetric analysis by means of a Shimadzu brand TGA 60H thermal analyzer in the temperature range up to 600°C, with a heating rate of 5°C/min to 100°C and 10°C/min to 600°C, with nitrogen atmosphere with flow of 50 ml / min, using nickel crucibles.

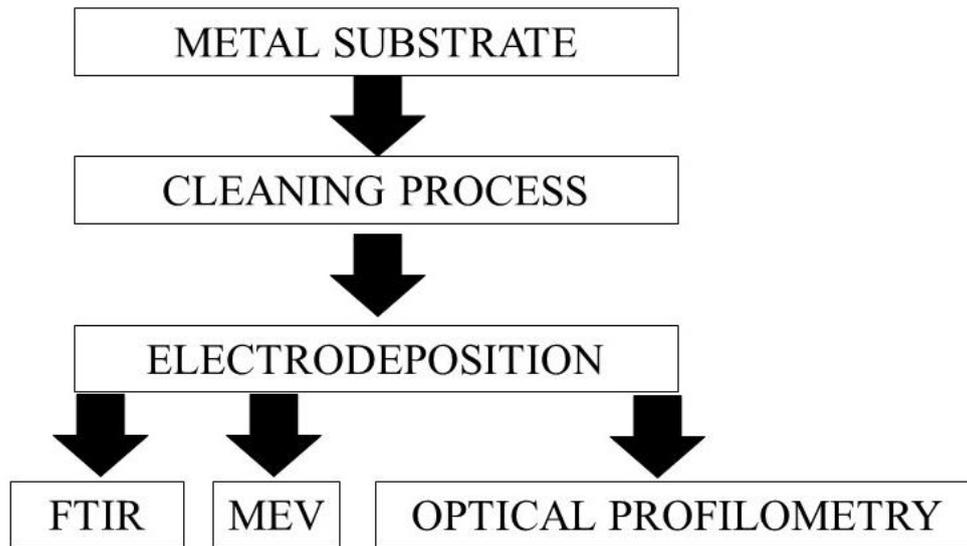The activity flowchart developed for this research can be seen in Fig. 1 below.

Figure 1. The activity flowchart

3. RESULTS

3.1 Vibrational Spectroscopy in the Medium Infrared by Fourier Transform by Transmittance (FTIR) of the films produced

Figure 2 represents the average infrared vibrational spectroscopy in terms of transmittance of the samples under study.
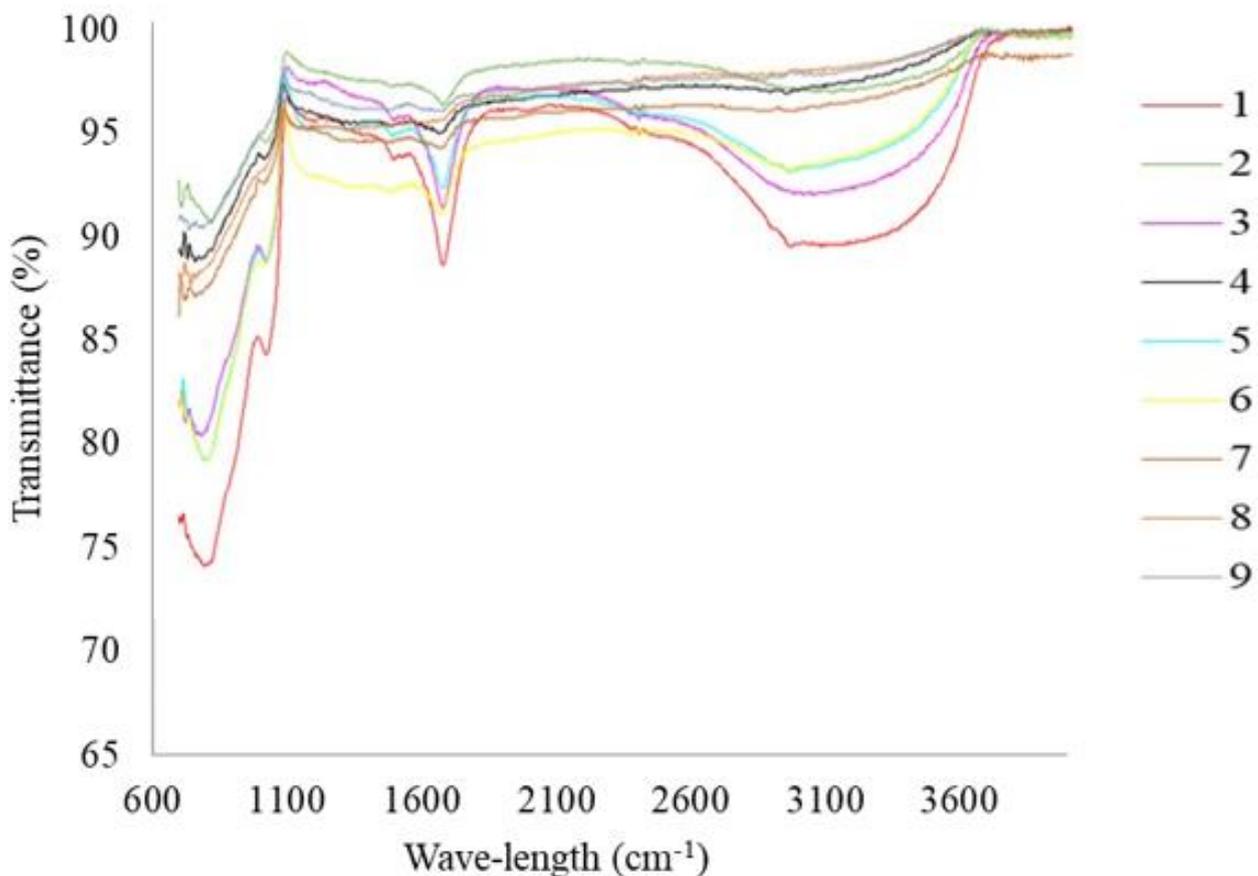

Figure 2. Vibrational Spectroscopy in the Medium Infrared by Fourier Transform (FTIR) of the films produced in terms of transmittance.

Analyzing Figure 2, it is observed that the wide bands are indicative of the practically amorphous nature of the absorber films. Bands corresponding to 1600 cm^{-1} and 2900 cm^{-1} were not identified. According to Madi (2007) in the first band, the peak near 600 cm^{-1} is indicative of the presence of Cr_2O_3. The smallest peak occurring at about 950 cm^{-1} that appears primarily in films from 30 seconds to 20 minutes should correspond to CrO_2.

3.2   Optical Profilometry

The optical profilometry was performed in all films in order to evaluate the roughness. Through the analysis the values of Rp, Rv and Ra presented in Tab. 2 were obtained.

Table 2. Values of Rp, Rv and Ra obtained through the Optical Profileometry.

Sample	Rp(μm)	Rv(μm)	Ra(μm)
1	0.162	0.123	0.049
2	0.101	0.129	0.037
3	0.136	0.167	0.026
4	0.818	0.543	0.196
5	2.125	1.367	0.337
6	0.297	0.255	0.073
7	6.815	5.786	0.989
8	7.169	7.058	1.111
9	11.444	9.902	1.405

The roughness is fundamental in the definition of the uniform absorption capacity of the radiation in the region of the visible and near the infrared (Medeiros et al., 2019), thus observing the roughness of the samples through the Tab. 2 it is observed that the roughness of the smaller samples time presented films with less roughness, this fact can be attributed to the lack of nucleation of the chromium throughout the steel substrate, thus interfering negatively in the performance of the surfaces.

The sample 5, even with high values of Rp and Rv, presented Ra within the range of interest of the cut length (0.25 to 2.5 μm) and low difference between the peaks and valleys, thus obtaining a high performance regarding the entrapment of radiation.

3.3   Scanning Electron Microscopy

Figure 3 shows the micrographs observed for the electrodeposited films for 1 and 10 minutes.
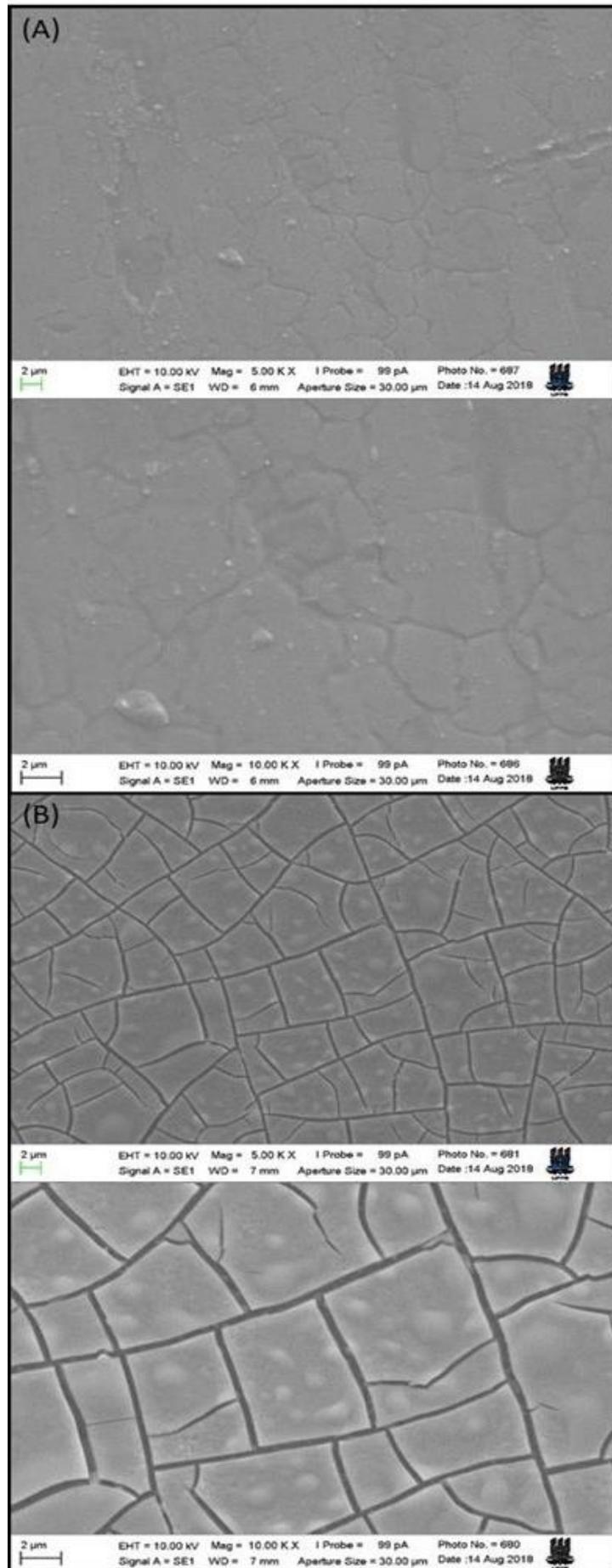
Figure 3. Micrograph with increase of 5,000 and 10,000 times of the films obtained by electrodeposition to: (a) 1 minute and (b) 10 minutes.

It can be seen from the micrographs presented in Fig. 3 (a) and (b) that the obtained films present different morphologies. This occurs as a function of the deposition time that makes the nucleation of chromium can develop

more markedly on surfaces with higher deposition times. As can be observed in the figures above, it is evident the greater cracreation in the morphology of the deposited films for 10 minutes. This, confirms the evidence in the literature, that for black chrome-based surfaces they present a cracked appearance.

The electrodeposited films in larger times have small peaks scattered along their entire surface, as can be observed by the number of white spots in the micrograph, this fact may have contributed to the phenomenon of optical traps, in which the multiple reflections of the incident radiation increase the probability of absorption, this result corroborates with the data obtained in the profilometry.

3.4 Thermogravimetry

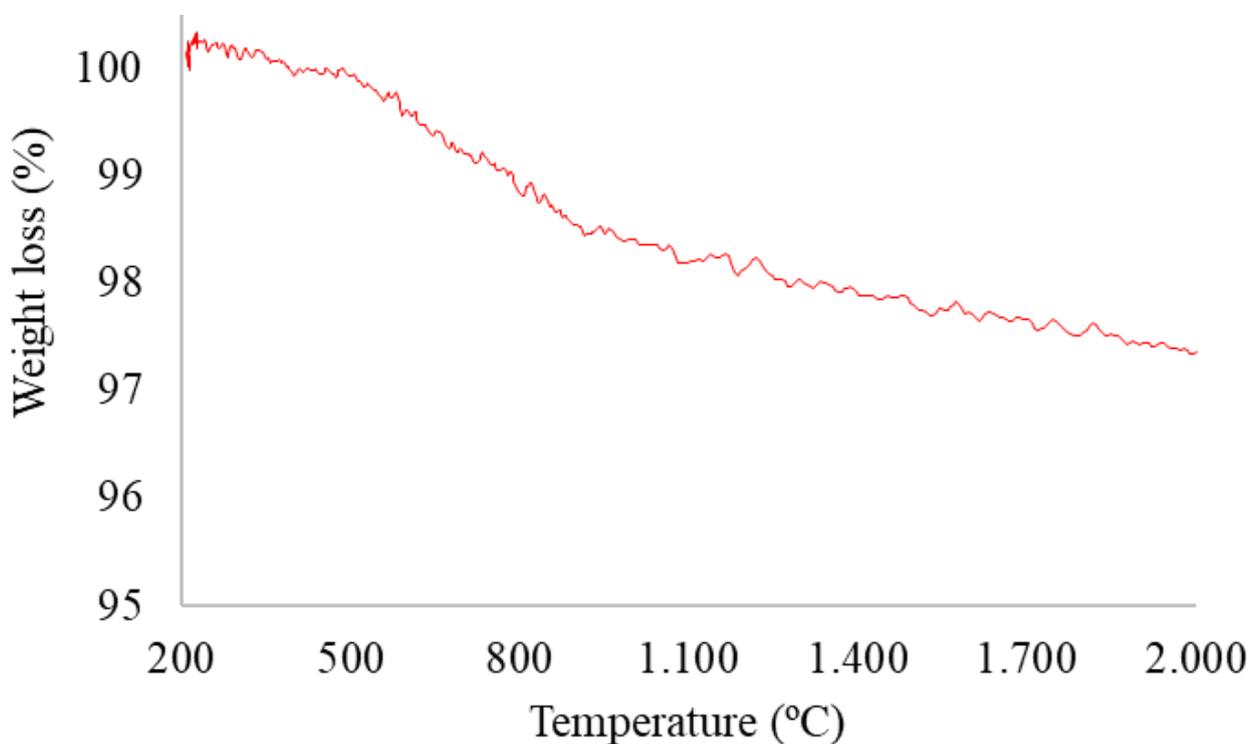The thermal stability of chromium can be seen in Fig. 4.

Figure 4. Thermal stability of chromium.

It is observed in Fig. 4 that the chromium presents a good thermal stability in the temperature range of interest (up to 400°C), since there is a small loss of mass due to the increase in temperature, being 5%. The existing mass loss can be mitigated by the use of another film (multilayer selective surface) with thermal and mechanical properties that provide the desired thermal stability for the solar collector.

4. CONCLUSIONS

The development of the present study allowed to observe the presence of several types of chromium oxides in the selective absorber films produced by black chromium electrodeposition, where the presence of Cr_2O_3 was increased as the deposition time increased. This parameter was also influential on the morphology of the film, since the shape of the film was modified with the increase of electrodeposition time.

Through the thermal characterization, it was observed that the loss of mass up to 400°C was approximately 5%, so it is interesting to use a selective surface of the multilayer type to increase the performance of the solar absorber film, where the other coating composes this selective surface must have excellent thermal properties, thus optimizing the selectivity.

5. ACKNOWLEDGEMENTS

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