Materials Research. 2018; 21(1): e20170556
DOI: http://dx.doi.org/10.1590/1980-5373-MR-2017-0556

Selective Surfaces of Black Chromium for Use in Solar Absorbers

Rogério Antônio Xavier Nunes[a]*, Vilma Conceição Costa[a], Wagner Sade[a], Frederico Resende Araújo[a], Guilherme Marconi Silva[a]

[a] Departamento de Engenharia Mecânica, Centro Federal de Educação Tecnológica de Minas Gerais - CEFET-MG, Belo Horizonte, MG, Brazil

Received: February 01, 2017; Revised: June 06, 2017; Accepted: September 17, 2017

One of the applications of selective surfaces is to improve performance of solar absorbers. The purpose of this work is to produces selective coatings with high absorption of solar radiation in the range of UV/Vis/NIR. It was prepared a selective surface composed of black chromium (Cr/Cr_2O_3) deposited on substrates of AISI 304 stainless steel using the technique of electrolytic deposition for application in solar thermal absorbers. The great parameters for deposition consisted of a continuous electric current of 2A for 90s, at a constant temperature of 40°C. After deposition, the samples under went to a heat treatment at 600°C for 2h for oxidation. The coatings thicknesses were determined. From the SEM analysis coupled with EDS, it was found that the microstructures reported sample of cermets. The XRD results show diffraction peaks related to metallic chromium (Cr) and chromium oxide (Cr_2O_3). Spectral absorptance values more 90.0% were found.

Keywords: *selective surfaces, solar absorbers, black chromium, electrolytic deposition*

1. Introduction

The solar energy is currently conceived as the most promising energetic resource to use in the next years, mainly the conversion of light energy into electrical energy[1]. One of the parameters to be optimized for this high use is increasing the energy conversion efficiency, whereas that in heliothermal power plants; which has as function, convert light energy into heat energy and then into electrical energy. The selective surfaces combine in high absorptance of radiation ultraviolet, visible and near infrared (UV/Vis/NIR regions), obtaining values more than 85.0%, with low emittance (medium/distant infrared regions), with values less than 15.0%. For the temperature range in which the surface emits radiation[2], obtaining then a factor known for selectivity, which is given by the ratio of absorptance and emittance, being non-dimension and that the higher is your module, better will be the optical characteristics of selective surface.

The goal of this work is establish the parameters that best provide the optical properties of absorptance more than 90.0% on the selective coatings. Black chromium is one of the most commonly studied and used solar selective coatings in solar collector systems for the efficient conversion of solar energy into thermal energy[3]. It has the required high absorptance in the visible spectral and low emissivity in the infrared spectral to make it a desirable solar selective coating[4]. A variety of deposition techniques such as chemical vacuum deposition, CVD, spray, sputtering and electroplating are available for coating preparation. Electroplating technique has advantages such as deposition on large areas, low cost and simplicity[5], being indicated for application in solar thermoelectric plants. In this paper, was studied the electrolytic deposition of black chromium varying the deposition parameters.

2. Experimental Techniques

The black chromium films were deposited by electrolytic deposition on substrates of stainless steel AISI 304[3] cut in the dimensions of 30mm x 20mm x 3mm.

2.1 The electrodeposition of black chromium

Mechanical polishing was done with a grinding paper of 240-600 mesh and polishing paste of 9μm and 3μm, in order to obtain smooth surfaces. After polishing, the steel substrates were immersed in alkaline solution of 10 vol% NaOH for 60 seconds to be degreased and then washed in distilled water for 30 seconds. In the sequence, the substrates were immersed in acid solution of 10 vol% HCl for 30 seconds to perform surface activation, followed by rinsing in distilled water[6]. The chemical bath for black chromium electrodeposition is showed by Table 1.

Several combinations of electric current and deposition time[6,7] were made to optimize the selective coating, according to Table 2. After coating, the sample was heated 600°C for 2 hours for oxidation and obtaining chromium oxide. The experiments were carried out in triplicates.

2.2 Characterization of the coatings

The thickness of the black chromium coatings was obtained using the thickness meter for ferrous and non-ferrous materials of the Digimess model TT-210. The surface morphology of the coating and the elemental analysis were

*e-mail: rogerioxavier@cefetmg.br

Table 1. Chemical bath for electrolytic deposition

Chemical Bath	Concentration
$CrCl_3$	250 g/l
$CoCl_2$	14.1 g/l
H_2SiF_6	7.50 g/l
NaH_2PO_4	3.80 g/l
NaF	19.7 g/l
H_2O	940 ml

Table 2. Parameters for black chromium electrolytic deposition

Samples	Time (s)	Current (A)	Tension (V)
1	90	2.0	4.0
2	300	2.0	4.0
3	150	4.0	8.0
4	90	4.0	8.0
5	120	2.0	4.0
6	180	2.0	4.0
7	60	2.0	4.0

determined using a scanning electron microscope (SEM), Shimadzu SSX-500 model, with energy dispersive X-ray spectroscopy (EDS). The crystalline structure and identify of phases of the deposited black chromium were studied by X-ray diffraction using a diffractometer Shimadzu, XRD 7000 model.

2.3 Spectroscopy analysis of UV/Vis/NIR

Spectral absorptance was measured using a UV-VIS-NIR spectrophotometer, Shimadzu UV-3600 model, operating with diffuse reflectance accessory using an integrating sphere. Spectral reflectance measurements in the UV/Vis/NIR regions were used to investigatethe optical selectivity of black chromium coating eletrodeposited on substrate.

The reflectance spectral of the coating was used to derive the absorptance spectral. Absorptance is the fraction of incident energy, at a given wavelength and direction, absorbed by the material. Absorptance and reflectance are related by the Equation 1, where "*r*" is the reflectance and the transmittance ("*t*") is zero for opaque materials[8].

$$\alpha = 1 - r \qquad (1)$$

The average absorptance ($\bar{\alpha}$) was calculated through the graph of the absorptance as function of the wavelength (λ) of the radiation (Equation 2).

$$\overline{\alpha} = \frac{\int_{\lambda_1}^{\lambda_2} \alpha d\lambda}{\lambda_2 - \lambda_1} \qquad (2)$$

3. Results and Discussion

The samples 1 and 5 presented the best results regarding solar absorptance in the UV/Vis/NIR regions. These results of solar absorptances were more than 90.0%.

3.1 Thicknesses of samples coated

The coatings thicknesses of the samples 1 and 5 are showed by Table 3. These are the best samples.

Table 3. Thicknesses of the samples 1 and 5 coated and heated.

Sample	1	5
Thickness (µm)	18.21±0.78	19.73±0.91

Bayati *et al*[7] assert that increasing the coating thickness to a critical value of 25.0 µm improves the absorptance. Then these values are as expected.

3.2 The X-ray diffraction

The X-ray diffraction measurements reveals that the structure of the black chromium film was mainly consisted of crystalline metallic chromium and chromium oxide. However, all the peaks that occurred coinciding with those given in the Joint Committee on Powder Diffraction Standards[9] "JCPDS" card 74-0326 of the Cr_2O_3 structure. The Fe-γ phase peak of the substrate is confirmed by "JCPDS" card 33-0397. The diffractograms taken on black chromium film (sample 1 and 5) electrodeposited and stainless steel AISI 304 substrate (reference) annealed at 600°C for 2 hours are reported in Figure 1. It can be seen, for the uncoated substrate (reference) that all peaks of the XRD pattern were found to be indexed to Fe-γ phase with peaks at 2θ = 43.3°, 50.5° and 74.3°. These peaks are related to the stainless steel AISI 304[10]. As Figure 1 shows, the diffraction pattern of black chromium film exhibited peaks that are assigned to crystalline metallic chromium, 2θ = 44.4° and 81.5°, and peaks of chromium oxide, 2 θ = 35.5° and 64.0°. Peaks characteristic of the substrate also can be seen at the coated sample[4,11].

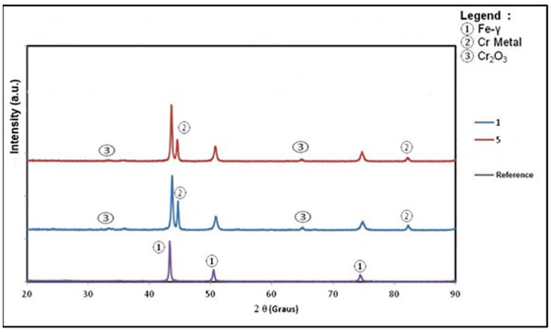

Figure 1. Diffractograms: of the substrate (reference) and of the samples 1 and 5.

3.3 Surface morphology of the coatings

The Figure 2 show that substrate before the coating with black chromium. It can be seen from the photomicrograph of the substrate that it presents a uniform and homogeneous surface. Surface microcracks resulting from the substrate preparation process can be seen with the sanding and polishing steps.

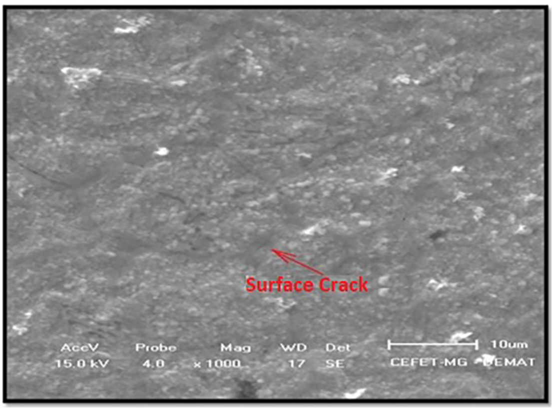

Figure 2. The substrate of stain steel after coating by black chromium.

Lira-Cantu *et al*[12] also observed similar surfaces in their analyzes. As the substrate is stainless steel it contains besides iron and carbon, metals such as nickel and chromium.

A typical surface morphology of prepared black chromium eletrodeposited (parameters 4V, 2A for 90s) on substrate after heat treatment a at 600°C for 2h, is shown in Figure 3.

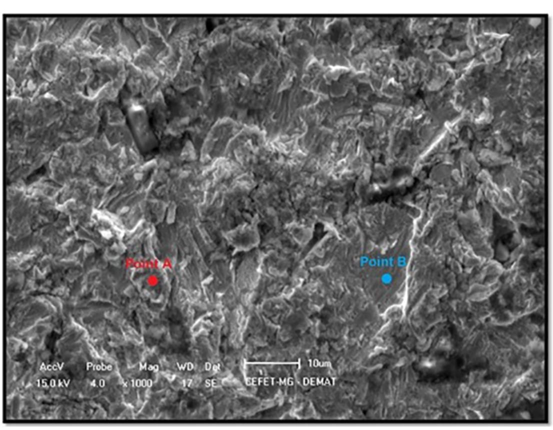

Figure 3. Microstructure of the sample 1 coated with black chromium.

This is the sample 1 that is presented by the scanning electron microscopy (SEM) of magnification 1000X for the black chromium films. The surface topography reveals particles highly irregular in size and shape.

The chemical composition is presented by Table 4 and these two points (A and B) show a very different composition. Therefore, is an inhomogeneous film.

In point "A" the chemical composition is rich in chromium (Cr) and poor in chromium oxide (Cr_2O_3), because the weight percentage of oxygen is low. Otherwise, in point "B" the composition is poor in chromium and rich in chromium oxide, because the weight percentage of oxygen is high. This is a heterogenous films of cermet (Cr/Cr_2O_3). This fact may have been caused by the adsorption of oxygen during the heat treatment of the sample. SEM and EDS results indicate that microstructure is mainly consist of metallic chromium and chromium oxide, which leads to black chromium coating.

A typical surface morphology of prepared black chromium eletrodeposited (parameters 4V, 2A for 120s) on substrate after heat treatment a at 600°C for 2h, is shown in Figure 4. This is the sample 5 that is presented by the scanning electron microscopy (SEM) of magnification 1000X for the black chromium films.

Sample 5 presented a morphology very similar to that of sample 1 in which the structure presented a rough and uniform shape, but with distinct regions that had their compositions analyzed by EDS.

The point "A" represents a region with a much more significant amount of chromium than that of oxygen, which also leads to the conclusion that the presence of chromium oxide at this point is quite significant.

The point "B" also indicates the presence rich in chromium oxide, because of the higher oxygen content in relation to chromium. Table 5 shows the chemical composition obtained by EDS for sample 5 at points "A" and "B".

Table 4. Chemical compositon of the sample 1 in differents points.

Elements	Quantity (wt %)	
	Point A	Point B
Cr	85.0	33.0
O	15.0	67.0

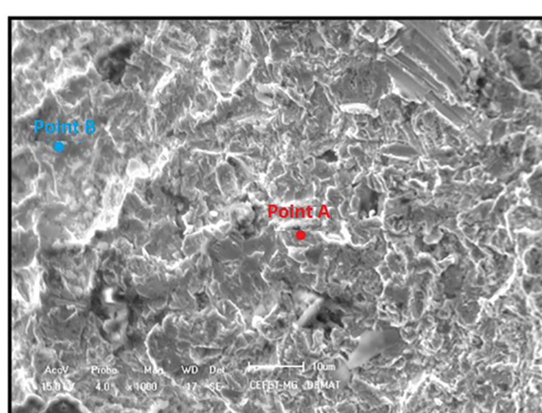

Figure 4. Microstructure of the sample 5 coated with black chromium.

Table 5. Chemical compositon of the sample 5 in differents points.

Elements	Quantity (wt %)	
	Point A	Point B
Cr	88.0	45.8
O	12.0	54.2

Table 6. Average absorptance of the substrate and sample 1 and 5.

Samples	$\bar{\alpha}$ (%)
Reference (Substrate)	39.7 ± 0.4
1	95.3 ± 0.5
5	93.2 ± 0.6

3.4 The UV-VIS spectroscopy

The Figure 5 shows the determined absorptance spectral for substrate (reference) and for black chromium coatings for the sample 1 and 5.

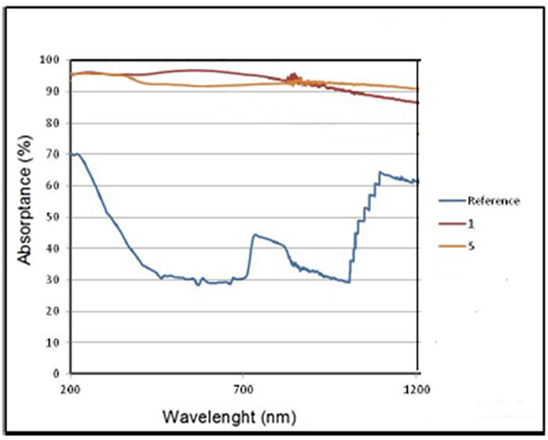

Figure 5. Spectroscopy of the substrate and the samples 1 and 5 coated.

In this work, it was verified that the changing on the deposition parameters, such as, electric current, deposition time, bath temperature and heat treatmente after deposition affect the optical absorptance values.

The samples selected to be shown, it was the best combination of the variables deposition. It was observed that spectral absorptance of the black chromium coatings heated at 600◦C for 2 hours was increased compared to the substrate. This is an indication that heat treatement step provides the formation of chromium oxide phase at the coating, since this phase is directly responsible for the quality of the deposited film[13,14]. It can be seen that the absorptance in UV/Vis/NIR regions is high for the selected black chromium thin film, sample 1, with lowest thickness value 18.21 µm.

The absorptance spectral for reference sample, uncoated substrate, has shown less values of spectral absorptance. The black chromium film has increased significantly the absorptance in the spectral region. The calculated average absorptance, in the range of UV/VIS/NIR for the uncoated substrate was 39.7% and for black chromium film was 95.3% (Sample 1). The Table 6 presents the results of absorptance of the sample 1 and 5.

The other samples from this experiment had average absorptance values less than 90.0%, outside of the purpose of this work. Lee[13] has prepared multilayer type Cr/Cr_2O_3 selective surfaces by electrolytic deposition with solar absorptance value of 80.0%. Also, Wijewardane and Goswami[14] reported the absorptance value for black chromium in stainless steel substrate of 85.0%.

4. Conclusions

Electrodeposited black chromium coatings were formed on stainless steel AISI 304 substrate using an electrodeposition technique. Among samples in which there was black chromium deposit by electrolytic deposition technique, the sample 1 and 5 was that achieved the prerequisites for selective surface with absorptance more than 90.0%.

The XRD measurements indicate that the structure of the black chromium film was mainly consisted of crystalline metallic chromium and chromium oxide. The black chromium films have good optical properties for solar energy absorption.

This work shows that the technique of electrolytic deposition of black chromium followed by a heat treatment for 2 hours at a temperature of 600°C used to produce coatings for application to selective absorbers for solar concentrator tubes. It been noticed from the results that the great tension is 4.0V, electric current is 2.0A and the deposition time is 90s.

The heat treatment influenced the optical properties in a positive manner, making the rate of absorptance obtained from samples. This is due to the increased phase of chromium oxide at 2θ=35.5ºand 2θ=64.0º.

Acknowledgement

Financial support for the present work was provided by the CAPES. The authors wish to thank Dr. M. P. Ferreira (CDTN) for helping with the reflectance measurements, as well the physical and personal structures of CEFET-MG.

5. References

1. Ferreira MAM, Filipe JA, Chavaglia J. Nanotechnology and processes the nanophotovoltaic panels. *Advanced Materials Research. 2014.* 837:694-698.

2. Madhukeshwara N, Prakash ES. An investigation on the performance characteristics of solar flat plate collector with different selective surface coatings. *International Journal of Energy and Environment.* 2012;3(1):99-108.

3. Kennedy CE. *Review of Mid- to High-Temperature Solar Selective Absorber Materials.* Golden: National Renewable Energy Laboratory; 2002.

4. Klamlich S, Nemraoui O, Mongwaketsi N, McCrindle R, Cingo N, Maaza M. Black Cr/α-Cr_2O_3 nanoparticles based solar absorbers. *Physica B: Condensed Matter.* 2012;407(10):1509-1512.

5. Jafari S, Rozati M. Characterization of black chrome films prepared by electroplating technique. 2011. In: *Procedings of World Renewable Energy Congress*; 2011 May 8-13; Linköping, Sweden.

6. Hamid ZA. Electrodeposition of black chromium from environmentally electrolyte based on trivalent chromium salt. *Surface and Coatings Technology.* 2009;203(22):3442-3449.

7. Bayati MR, Shariat MH, Janghorban K. Design of chemical composition and optimum working conditions for trivalent black chromium electroplating bath used for solar thermal collectors. *Renewable Energy.* 2005;30(14):2163-2178.

8. Incropera FP, DeWitt DP. *Fundamentos de Transferência de Calor e de Massa.* Rio de Janeiro: LTC; 2014.

9. JCPDS - International Center for Diffraction Data. *Powder Diffraction File: Alphabetical Index, Inorganic Phases.* Swarthmore: JCPDS; 1982.

10. Ghoraneviss M, Shokouhy A, Larijani MM, Haji Hosseini SH, Yari M, Anvari A, et al. Corrosion behavior of low energy, high temperature nitrogen ion-implanted AISI 304 stainless steel. *Pramana: Journal of Physics.* 2007;68(1):135-140.

11. Anastácio FC, Pires AM, Cardoso CX. Propriedades ópticas do compósito PVDF/Cr_2O_3. 2011. In: *11º Congresso Brasileiro de Polímeros*; 2011 Oct 16-20; Campos do Jordão, SP, Brazil.

12. Lira-Cantu M, Sabio AM, Brustenga A, Gómez-Romero P. Electrochemical deposition of black nickel solar absorber coatings on stainless steel AISI316L for thermal solar cells. *Solar Energy Materials and Solar Cells.* 2005;87(1-4):685-697.

13. Lee KD. Preparation and characterization of black chrome solar selective coatings. *Journal of the Korean Physical Society.* 2007;51(1):135-144.

14. Wijewardane S, Goswami DY. A review on surface control of thermal radiation by paints and coatings for new energy applications. *Renewable and Sustainable Energy Reviews.* 2012;16(4):1863-1873.