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# HOLLOW CATHODE DISCHARGE FOR ABSORBER FILM DEPOSITION

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**Abstract.** *The solar thermal collectors have limitations associated with the fact that the higher the temperature of the solar collector, the greater the amount of heat emitted by radiation. The use of selective surfaces is one of the alternatives found to increase radiation absorption and, above all, to reduce thermal emission losses. Considering that radiation absorption is a surface phenomenon of the material, many techniques are being studied for the deposition of the material, with favorable optical properties, on the substrate. The present study is aimed at produce selective coatings with high absorption in UV/Vis range, composed of ilmenite deposited on AISI 304 stainless steel substrates and aluminum substrates, using cathodic cage plasma nitriding/deposition technique for application in solar thermal absorbers. Ilmenite was initially characterized by X-Ray Fluorescence (XRF), X-Ray Diffractometry (XRD) and Thermal Analysis (TGA). The coatings produced were optically characterized in range UV/Vis, the microstructural evaluation of coatings by Scanning Electron Microscopy (SEM) and data on them roughness parameters of the films produced were obtained by Optical Profilometry. Uniform selective surfaces with high solar absorbance (87%) were obtained in the ilmenite samples deposited on stainless steel substrate, but the material was not deposited in the aluminum substrates in a satisfactory manner.*

**Keywords:** *Hollow Cathode Deposition, Selective Surfaces, Solar Absorbers, Ilmenite.*

## 1. INTRODUCTION

The implementation of renewable energy is the alternative that provides greater benefits, for its wide variety of energy sources found in nature cyclically (Gazoli, 2013). Among these sources, solar energy stands out. Sunlight is readily available and free from geopolitical tensions, and does not pose a threat to our environment.

About the use of sunlight as energy source, the simplest, clean and direct way is through its thermal conversion, where heat transmitted by solar radiation is used to heat water for residential use and to generate steam for industrial use, saving other energy resources such as natural gas, coal and electricity (Medeiros, 2020). As the emission of heat by radiation is a surface phenomenon, several authors (Shaffer, 1958; Tabor *et al.*, 1961; Kokoropoulos *et al.*, 1980) have proposed that the solar collectors be coated with materials that are good absorbers of radiation and on the other hand emit little heat by this same mechanism. These coatings, which are called solar selective surfaces, are characterized according to their interaction with solar radiation in specific regions of the electromagnetic spectrum (Atkinson *et al.*, 2015).

The use of selective surfaces is one of the alternatives found to increase radiation absorption and, above all, to reduce thermal emission losses (Martins, 2010). In addition to increasing the efficiency of the collectors, surface coatings allow a higher temperature at the equipment outlet, increasing the application horizon and significantly reducing the emission of thermal radiation (Gomes, 2001).

Many techniques are being studied for the deposition of the material, with favorable optical properties, on the surface of the solar collector. Some processes have been studied over the years in order to have a homogeneous selective surface, with uniform and controlled thickness and with lower manufacturing cost.

The hollow cathode plasma nitriding/deposition is an adaptation of ionic nitriding technique to reduce undesirable problems of the conventional process, mainly obtaining a homogeneous film (Daudt *et al.*, 2014). This technique uses a discharge produced between close enough cathodes to produce an intensification of ionic density due to the trapping of electrons between the electrodes. Ions generated by collision with electrons in this region, will be accelerated to the electrodes, producing localized heating, sputtering and atomic diffusion.

Hollow cathode deposition is a technique that uses a discharge produced between cathodes close enough to produce an intensification of ionic density due to electron entrapment between the electrodes. Ions generated by collision with electrons in this region will be accelerated to the electrodes, producing localized squeezing, sputtering and atomic

diffusion. Depending on the existing gas type and the material that makes up the cathodes, different structures and surface compositions can be obtained through the combined effect of atomic deposition and diffusion. This process generates the stripping of atoms of the material to be deposited (target), which can be combined with the reactive gas in the plasma atmosphere resulting in the deposition of the material on the substrate (Araújo, 2006). The control of the hollow cathode effect in deposition processes offers the advantage of controlling the deposition rates of the atoms sprayed from the cathode.

Another variable to be considered in the production of selective solar surfaces is the selection of the material to be deposited. Ilmenite is a titanium-iron ore ( $\text{FeTiO}_3$ ) that has been gaining scientific interest for its mineralogical importance and technological applications in the area of pigmentation. It is an opaque material, with theoretical composition of Fe (36.8%), Ti (31.6%) and O (31.6%), characterized by conducting bands of iron and titanium oxide that extend throughout the spectrum (Barth and Posnjak, 2014). The direct use of this ore becomes important since the production of pure metallic titanium implies the use of sophisticated chemical processes and high cost, and ilmenite is a common mineral with large reserves worldwide.

## 2. MATERIALS AND METHODS

### 2.1 Sample Preparation

Ilmenite samples were made in two configurations, partly following the particle size control suggested by Medeiros (2020), using a particle size analysis sieve with 53  $\mu\text{m}$  aperture (Samples 1 and 2) and part following its original state of industrial processing (Samples 3 and 4).

Ilmenite inserts were sintered for deposition following two methodologies. Samples 1 and 4 were heated to a temperature of 500°C at a rate of 20°C per minute and then reached the level of 900°C at a rate of 10°C per minute. And samples 2 and 3 were subjected to a temperature of 900°C at a constant heating rate of 5°C per minute. The samples remained at 900°C for 120 minutes.

The substrates used in this work were aluminum and 304 stainless steels. Aluminum was chosen for this application due to the relatively low cost combined with a good thermal conductivity. Stainless steel 304 was chosen because it has high corrosion resistance and high temperatures, which favors its use in solar concentrator systems. Substrate sizes were maintained as received from suppliers. Aluminum samples with dimensions 30 x 30 x 5 mm and Stainless Steel AISI 304 cuts in the dimensions of 25 x 25 x 1 mm. This condition makes it possible to evaluate the influence of the sample geometry on the target-substrate deposition process. The substrates were polished and washed in an ultrasonic bath using enzymatic detergent for degreasing and cleaning, according to recommendations by Silva *et al.* (2018).

### 2.2 Deposition

The conventional nitriding chamber was adapted for hollow cathode deposition configuration using a different configuration for the electrodes. The equipment consists of a stainless-steel vacuum chamber in the form of a cylinder, 300 mm in diameter and 400 mm high, with a side window for observation of the samples. A table composed of holes of 15 mm in diameter was used to place ilmenite tablets (target). The substrate designed to deposit the ilmenite film was placed on the sample holder. The pressure and voltage were adjusted until a high light discharge appeared between the two electrodes. The hollow cathode discharge conditions were set at a voltage of 400 V and a current of 0.10 A. The pressure inside the chamber was approximately 0.3 mbar and the flow of oxygen gas ( $\text{O}_2$ ) was kept constant at 30 s.c.c.m. at a working temperature of 180°C. Thereafter, the conditions were fixed and maintained for 5 hours. The oxygen used was manufactured by White Martins and has 99.5% pure.

### 2.3 Characterization of the coatings

Analysis of the optical properties of the ilmenite coatings were performed on the Shimadzu UV/Vis/NIR Spectrophotometer, UV 2600 model operating with the integration sphere accessory with a sweep from 220 to 1400 nm. The surface morphology of the coating was determined using a scanning electron microscope (SEM), FEI ESEM Quanta 450 model.

The determination of the surface roughness of the deposited films, was identified by the CCI MP non-contact optical profiling device, manufactured by Taylor Hobson, connected to a computerized unit containing the Talysurf CCI software (Taylor Hobson, 95 England) to obtain and analyze the data.

## 3. RESULTS AND DISCUSSIONS

Figure 1 shows the results of absorbance spectroscopy in the UV-Vis range for absorber films produced on aluminum substrate.

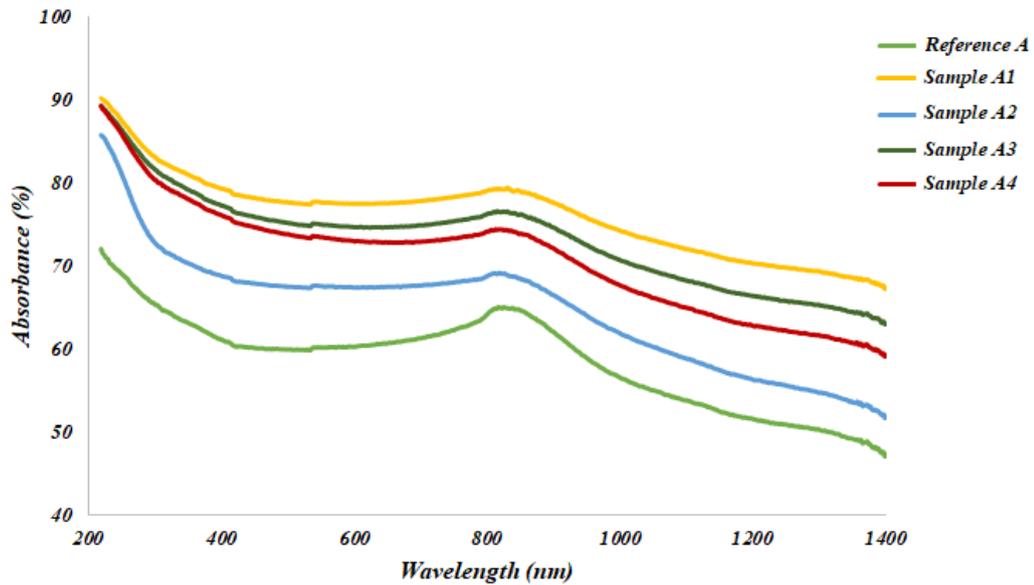


Figure 1. Absorbance spectroscopy in the UV-Vis range of ilmenite films deposited on aluminum substrate.

Note that the absorbance curves of the samples presented similar behaviors to the reference substrate curve. However, it is possible to observe an absorbance gain on substrates with coatings. The "A1" and "A3" samples obtained the best results in their configurations. The means of absorbance of ilmenite films deposited on aluminum substrate can be found in Table 1.

Table 1. Average absorbance of thin films deposited on aluminum substrate.

Samples	Reference A	A1	A2	A3	A4
<b>Absorbance (%)</b>	58,67±2,53	76,25±4,84	64,76±6,87	73,13±5,65	70,94±6,57

In Figure 2, we can observe the results for the surfaces on 304 stainless steel substrates, evaluated in the UV-Vis radiation bands.

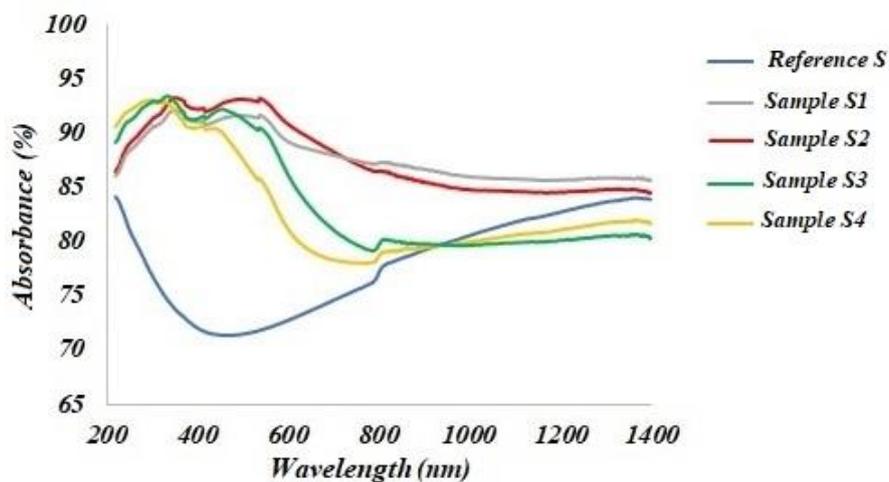


Figure 2. UV-Vis absorbance spectroscopy of ilmenite films deposited on 304 stainless steel substrates.

It is noticeable that the deposited films presented different behavior from the reference substrate. It is observed that the samples that went through the sieving process acquired a greater gain in absorption. The absorbance averages of ilmenite films deposited on 304 stainless steel substrates can be observed in Table 2.

Table 41. Average absorbance of fine films deposited on 304 stainless steel substrates.

Samples	Reference S	S1	S2	S3	S4
<b>Absorbance (%)</b>	77,95±2,38	87,68±3,24	87,84±2,24	83,86±2,91	83,10±3,23

Comparing these results with the films deposited in aluminum, it can be seen that the selective surfaces deposited in steel substrate obtained a better outcome. Comparing these results with the films deposited in aluminum, it is noticed that the selective surfaces deposited in steel substrate obtained better performances.

The absorber films produced were submitted to optical profilometry analysis and the results of the measurement of the roughness parameter (Ra) of the films deposited on steel and aluminum substrates can be seen in Table 3.

Table 3. Parameter Ra of thin films on steel and aluminum substrate and film thicknesses.

Samples	Ra (µm)
S1	0,44
S2	0,25
S3	0,24
S4	0,30
A1	2,18
A2	5,20
A3	2,84
A4	4,59

From Table 3, there is a discrepant difference between the roughness (Ra parameter) of films deposited on steel substrate in relation to films deposited on aluminum substrate. In the ilmenite deposition on the aluminum substrate, it was noted that the atoms removed from the ilmenite target were not being deposited uniformly on the substrate, as occurred in the deposition with the steel substrates. The reaction caused the removal of some atoms from its surface, causing an increase in its roughness.

As the same deposition parameters were used for both substrates, it is possible to state that the thickness of the aluminum substrate has hindered the hollow cathode deposition, which depends on the arrangement between the target and the substrate to generate intensified plasma. Therefore, the absorption gain highlighted in Figure 1 is due to optical traps caused by increased roughness on the aluminum surface. Note that the best absorbance results with the aluminum substrate came from samples "A1" and "A3" with their roughness parameters, respectively, 2.18 and 2.84 µm, values closer to 2.5 µm, upper limit of the solar spectrum, corroborating the studies of Silva et al. (2018).

The SEM analyses allowed the characterization of the absorber film surfaces produced from the mineral under study, ilmenite, in relation to its morphology. Figure 3 exposes in different magnitudes the micrography of films produced with better absorption in steel substrate and aluminum substrate.

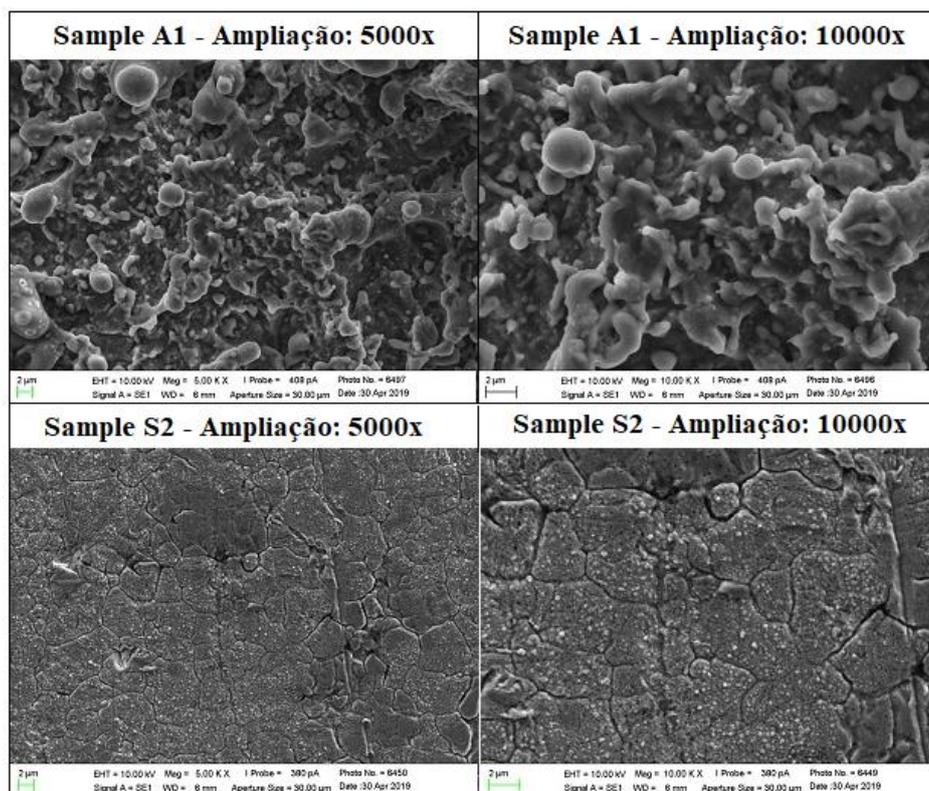


Figure 3. Micrographs of the samples that obtained the best results in absorbance on steel substrates and aluminum substrate.

The micrographs of the present study verified better geometric uniformity of the grains for the sample "S2", ilmenite sieve deposited on AISI 304 stainless steel substrate the illustrated films presented a porous structure with grains on the micro scale. It is possible to verify by micrography that the parameters used in film deposition led to the surface of the coating becoming rougher and with more cracks. This is due to the time of deposition and the thickness of the coatings.

The micrograph of the films deposited in aluminum presents a "cauliflower" type structure consisting of microspherical grains, which has been attributed to the oxidation phenomenon caused by the attempt of deposition target-substrate by the hollow cathode method. Although both micrographs were analyzed only from the selective surface layer, the difference between the images of ilmenite on steel substrate and the images on aluminum substrate is noticeable. The morphology presented by the films deposited in aluminum is recurrent of the presence of aluminum compounds in the surface layer, due to ilmenite not having been deposited totally in the substrate.

#### 4. CONCLUSIONS

The deposition technique employed was satisfactory for stainless steel substrates. The films were deposited uniformly and with a moderate control of their thickness, coming from the employed deposition parameters. Ilmenite absorber films were produced with a good absorption rate (higher than 85%) and were produced using the hollow cathode deposition technique.

It was observed that the optical behavior of films deposited on aluminum substrate, even with better absorbance results, were similar to the reference substrate curve. It was also noted, from the morphology presented, the presence of aluminum compounds in the surface layer. It is understood that in the ilmenite deposition on the aluminum substrate, the atoms removed from the target were not deposited correctly in the substrate and the reaction caused the removal of some atoms from its surface, causing an increase in the roughness of the substrate. The absorption gain acquired by the samples came from optical traps created with the increase in roughness.

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