Materials Research. 2018; 21(3): e20170970
DOI: http://dx.doi.org/10.1590/1980-5373-MR-2017-0970

Preparation of Antireflective Silica Coating by the Sol-Gel Method for Heliothermic Power Plants

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Received: October 30, 2017; Revised: February 15, 2018; Accepted: March 08, 2018

This work deals with the deposition of a thin layer of porous silica antireflective coating onto glass substrates. The films were deposited with different withdrawal speeds and heat-treated at 425°C for 30 minutes. The effects of heat treatment and film deposition rate on the films reflectance were evaluated. The diffuse reflectance was measured using ultraviolet-visible (UV-Vis) spectroscopy. Scanning electron microscopy (SEM) was used for microstructural evaluation of the films. The water contact angle upon the films surface was evaluated using a tensiometer and was based on the sessile drop technique. The mechanical characteristics of the films were evaluated by tape test and pencil hardness. The obtained sol-gel silica coatings were homogeneous and free of cracks. UV-Vis analysis of the glass substrate revealed a reflectance value of 3.86%, whereas the lowest reflectance value obtained for antireflective coatings was 2.72%. The contact angle measurement showed that, for all films, there was wetting of the film by water, characterizing them as hydrophilic. The adhesion of the films were 4B and the pencil hardness were 3H.

Keywords: *Antireflective coating, silica thin film, sol-gel, heliothermic power plants.*

1. Introduction

Antireflective coatings have attracted attention of technological and scientific community due to the possibility of improving the optical properties of different materials for a variety of applications such as solar panels, solar collectors, video display screens, eyeglass, etc.[1-4]. To produce electricity, either in heliothermic power plants or photovoltaic systems, antireflective coatings play an important role reducing losses due to reflection of sunlight. Calculations have shown that the yearly energy produced in a solar thermal plant, where the temperature of the solar collector fluid is 100°C, can be increased by about 20% with the application of an antireflective coating on the solar glass cover[5].

Heliothermic plants are responsible for the solar irradiation conversion and subsequent use for the production of electricity. This process comprises four steps: irradiation collection, heat conversion, transport and storage, and finally conversion to electricity. In the solar radiation collection stage, large mirrors or parabolic troughs concentrate the sunlight on a single line or point, the absorber tubes that hold the heat transfer fluid.

The absorber tubes are coated by vitreous material which reduces energy losses by convection and irradiation, but which can lead to a loss of approximately 10% due to solar radiation reflection. To achieve higher efficiency and energy cost reduction of the plant it is fundamental that the losses due to the reflection on the glass surface of the receivers are the smallest as possible. Such loss is related to the difference between the refractive indexes of the environment and the optical material. With the insertion of a porous coating layer it is possible to provide a more gradual transition of light from one medium to another, thus eliminating much of the reflection[6].

The absorber tube (Fig.1) is the most important component of the heliothermic plant. The optical properties of the absorber coating are crucial for the collector performance[7].

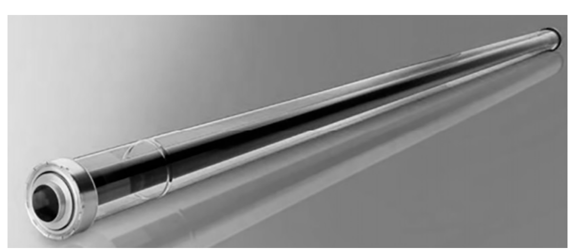

Figure 1. Absorber tube receiver

Various materials and processes have been studied for obtaining antireflective surfaces, and silicon oxide (SiO_2) obtained by the sol-gel process is the one that provides the best results of reflectance[1-5]. In the sol-gel process is a transition occurs from a sol system to a gel system through the establishment of connections between colloidal particles or polymeric chains with the formation of a three-dimensional solid network[8]. Usually, the synthesis of silica particles, by

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sol-gel process, is done through hydrolysis and condensation of alkoxysilanes such as tetramethyl orthosilicate (TMOS) or tetraethyl orthosilicate (TEOS), with the addition of water, alcohol and an acid or basic catalyst[1,9-10].

A particularly attractive feature of the sol-gel method is the fact that coating materials with a wide application can be synthezised at ambiente temperature from the as prepared solution. Thus, it is possible to have a precise control over the film microstructure, such as surface area, volume and pore size[1,8,11]. The low reflectance of the silica film obtained by the sol-gel process is a result of the porous structure formed during the film deposition; it makes the layer's refractive index achieve sufficiently low values reaching up to zero reflection of light by the surface, for a single wavelength[1-3,5].

Different techniques can be employed in production of antireflective films, such as dip-coating, sputtering and spin-coating. Among these the dip-coating technique is the most indicated and used to produce antireflective coatings by sol-gel process, especially when it is required the coverage of large areas or materials with complex shapes, furthermore it has low cost of deployment and operation if compared to the others techniques[2-3,5,9,12,13].

The Federal Center for Technological Education of Minas Gerais (Cefet-MG) was the first in Brazil to develop a project for the creation and operation of a heliothermic power plant.

In this work, we report the deposition, by the sol-gel method, of a thin layer of antireflective coating consisted of porous silica on the surface of a glass substrate in order to increase its transmissivity to solar radiation by the reduction in reflection losses. The effects of heat treatment and film deposition rate on the samples reflectance were evaluated.

2. Experimental Procedures

2.1 Preparation of silica sol and antireflective coating

The silica sol was prepared by mixing tetraethyl orthosilicate (TEOS, 99%, Merck), water and ethyl alcohol. Hydrochloric acid was used as a catalyst to obtain acidic conditions. The synthesis was conducted at room temperature.

The silica sol was deposited on well-cleaned glass microscope slides by the dip-coating process at withdrawal rates of 2, 4, 6, 8, 10 and 12 cm/min. The films remained drying at room temperature for 7 days. Then, a sample of each deposition rate was treated at 425°C for 30 minutes under ambient atmosphere. In total, twelve samples were prepared with six different withdrawal rates, in which, one group was heat treatment and the other group aged at room temperature.

2.2 Characterization of silica coatings

The diffuse reflectance spectra were measured with an UV-Vis spectrophotometer (Shimadzu, UV-2600 Plus). The average reflectance was calculated using the mean value theorem to the integral of the reflectance curve in the wavelength range of 350 to 900 nm according to Eq. 1.

$$R_{mid} = \frac{1}{\lambda_f - \lambda_i} \int_{\lambda_i}^{\lambda_f} R(\lambda) d\lambda \qquad (1)$$

Where R_{mid} is the reflectance in the wavelength range analyzed; λ_i and λ_f are respectively the initial and final wavelength of the analysis interval; R is the reflectance for each wavelength.

Surface topographies of films were carried out using a scanning electron microscope (Shimadzu, SSX-550). The scan along the sample was conducted with a magnification of 50X, 100X and 2000X. Wettability tests were carried out and the contact angle measurements made using a tensiometer (Krüss DSA100). The performance of the tests was based on the technique of sessile drop to measure the advancement of contact angle, as described in ASTM D7334-08 standard[14].

The adherence between the film and the substrate was evaluated by the tape test using the cross cut method as described in ASTM D3359-09[15]. The silica films hardness was measured by the pencil test in accordance with ASTM D3363-05[16]. The test was conducted using an apparatus for hardness testing Wolff-Wilborn pencil, European model, which is based on 14 different levels of pencil hardness (6B-6H).

3. Results and Discussion

3.1 Spectroscopy in the ultraviolet-visible region

Fig. 2 shows the reflectance spectra in the ultraviolet-visible region of the glass substrate, antireflective films that did not received heat treatment (Fig. 2-A) and antireflective films with heat treatment (Fig. 2-B). It can be seen that the antireflective films exhibited lower reflectance than the glass substrate for all wavelengths values. The sample that had the lowest value of reflectance was the one with a deposition rate of 12 cm/min and without heat treatment, its lower value of reflectance was 2.23% in 596.5 nm.

Fig. 3 shows the results of average diffuse reflectance in the wavelength of 350 to 900 nm for the glass substrate and antireflective films, according to Eq. 1. All silica films presented a lower reflectance than the glass substrate (3.86%), proving their antireflective property. The lowest diffuse reflectance value (2.72%) was obtained for the film with a deposition rate of 4 cm/min and heat-treated at a temperature of 425ºC for 30 minutes. These results indicate that deposition

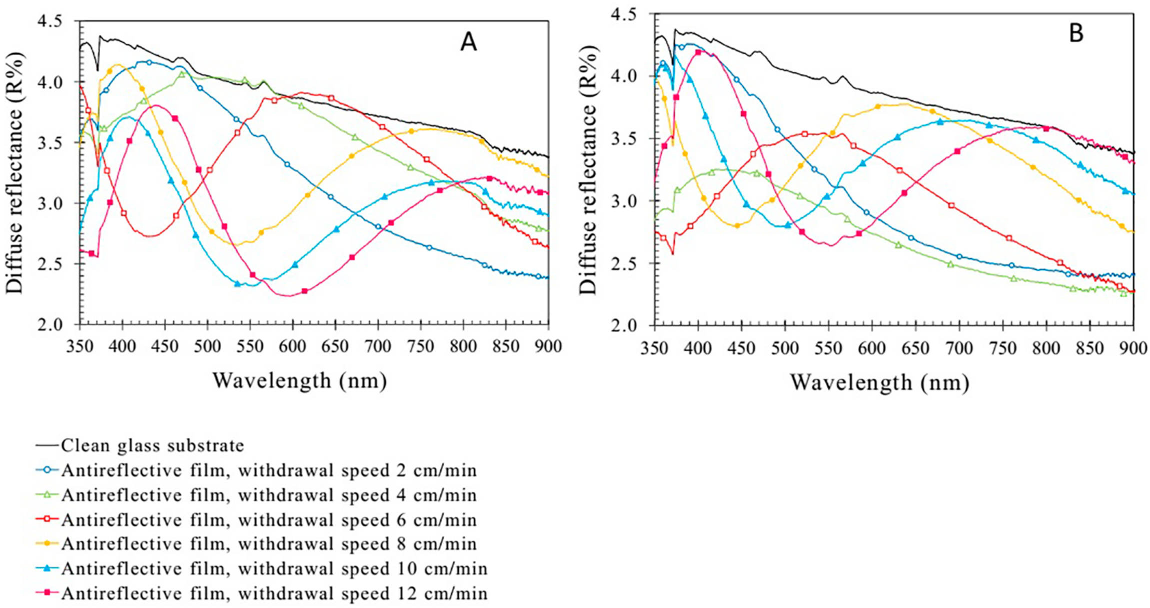

Figure 2. Diffuse reflectance spectrum of the glass substrate and the antireflective films without heat treatment (A) and antireflective films with heat treatment (B)

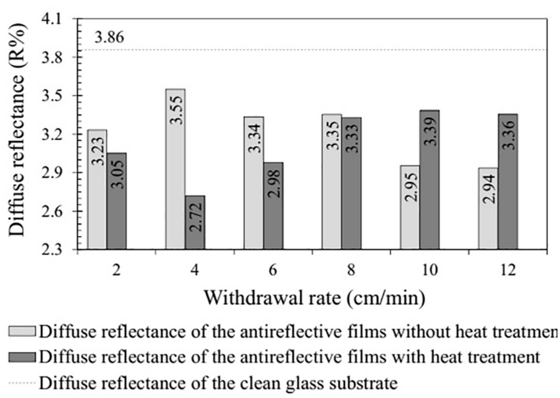

Figure 3. Average diffuse reflectance of the clean glass substrate and antireflective films at different withdrawal rates

rates around 4 cm/min result in films with refractive indexes close to the refractive index of air, ensuring a lower light reflection on their surface.

3.2 Scanning electron microscopy

Fig. 4 shows the images obtained by scanning electron microscopy (SEM) of the antireflective films. On Fig. 4-A, there is the image corresponding to the sample with a withdrawal rate of 4 cm/min, without heat treatment, with a magnification of 100X at the central region of the sample. The Figs. 4-B, 4-C and 4-D show the images obtained by SEM of the sample with a withdrawal rate of 4 cm/min, with heat treatment, with a magnification of 50X at the film-glass interface region, with a magnification of 100X and 2000X at the central region of the sample respectively.

On Fig. 4-B the dark area represents the silica film, while the light area is the glass substrate. Cracks and detachment points are observed on the film-substrate interface region; these are expected since it is a zone of great tension during the drying. Furthermore it can be seen, within the limits allowed by the equipment, that all films are homogeneous and without cracks. No clear changes were observed on the films surface with the use of heat treatment or variation in the withdrawal speed on the dip-coating.

3.3 Wettability

Fig. 5 presents the results of wettability tests. For all samples the contact angle value was below 90º, indicating that the water wets the films surface, characterizing them as hydrophilic.

The silica film hydrophilicity was expected, since its surface is made of vicinal silanol groups (Si-OH) and germinal silanol groups (HO-Si-OH). These silanol groups make the film surface polar and reactive, allowing interaction with water molecules physically adsorbed or bounded by hydrogen bonds[2,9-11].

Fig. 6 shows the drop profile images obtained during the wettability tests for the samples with withdrawal speed of 2 cm/min, without heat treatment (Fig. 6-A) and the sample with withdrawal speed of 4 cm/min, with heat treatment (Fig. 6-B). Those are the samples that presented the lowest and highest contact angle respectively.

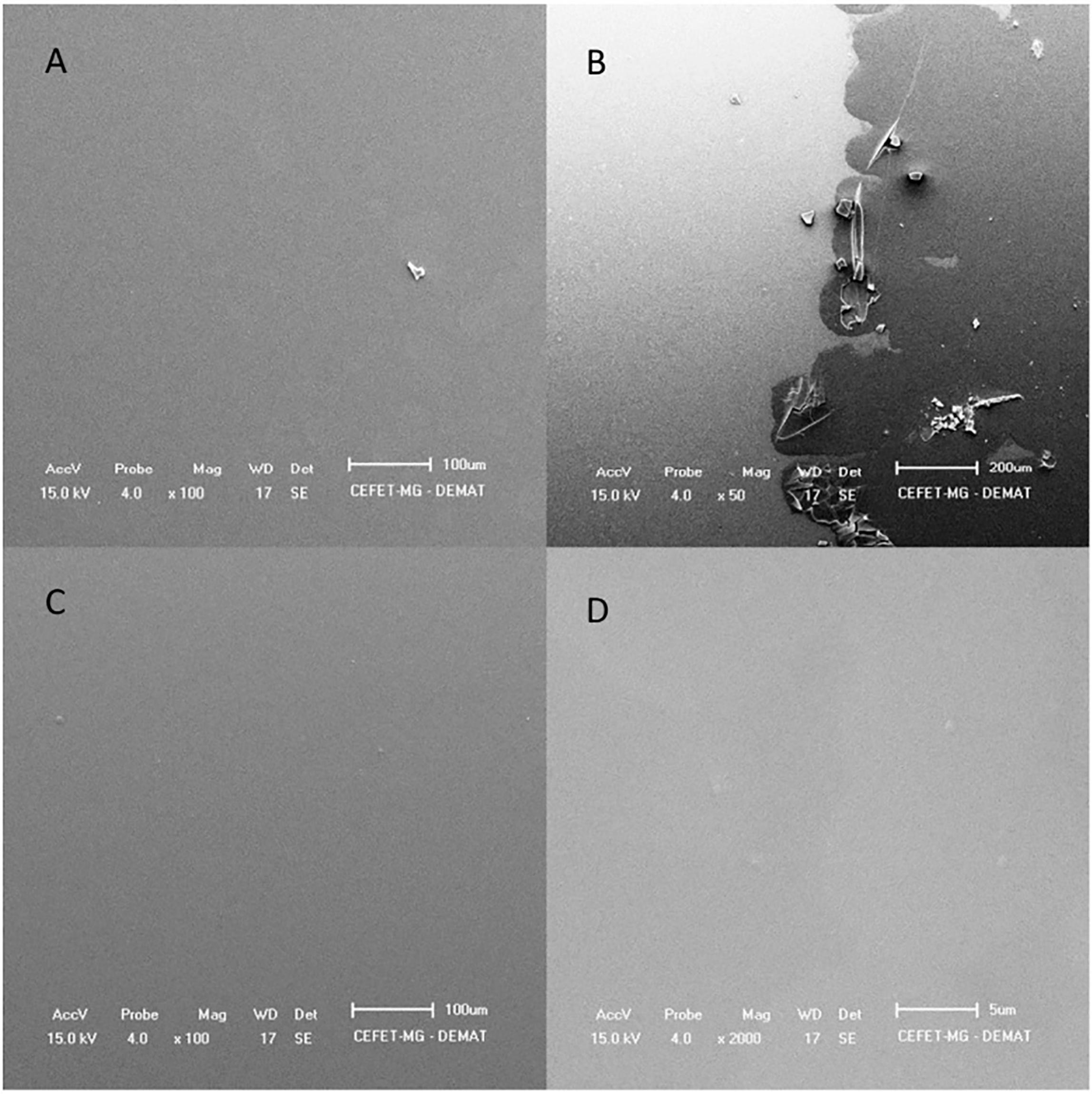

Figure 4. SEM images of antireflective films corresponding to the sample with a withdrawal rate of 4 cm/min, without heat treatment, with a magnification of 100X at the central region of the sample (A) and sample with withdrawal rate of 4 cm/min, with heat treatment, with a magnification of 50X at film-glass interface region (B), with a magnification of 100X (C) and 2000X (D) at the central region of the sample

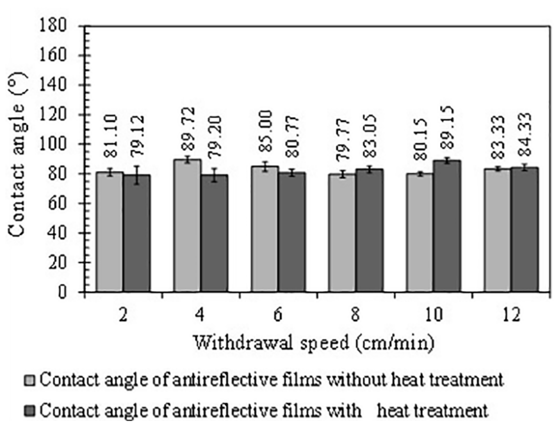

Figure 5. Results of wettability tests for all antireflective films

3.4 Adhesion

The antireflective films that did not receive heat treatment and the ones heat treated presented an adhesion of 4B, which is considered as a good bond strength of the film to the substrate. The films hardness also remained the same for the films with and without heat treatment, determined as 3H and also considered as a good scratching resistance[4].

Fig. 7 presents images of the sample with a withdrawal speed of 4 cm/min after the adhesion tape test. In the Fig. 7-A are shown points where, even after performing the test, no detachment of the film was verified. In the Fig. 7-B is shown a point where there was detachment of the film. It is noticed that the area where there was detachment of the film is

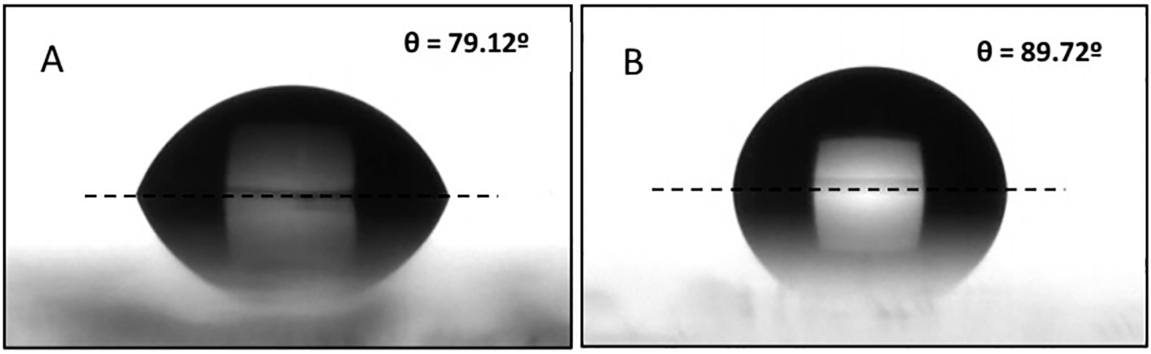

Figure 6. Images of drop profile obtained in the wettability test for the samples with withdrawal speed of 2 cm/min, without heat treatment (A) and the sample with withdrawal speed of 4 cm/min, with heat treatment (B)

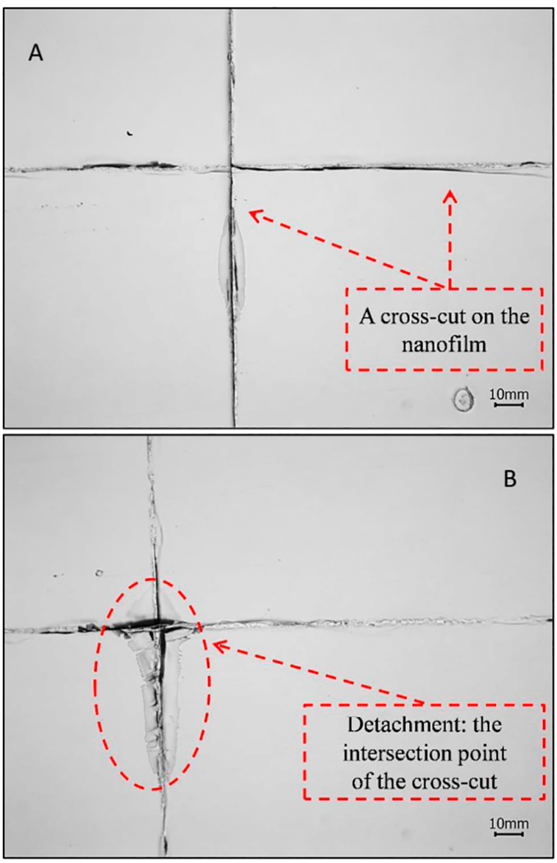

Figure 7. Sample after the adhesion tape test: image (A) the region where there was no detachment of the film; at image (B) the region where there was detachment of the film at the intersection of the cross-cut

preferably at the intersection point of the cuts, characterized by a weakened region. The total percentage of removed film was less than 5% according to the ASTM standard[16].

4. Conclusions

Thin silica films were prepared with antireflective properties. SEM images revealed that the films surface is homogeneous and free of cracks. For all films the contact angle value was below 90º, characterizing them as hydrophilic. The best reflectance result was obtained for the silica film with a withdrawal rate of 4 cm/min and with heat treatment, presenting a diffuse reflectance in wavelength range of 350 to 900 nm of 2.72%. The films exhibited good mechanical properties with adhesion of 4B and hardness of 3H. These results indicate parameters for future work required to improve the antoreflective properties of the sílica films applied the conversion of solar energy in heliothermic plants.

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