Preparation and Characterization of Absorbent Films by Ultrasonic Spray Pyrolysis Technique

C.D. Hernández - Pérez[1], E. Barrera-Calva[1], F. González[1] A.M. Soto[2] and R. Rosas[1]

[1] Universidad Autónoma Metropolitana - Iztapalapa, CBI, IPH, IRE, CDMX, México

[2] Universidad Autónoma Metropolitana - Iztapalapa, CBI, Quimica, CDMX, México

Abstract

Films of Fe_2O_3: Mn were obtained using ultrasonic spray pyrolysis technique. Deposits of this material were made on Titanium plates in a temperature range of 350 to 600 °C in steps of 50 °C. The concentrations of Fe and Mn varied in the solutions to be sprayed. For the concentration of 0.0015 molar of Fe and 0.0035 molar of Mn and at a temperature of 600 ° C it was obtained that the absorpbance has a value of 0.943 and the emittance value of 0.07, which are competitive to the commercial absorber $TiNO_x$. X-ray diffraction analysis shows that the phase that this material presents corresponds to the structure of the hematite, on the other hand, the roughness analysis of the films show that this parameter varies depending on the deposition temperature, being fundamental in the optical response of the material.

Keywords: Spray Pyrolysis, Hematite, Solar Absorber, $TiNO_X$

1. Introduction

The global energy demand has increased over the years, and solar energy considered as an option to support more intensely in meeting the annual energy demand that required at this time (630 EJ/year). Currently, research is being carried out on various materials for its application in efficient solar energy technology to bring it to an industrial scale. In the case of solar absorber materials, it is necessary to achieve high standards in solar absorpbance and thermal emittance. Additionally, this type of material is required to be stable, non-toxic, abundant in nature, absorb ultraviolet wavelengths, and high energy. An example of this type of s olar reference material is TiNOx, which achieves a solar absorptance of 0.95 and an emittance of the order of 0.06. M.S. Tomar and F.J. García (1981).

A material that potentially used in these applications has been Hematite (α-Fe2O3), which is considered an n-type semiconductor with the closed-package hexagonal crystal structure, has a high corrosion resistivity and its production is low-cost, J. Chen et al. (2005). This material allows taking 40 % of the incident solar radiation. As reported by S. Kumari et al. (2007) the properties of iron oxide can be altered by varying some parameters such as the introduction of extrinsic defects and/or the alteration of extrinsic defects by doping. Another advantage of this material is the diversity of preparation methods to synthesize it and various techniques have been used to obtain it. On the other hand, Gurudayal et al. (2014), it shows that Mn is an excellent option to doped Fe_2O_3. Due to its position in the periodic table the atomic radii of the Fe^{3+} and Mn^{2+} ions are similar between them which implies that there no significant distortion of host lattice, it is also known that Mn generates states within the Band Gap of Fe_2O_3 P. Liao and E. Carter (2012) and B.A. Balko et al. (2001) which are used to make solar absorption more efficient. Reports shown by F. Achouri et al. (2014) show that Mn is an excellent solar absorber because it are in the spectral region of UV-VIS M.

doi:10.18086/swc.2019.01.02 Available at http://proceedings.ises.org

In the specialized literature are few reports of this material and its obtaining in Manganese-doped Hematite structure as well as study of its response as a solar absorber. Obtaining materials in film form is an important research branch, which has allowed the development of various physical and chemical techniques to obtain materials in this form for various applications. The spray pyrolysis technique corresponds to a technique of chemical type that uses precursors in solution Gurudayal et al. (2014), this technique stands out from others because it does not require expensive accessories or some atmosphere to perform the synthesis of the materials. The advantages of technique are obtaining of material in the form of a film with high adhesion and chemical stability, characteristics that have allowed the obtaining of porous, dense, multilayer films and even the production of powders. The use of this technique has had successful results in obtaining materials for use in solar cells as well as semiconductors R.R. Chamberlin and J.S. Skarman (1966) and J.E. Hill and R.R. Chemberlin (1964)

In this research, the results obtained from films of α-Fe_2O_3 doped with different concentrations of manganese synthesized employing the ultrasonic spray pyrolysis technique to obtain of a material that has the properties of good solar absorber. The preparation method described, the solar absorptive analysis, thermal emittance, the characterization of the material by XRD as well as the Perfilometry studies are carried out and reported. As far as we know the research of these films of Fe_2O_3: Mn is practically non-existent in the literature on this subject.

2. Experimental Methodology

The substrates used for depositing the film material by the pyrolytic reaction are high purity titanium sheets, 99.9%, cut into 2 x 2 cm^2 samples. The substrates were washed with water and detergent. After that, the samples were dipped in ethanol and a second wash is carried out by immersing the samples in hot acetone to remove the remaining residues of fat on the surface.

To obtain Fe_2O_3 films contaminated with manganese, the following substances were used as precursors; $FeCl_3$ $6H_2O$ (Meyer 97%) in a concentration of 0.0015 mol / l and $MnCl_2$ $4H_2O$ (Tecsiquim 98%) in a concentration of 0.0035 mol / l. In all cases deionized water was used as a solvent. To obtain the solution to be sprayed, proportional volumes of the precursor are mix to obtain 100 ml of the solution to be spray. The solution is spray for 15 minutes at a flow of 5 L / min, using dry air as the entraining gas, at temperature ranging from 350 °C to 600 °C, at 50 °C intervals to deposit various samples.

The titanium sheets as substrates were placed on the tin bed and the material immediately deposited. The deposits made inside an air hood so that the vapors of the reaction come out and do not affect in the reaction that it is happening. It is shown that this procedure is the ideal one for the coating deposit in order to reach the good optical response of the material.

Once each sample obtained, it was cooled and then subjected to a heat treatment for two more hours at the preparation temperature to stabilize the phase. Subsequently, each sample passed to structural, optical, and morphological characterization. The total spectral reflectance of the samples were obtained with the Varian Cary 5E UV-VIS Spectrophotometer using an integration sphere. Based on this measurement, the total solar absorptance of the samples evaluated by the integration of the reflectance spectrum. UV- VIS Spectrophotometer was initially calibrated using NASA international Standard equivalent to $(BaSO_4)_3$ as base line. FTIR was calibrated using an international standard for emittance value (Device and services Co Standard).

To determine the thermal emittance of the samples, we start by manipulating the reflectance spectra of the samples in the infrared region. Such spectra are performed with an Infrared spectrophotometer with FTIR Fourier transform from Thermo Scientific, model IS50 FT-IR

In the case of profilometry analysis, a Stylus Profilometer Bruker Dektak XT was used for areas of 1000 mm^2, while the Atomic Force Microscopy analyses were performed using an Ambios Technology Inc Q Scope 250/400.

The structural characterization analyses of the samples was measure using a Bruker D8 Advance X-ray diffractometer.

The measurements of optical properties of commercial TiNOx made from a sample of this material on glass, which is the material used in the manufacture of the evacuated tubes of commercial solar collectors.

3. Experimental Methodology

The experimental process consisted of making deposits of Fe_2O_3: Mn on titanium substrates for different concentrations of Fe and Mn ions. Preliminary analyzes allowed to fix a concentration of Fe in 0.0015 mol/l and Mn in 0.0035 mol/l in solution to use in this research. The first analyzes focused on knowing how to modify the appearance of deposit as well as the roughness of filmas a function of temperature. The results are shown in Table 1.

Table 1. Thickness and appearance of samples prepared at a concentration of Fe and Mn, (0.0015: 0.0035 in mol), as a function of the temperature

Sample	Thermal temperature (°C)	Colour and homogeneity	Film Roughness (μm)
(a)	350	Redish	1.011
(b)	400	Redish	0.749
(c)	450	Redish	1.170
(d)	500	Dark redish	1.008
(e)	600	Black color uniform	0.450

Table 1 indicate how the color modified as the roughness of Fe_2O_3: Mn as a function of the deposition temperature. Whenever the deposit made at 350 °C, the reddish color is predominant over the deposits made. It can be observed that the roughness does not present any regularity as a function of the deposition temperature.

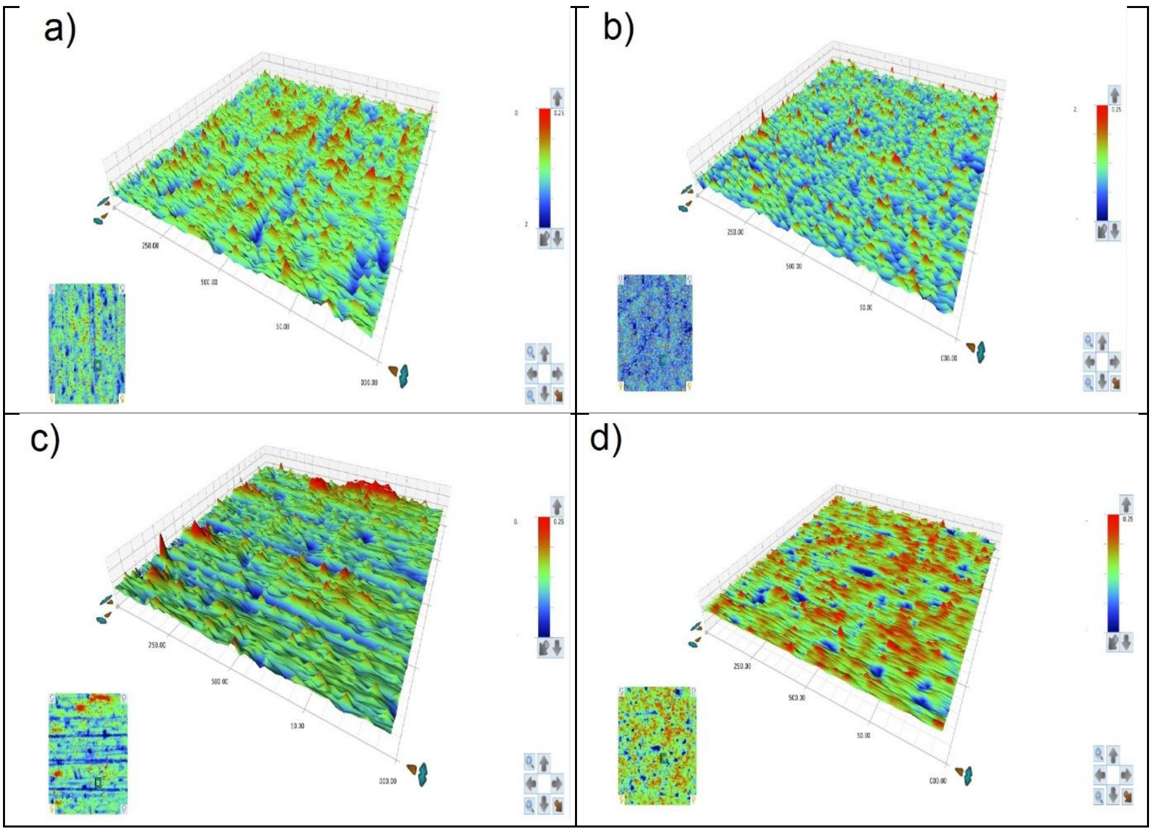

Figure 1 shows some representative images of the surfaces roughness analysis. a) 350 °C, b) 450°C, c) 500°C y d) 600 °C

Figure 1 shows the roughness of Fe_2O_3: Mn deposited at different temperatures. It can be seen that the deposits do not present any type of regularity either on the surface or in the roughness values. With increasing temperature, a decrease in surface roughness is noticeable, which is most likely the cause of the increase in solar absorpbance, by a trapping the incident solar irradiation of the same wavelength range that the roughness surface.

The previously analyzes the storage temperature to be set at 600 °C. For the study of absorpbance and emittance, deposits are made for different concentrations of Fe and Mn. It starts with the calculation of absorptance, as shown in table 2.

Table 2. Values were resulting from solar absorption of various samples prepared by ultrasonic spray pyrolisis, as a function of various concentrations of Fe and Mn, deposit at 600 °C.

Sample	**Fe (mol)**	**Mn (mol)**	**Solar Absorpbance**
(a)	0.0015	0.0035	0.943
(b)	0.025	0.0025	0.771
(c)	0.02	0.003	0.697
(d)	0.015	0.0035	0.755
(e)	0.01	0.004	0.692
(f)	0.05	0.0045	0.722

The optimum solar absorptance value is obtained for the concentration of 0.0035 mol of Mn and 0.0015 mol of Fe, obtaining a value of 0.943 that is comparable with that reported by commercial TiNOx whose reported value is 0.95 [13], for the remaining concentrations this parameter does not exceed a value from 0.77

As mentioned, a variation in temperature modifies the roughness and reflectance of the material obtained. Figure 2 shows this behavior of the material obtained as a function of temperature compared to the commercial reference TiNOx.

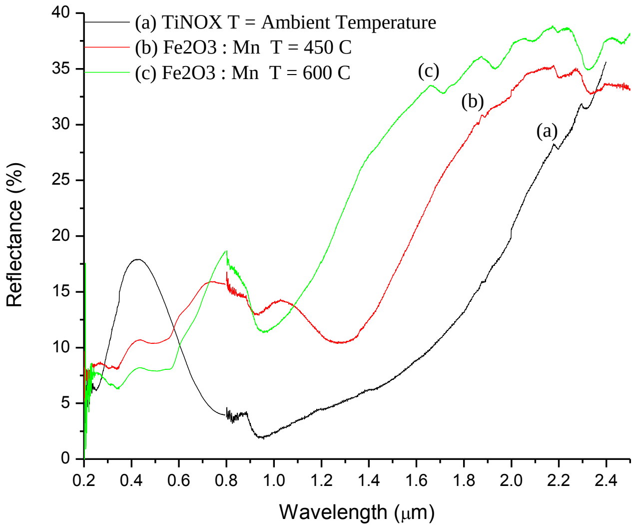

Figure 2. Spectral total reflectance of Fe_2O_3: Mn with the fixed molar concentration of Fe in 0.0015 mol and Mn in 0.0035 mol as a function of temperature.

From the results shown in table 2, as well as that shown in graph 2, the concentrations of 0.0015 mol of Fe and 0.0035of Mn in the solution to be deposited via the ultrasonic spray pyrolysis technique guarantee the maximum value of solar absorptance. To complement the analyzes, reflectance measurements made as a function of temperature for these concentrations of Fe and Mn. Figure 3 shows the response for some selected temperatures.

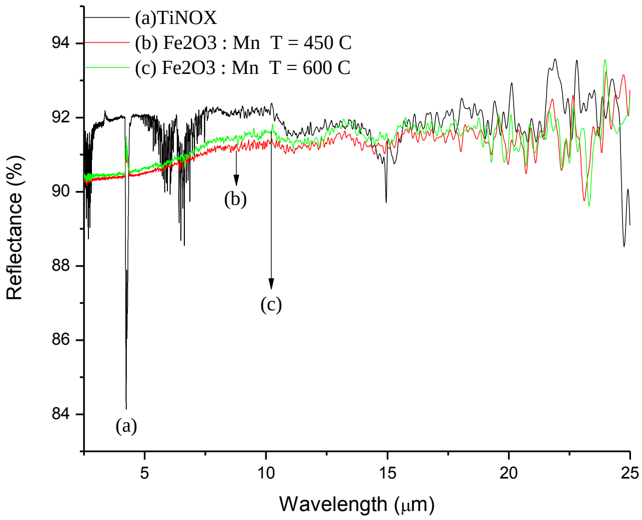

Figure 3. Spectral specular reflectance of Fe_2O_3: Mn in the infrared region, for different temperatures and a fixed concentration of Fe and Mn.

Table 3 indicates the values calculated for the emittance for different temperature conditions and the fixed concentration of Fe and Mn.

Table 3. Emittance values as a function of temperature.

Sample	Temperature (°C)	Emittance
(a)	600	0.07
(b)	500	0.10
(c)	450	0.075
(d)	400	0.038
(e)	350	0.15

The value of the absorptance of the material obtained utilizing the ultrasonic spray pyrolysis technique, when compared with the commercial TiNOx absorber, a deviation of 7% is obtained. This value shows that the technique used is an excellent procedure for obtaining this type of materials. In the case of the emittance, the experimentally reached value shown in Table 3 is comparable to that reported for the TiNOx absorber. Experimentally it has been shown that the values of both emittance and absorptance are comparable concerning the TiNOx commercial reference. As mentioned in the introduction, several techniques have been used to obtain this material; however, the values obtained are far below those offered by TiNOx.

The use of the ultrasonic spray pyrolysis technique for the deposit of these coatings presents advantages in comparison with the techniques reported in the literature because the materials obtained by this technique are uniform, homogeneous, have high adhesion, are physically and chemically stable and can be deposited in areas of several meters and therefore can be used in the manufacture of solar cells or solar panels for finned tube solar collectors.

The results mentioned above are related to the phase that has α-Fe_2O_3, so it is necessary to show that the synthesis process allows obtaining the hematite phase. Figure 4 shows the diffraction pattern of both the substrate (titanium plates) where the deposit made and the Hematite phase corresponding to the material studied. As the storage temperature increases, the intensities associated with these two phases also increase as a natural consequence of a high level of crystallization of Fe_2O_3: Mn.

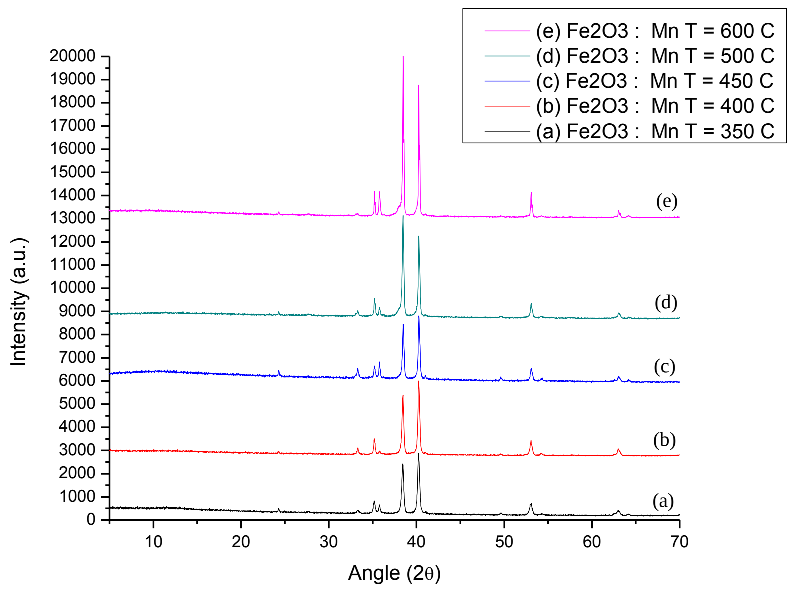

Figure 4. XRD patterns as function of temperature

The peaks associated with the phases listed are presented in Table 4 (a) and 4 (b) respectively.

Table 4 (a): Diffraction planes for the Ti, according to the standards

Angle (°)	Diffraction planes	Size Crystal (nm)
35.09	(100)	81.51
38.42	(002)	84.43
40.17	(101)	159.9
53.00	(102)	83.56
62.94	(110)	53.36

Table 4 (b): Diffraction planes for Hematite

Angle (°)	Diffraction planes	Size Crystal (nm)
24.29	(012)	65.34
33.15	(104)	79.74
35.61	(110)	52.79
49.47	(024)	63.74
54.08	(116)	81.08

Conclusions

This research shows that the Ultrasonic Spray Pyrolysis technique is acceptable for depositing thin Fe_2O_3 absorbent films doped with Mn. Analyzes performed for different concentrations of Fe and Mn. The concentration of Fe and Mn 0.0015 mol/l and 0.0035 mol/l respectively offer the best values of emittance and absorptance that lead us to a high solar selectivity. The values obtained 0.94 (3) for the absorbance, and 0.07 for the emittance are around to the commercial reference TiNOx, which is used commercially as an absorber coating. X-ray diffraction analysis indicates that the technique used guarantees obtaining the hematite phase, a fundamental element for absorption analysis. The diffractograms show that increase of temperature in steps of 50 ˚C does not modify in any sense the structure of the material remaining constant in the process of depositing Fe_2O_3:Mn, a fact that stands out about the temperature of deposit of the material is that the roughness is modified depending on the temperature. Concerning the optical properties, the reflectance spectra measured and shown in this work allow us to appreciate the potential solar absorber selectivity of this type of systems for the use of solar energy in solar collectors, as shown in Figure 2. The relatively simple technique can be considered as an option for the production of this material to deposit in large areas as required by the manufacturer of solar collectors, that continuing with an increased interest all over the world.

References

[1] M.S. Tomar and F.J. García, Spray pyrolysis in solar cells and gas sensors
Progress in Crystal Growth and Characterization of Materials, 4(3), 221 (1981)

[2] J. Chen, L. Xu, W. Li, and X. Gou, α-Fe_2O_3 Nanotubes in Gas Sensor and Lithium-Ion Battery Applications, Adv. Mater. 17, 582 (2005)

[3] S. Kumari, Aadesh, P. Singh, C.Tripathi, D. Chauhan, S. Dass, R. Shrivastav, V. Gupta, K. Sreenivas, and V. R. Satsangi, Enhanced Photoelectrochemical Response of Zn-Dotted Hematite, Int. J. Photo. Vol. 2007. Article ID 87467, 6 Pages

[4] Gurudayal, S. Y. Chiam, M. H. Kumar, P. S. Bassi, H. L. Seng, J. Barber, L. H. Wong. Improving the Efficiency of Hematite Nanorods for Photoelectrochemical Water Splitting by Doping with Manganese, Appl. Mater. Interfaces 2014, 6, 5852−5859

[5] Liao, P.; Carter, E. A. Hole Transport in Pure and Doped Hematite.J. Appl. Phys.2012,112, 013701-1−013701-13.

[6] Balko, B. A.; Clarkson, K. M. The Effect of Doping with Ti(IV) and Sn(IV) on Oxygen Reduction at Hematite Electrodes. J.Electrochem. Soc. 2001,148, E85−E91

[7] F. Achouri, S. Corbel, L. Balan, K. Mozet, E. Girot, G. Medjahdi, M. B. Said, A. Ghrabi, R. Schneider. Porous Mn-doped ZnO nanoparticles for enhanced solar and visible light photocatalysis. Appl. Mater. Interfaces. 2014, 6, 5852−5859.

[8] M. Kawano, H. Takebe, M. Kuwabara, Compositional dependence of the luminescence properties of Mn^{2+}-doped metaphosphate glasses, Opt. Mater. 32 (2009) 277.

[9] Gurudayal, Sing Yang Chiam, Mulmudi Hemant Kumar, Prince Saurabh Bassi, Hwee Leng Seng, James Barber, and Lydia Helena Wong. Improving the Efficiency of Hematite Nanorods for Photoelectrochemical Water Splitting by Doping with Manganese *ACS Appl. Mater. Interfaces*, 2014, 6 (8), pp 5852–5859

[10] R.R. Chamberlin and J.S. Skarman, Chemical spray deposition process for inorganic films, *J. Electrochem. Soc.*, 113(1) 86 (1966).

[11] J.E. Hill and R.R. Chemberlin, US Patent 3, 148, 084 (1964).

[12] Almeco Group. Official web. www.almecogroup.com

[13] Vayssieres, L., Sathe, C. Butorin, S., et al. One dimensional quantum confinement effect in α- Fe_2O_3 ultrafine nanorod array. Adv. Mater. 2005. (17) 2320-2323.