American Journal of Energy Research, 2016, Vol. 4, No. 1, 11-15
Available online at http://pubs.sciepub.com/ajer/4/1/2

DOI:10.12691/ajer-4-1-2

Optical Characterization of TiO_2-bound ($CuFeMnO_4$) Absorber Paint for Solar Thermal Applications

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Abstract A composite thin film consisting of TiO_2 (binder), uniformly mixed $CuFeMnO_4$ paint (solar absorber) was coated on textured aluminum sheets by dip coating. The film's elemental analysis was done using energy dispersive x-ray (EDX) and the surface of the film characterized using scanning electron microscope (SEM). Optical properties of the $TiO_2/CuFeMnO_4$ composite film were also studied using computerized double beam solid-spec 3700 DUV Shimadzu Spectrophotometer. Reflectance was obtained by spectrophotometric measurements, and thermal emmittance was determined using heat flux- based technique respectively. Reflectance measurement values less than 0.03 in the solar wavelength (290 nm < λ < 2500 nm) and low thermal emmittance less than 0.016 for temperatures between 24°C and 100°C were obtained.

Keywords: *$CuFeMnO_4$ paint, TiO_2- bound, reflectance, thermal emmittance, solar thermal*

Cite This Article: C. O. Ayieko, R. J. Musembi, A. A. Ogacho, B. O. Aduda, B. M. Muthoka, and P. K. Jain, "Optical Characterization of TiO_2-bound ($CuFeMnO_4$) Absorber Paint for Solar Thermal Applications." *American Journal of Energy Research*, vol. 4, no. 1 (2016): 11-15. doi: 10.12691/ajer-4-1-2.

1. Introduction

Solar thermal absorbers such as paint-based $CuFeMnO_4$ has gained attention of researchers and manufacturers as one of the solar absorber paint coatings due to its low cost and ease to coat on various substrates [1]. It is therefore suitable for applications such as household solar water heating. Performance evaluation of any solar thermal absorber coating is evaluated by calculating the absorptance-emmittance ratio, α/ε. This is the spectral selectivity test requires that a good solar absorber absorbs more in the solar wavelength range (290 nm < λ < 2500 nm) but emits less in the far infrared range. Based on this criterion efficient selective solar absorbers should have high absorptance, $\alpha > 0.9$ in the wavelength range from 290 nm – 2500 nm and low emmittance, $\varepsilon < 0.1$ in the wavelength greater than 2500 nm, implying that the ratio α/ε should be high for good quality solar absorber [2].

Absorptance values of 0.86 and 0.93 have been reported for unbound and bound (SiO_2 – bound layer) $CuFeMnO_4$ paint respectively [1].

Even with significant improvement of absorptance for paint bound in SiO_2 layer, a thermal emmitance of 0.62 obtained was unfavourable for solar thermal absorber application. This high value of thermal emmittance was attributed to the SiO_2 binder layer. Improving solar spectral selectivity of $CuFeMnO_4$-paint as a means of boosting its absorber efficiency, calls for efforts to increase its absorptance-emmittance ratio, α/ε. This can be achieved by choosing low infrared (IR) transmitting binders to lower its thermal emmittance, ε. Our earlier study [3] shows that TiO_2 has high infrared transmittance and high absorptance in the visible region of the solar spectrum. In this report, the results of optical characteristics of $TiO_2/CuFeMnO_4$ absorber layer for solar thermal applications are presented. Optical properties of $CuFeMnO_4$-paint mixed with the IR transmitting titanium dioxide, TiO_2, binder coated on aluminium (Al) substrates was studied to test the feasibility of TiO_2-modified $CuFeMnO_4$-paint as a candidate for solar thermal application.

2. Experimental Procedures

2.1. Preparation of Titanium Dioxide (TiO_2) Solution and Thin Film Formation by dip Coating

One molar (1 M) solution of titanium (IV) isopropoxide (99.7% pure) in isopropanol (99.7% pure) from Fluka Ltd was prepared and 28 ml of the solution added gradually to 72 ml of distilled water under vigorous stirring to disperse the white coagulates. This mixture was stirred for 1 hour at 30°C to ensure complete hydrolysis. One molar (1 M) solution of nitric acid of volume 5 ml was then added to the mixture to speed up peptization and stirred at 70°C for 7 hrs to ensure that isopropanol evaporated and left to cool to room temperature. This solution was then left to cool to room temperature and forms a stable clear solution of TiO_2 [4]. TiO_{2}- bound ($FeMnCuO_4$) absorber paint was prepared by mixing $FeMnCuO_4$ solution with TiO_2 solution in varying ratios. Deposition of the TiO_2 film and TiO_{2}- bound ($FeMnCuO_4$) absorber paint was done by dip coating.

2.2. Thermal Emmittance Measurement.

Thermal emmittance of the absorber is a very important parameter for spectral selectivity. Because the collector plate consists of the plate itself, the binder (TiO_2) and the absorber paint, it is imperative to know how thermal emittance changes every time each of these components is introduced. Determination of thermal emmittance of aluminum sheet from room temperature to slightly above 100°C is done because this is the range of operation for the household flat plate solar thermal collector. The heat flux method of determining thermal emmitance that relies on the heat flux from a surface and does not require temperature history of the surface was used [5]. A heat flux sensor which consists of a layer of thermocouples infused into a 0.2 mm thick material was used to generate a potential difference proportional to the heat flux across the sensor. The relationship is represented as

$$Q = \frac{V}{c} \tag{1}$$

Where Q is heat flux, V is the electrical potential difference across the sensor terminals and c is the sensor constant. Having determined the heat flux, Q, the Stefan Boltzmann law is applied to give thermal emittance, in this case it is given by the following equation [6]:

$$\varepsilon = \frac{Q}{\sigma\left(T^4 - T_a^4\right)} \tag{2}$$

Where T is the temperature of the plate, T_a is the ambient temperature, ε is thermal emmittance and σ is the Stefan Boltzmann constant.

Figure 1 shows the set up used for thermal emmittance measurement. Current of different values was passed through the aluminum sheet of size (4.5 X 1.5) cm^2 which gradually heated the plate from room temperature to temperatures over 100 ^{o}C. An alternating current through the plate was regulated by a variac. After heating slightly above 100 ^{o}C, supply of electric power was stopped. As the sample cooled to room temperature, sensor voltage and surface temperature are measured using a thermometer simultaneously. Ambient temperature is also monitored using a thermometer. A temperature resistant tape was used to clamp the heat flux sensor on the plate during the measurement.

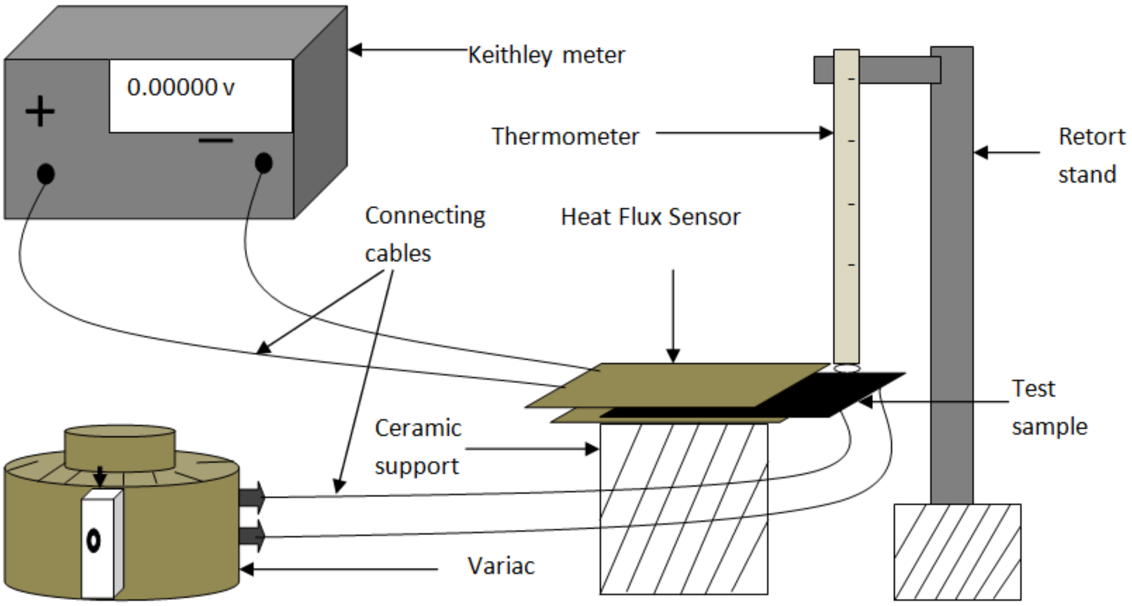

Figure 1. Set up for thermal emmittance measurement

2.3. Optical and Morphological Characterization

Reflectance of the aluminum substrate surface was studied at near normal incidence in the wavelength range of 300 nm to 2500 nm being the range of interest for solar applications. Reflectance and absorptance measurements were done using a computerized double beam solid-spec 3700 DUV Shimadzu Spectrophotometer with highly reflecting aluminum mirror as a reference. Micrographs of the samples were also obtained from light microscope and Carl Zeiss SIGMA FE-SEM OXFORD X-ACT equipped with EDS Detector (SEM).

3. Results and Discussion

Table 1. EDX analysis for the dip coated TiO_2- bound, $CuFeMnO_4$ paint on textured aluminum surface

Element	O	Al	Cl	Ti	Mn	Fe	Cu	Totals
Weight%	33.85	8.03	1.42	25.60	9.68	12.82	8.60	100.00
Atomic%	59.95	8.43	1.14	15.15	4.99	6.50	3.83	100.00

Surface morphology of TiO_2-bound, $CuFeMnO_4$ paint was studied and the micrographs shown in Figure 2. It is observed that the TiO_2-bound, $CuFeMnO_4$ paint surface is cracked into blocks. The cracks are as big as 1 μm while the blocks are predominantly more than 2 μm with individual blocks having pores less than 500 nm in size. EDX analysis was done on the coatings and the presence of the elements in the absorber matrix was presented by atomic percentages as in Table 1. From the table, chlorine is detected but forms the least part in the composite. Presence of chlorine could be due to the residues of either copper chloride or iron chloride which formed part of the reagent for preparation of $CuFeMnO_4$ absorber.

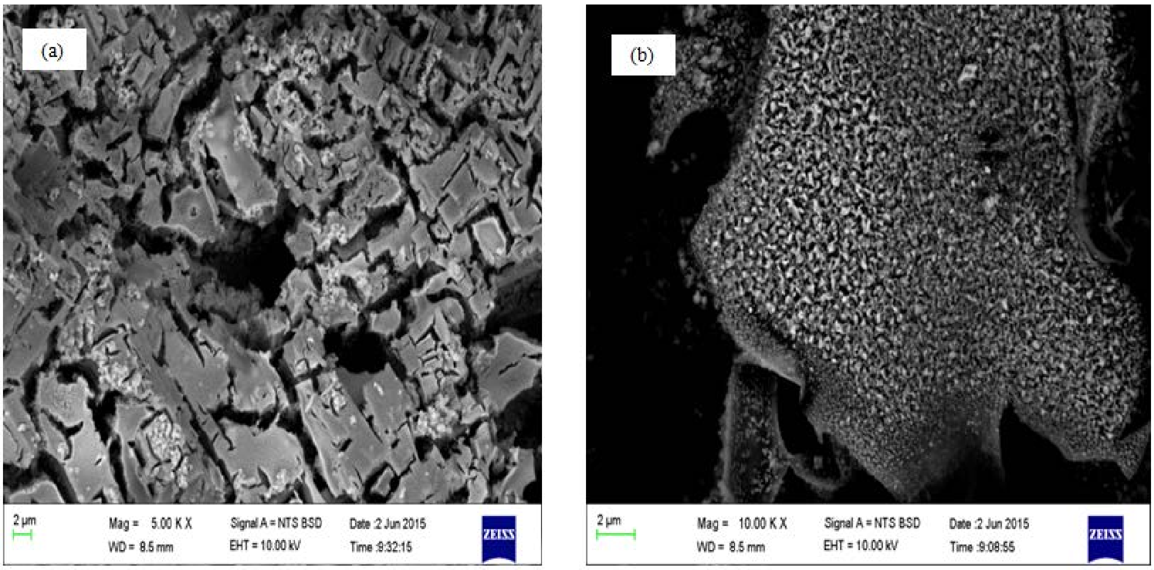

Figure 2. SEM micrograph of (a) dip coated TiO_2- bound, $CuFeMnO_4$ paint on textured aluminum surface at X 5000 magnification (b) porous block of the TiO_2- bound, $CuFeMnO_4$ paint coating formed on the textured aluminum surface taken at X 10 000 magnification

Figure 3 shows two sets of reflectance spectra; (i) films of TiO_2-coated on textured aluminum surface, (ii) dip coated, TiO_2-bound, $CuFeMnO_4$ paint film on textured aluminum surface. The upper set of graphs indicate that the reflectance of the films of TiO_2 coated with same thickness of 0.0014g/cm^2 on textured aluminum ranges from 41% to 71%. It is observed that the graphs within the spectral range of 250 nm to 2500 nm have small deviation of less than 4% reflectance attributed to the concentration of the etchant used for texturing aluminum substrates. The etchant concentration is presented in Figure 3 as a ratio of perchloric acid to ethanol by volume. The lower set of graphs shows that upon coating the textured aluminum surface with TiO_2-bound, $CuFeMnO_4$ paint, reflectance drastically decreases indicating that absorption is enhanced. It is further noted that reflectance is lower than 15 % in the visible spectral range from the lower set of graphs and increases in the infrared which is expected for a selective solar absorber.

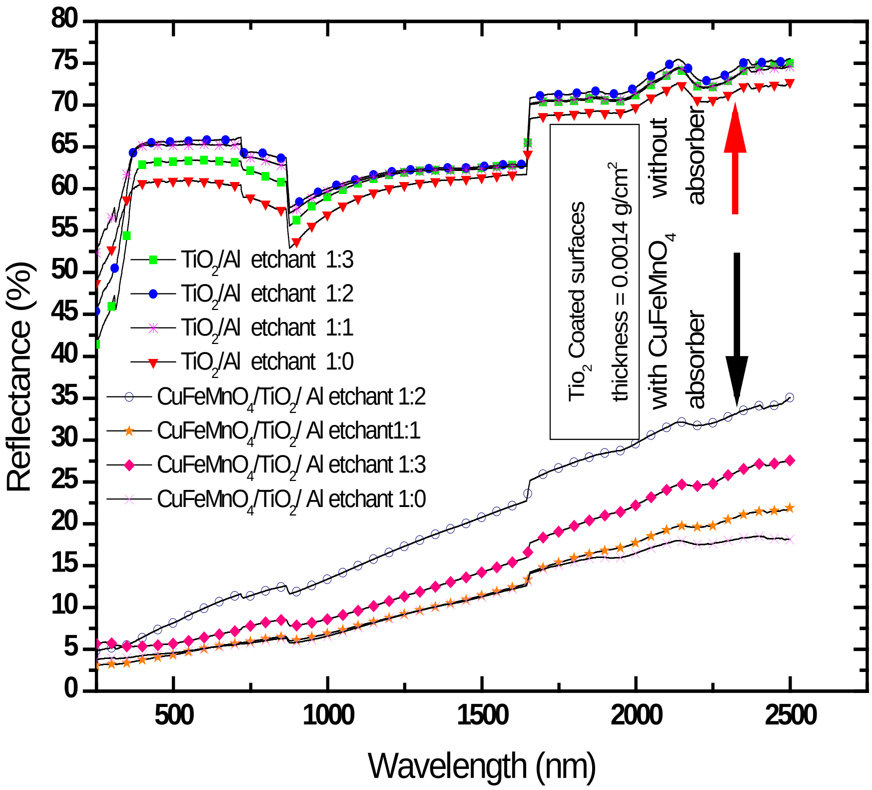

Figure 3. Reflectance spectra for; (i) TiO_2- coated textured aluminum surface (top), and (ii) dip coated TiO_2- bound, $CuFeMnO_4$ paint on textured aluminum surface (bottom)

It is clear from both upper and lower set of the graphs in Figure 3 that much as the etchant concentration affects reflectance, it does not have any consistent pattern on reflectance. The highest reflectance recorded for the dip coated TiO_2-bound, $CuFeMnO_4$ paint on textured aluminum surface is 35 %, meaning that more than 65 % absorption has been realized. The values of reflectance recorded for the dip coated TiO_2-bound, $CuFeMnO_4$ paint on textured aluminum surface as shown in lower set in Figure 3 which ranges between 2.5 % to 30 % are far much below the values (15 % to 60 %) obtained by [7] in the same wavelength range of 250 nm and 2500 nm. Therefore, there is a significant improvement in absorption when $CuFeMnO_4$ paint is modified with TiO_2.

The heat flux-based technique which was adopted in this work measures emissivity over all wavelengths and all angles, total hemispherical emissivity in a single test, which is not the case with optical techniques [8]. Figure 4 shows thermal emmittance of various treatments of aluminum surface at 24°C, the ambient temperature. It can be inferred that the thermal emmittance for all the surfaces studied lie in the range 0.005 to 0.016. The graphs depict a trend where with increase in sample temperature, thermal emmittance increases. Bare polished aluminum has the highest thermal emmittance values whereas coating the textured surface with TiO_2 reduces thermal emmitance which is even further reduced by coating the surfaces with the absorber paint, $CuFeMnO_4$. The thermal emmittance for aluminum has been reported by [5] to be between 0.03 and 0.06, which is far above the values obtained in this work. The variation could be due to the environment under which the measurements were taken: their measurements were done in a vacuum as opposed to our measurements which were made under the laboratory atmosphere. They also made measurements on aluminum coated foil whereas we worked with aluminum plate. The emmitance values for bare polished surface, TiO_2 coated surface and absorber coated surface are low to the extent that qualifies the dip coated TiO_2-bound, $CuFeMnO_4$ paint to be a good material for solar thermal collector now that its absorptance is as high as depicted from Figure 3 with over 65% absorption.

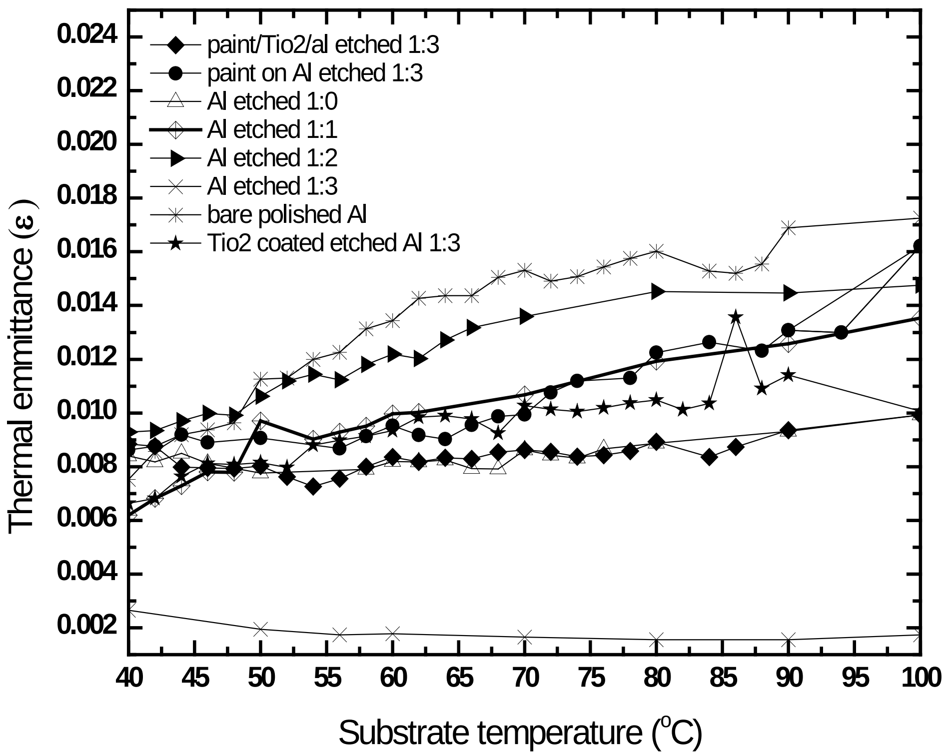

Figure 4. Thermal emmitance of aluminum taken at 24°C

It is also notable from Figure 3 that the lower set of graphs shows a pattern in which reflectance increases with wavelengths and as such high reflectance is expected in the far infrared region. This pattern is corroborated by [7], who did measurement beyond 3000 nm as their spectrophotometer could accommodate these longer wavelengths using a Perkin–Elmer Spectrum 2000 IR spectrophotometer. They recorded reflectance of more than 40 % for the wavelength range of 2500 nm to 25000 nm. The higher reflectance in the far infrared range is an indication that thermal emmitance reduces hence characterizing the film as spectrally selective. The low values of thermal emmitance indicated in Figure 4 obtained by heat flux-based technique supports the rising trend of reflectance with wavelength in Figure 3.

4. Conclusion

TiO_2-bound, $CuFeMnO_4$ coating on etched aluminum substrates forms porous blocks with high absorptance in the solar wavelength. Aluminum substrates are opaque and therefore with a record of between 15 % to 35 % reflectance obtained, it implies that TiO_2-bound, $CuFeMnO_4$ coating on etched aluminum substrates achieves between 65 %to 85 % absorbance. For the substrate temperature range between 40°C to 100°C, TiO_2-bound, $CuFeMnO_4$ coating recorded thermal emmittance values in the range of 0.005 to 0.016. With these high absorptance and low thermal emmittance values for TiO_2-bound $CuFeMnO_4$ coating, there is found a high absorptance-emmittance ratio, α/ε, making the coating a selective solar absorber suitable for solar thermal application.

Acknowledgements

This work is supported by African Materials Science and Engineering Network (AMSEN) and International Programme in the Physical Sciences (IPPS), Uppsala University (Sweden) and University of Nairobi (Kenya).

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