Effect of Sol-Gel Process Parameters on Optical Properties of $CuCoMnO_x$ Selective Coat for Solar Energy Applications

Nahed El Mahallawy [1], Madiha Shoeib [2] and Sandra Eletriby [1]

[1] Design and Production Engineering Department Faculty of Engineering, Ain Shams University, Abasia, Cairo, Egypt.
[2]Central Metallurgical Research Center, El-Tebbin.Helwan, Cairo, Egypt
sandraeletriby@hotmail.com

Abstract: A solar thermal collector collects heat by absorbing sunlight. It has many industrial and domestic applications. The main part of the solar thermal collector is the absorber surface which must have a maximum absorptivity and minimum emissivity of solar radiation. This is achieved by application of $CoCuMnO_x$ selective coating on the stainless steel absorber surface using dip coating sol gel technique; in this technique the substrate is dipped in a gel solution and withdrawn with a predetermined rate. This study is directed towards the effect of the different coating process parameters on the optical properties and selectivity of the selective $CoCuMnO_x$ coating. The process parameters include different concentrations of the solution, different withdrawal rates and different number of dips. The coated samples were heat treated at 450 ˚ C for 30 minutes. Absorptivity (α) and emissivity (Ɛ) of the coat were the optical properties studied in order to find the maximum selectivity (α / Ɛ) values. The coat properties were characterized by measuring its thickness and roughness. It was found from the results that when applying the coat on stainless steel substrates, a maximum selectivity value of (α/Ɛ) = 0.91/0.09=10.1 was realized. The results indicate that the roughness improves the absorbitivity while it has no sensible effect on the emissivity.
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Keywords: Sol-gel, $CuCoMnO_x$ selective coating, Optical properties.

1. Introduction:

The conversion of solar radiation is considered as a very efficient way to provide space heating, domestic hot water, and electricity production by using solar absorbers. Selective coating is an optical coating applied to the surface of a solar energy device to increase the absorption of thermal radiation and reduce its losse. The selective coat must have a high absorptivity (α) in the UV range and low thermal emissivity (Ɛ) in the near infrared (NIR) and far-infrared (FIR) wavelength ranges. These can be obtained by a material that has a reflectance of less than 10% in the UV range and greater than 90% in the IR range. By combining absorptivity and emissivity together, a selectivity factor can be defined by absorptivity/ emissivity ratio (α/ Ɛ); the higher the selectivity ratio the more promising the material will be for such solar applications [1].

There are many techniques to apply the selective coating for these solar absorbers such as electroplating [2], sol-gel [3], CVD [4], PVD [5] and [6], electroless plating techniques and magnetron sputtering [7], electro deposition of black chrome or an ordinary black paint. In the electroplating process, toxic Cr (VI) ions are used and care must be taken to avoid environmental pollution. Despite the fact that this product is very durable, it is problematic due to the environmental impact. On the other hand the vacuum deposition is a high cost process due to the expensive equipment required and can be out of reach for potential producers in certain situations [8]. This explains the interest in developing a sol-gel process for the production of nanocomposite selective solar absorber coatings. Indeed it doesn't require expensive vacuum equipment as it is very easy to be formed simply by dipping the substrate into an appropriate colloidal solution and withdrawing in a controlled manner and definitely avoid the use of toxic materials. Another advantage of the sol-gel film deposition process is that the sol-gel technique allows for the deposition of thin films with a uniform chemical composition [9] Today, Sol-gel technique has been established at a laboratory scale for low cost production of high efficient selective solar absorbers which has many applications such as optics, electronics and sensor devices [10] and [11] However, the application of sol gel for selective coating was mentioned to remains an uncommon practice likely due to the fact that inadequate film thicknesses could be obtained as in reference [12].

Due to its mechanical stability and the possibility of using it as a high temperature application, stainless steel is an interesting substrate material. It can be used as absorbers for domestic hot water generation, for receiver tubes in concentrated solar power and can be used for high temperature applications [8].

Cobalt oxides, copper oxides and manganese oxides are among the most interesting in the research field of selective coatings using sol gel techniques [13], [14], [15] and [16] for solar heating applications due to ease of applications and attractive optical properties. Selective coat is required to have a high absorptivity (α) in the solar wavelength range and an accompanying low thermal emissivity (Ɛ) in the near wavelength ranges. These requirements correspond to a material that has a reflectance of less than 10% in the UV range and greater than 90% in the IR range (wavelength >2.5 lm) [17].

Previous work [18] demonstrated that it is possible to reach a solar absorptivity of 0.86 and a thermal emissivity of 0.11 by sol-gel method with a single layer of CuCoMnOx on aluminum substrate. While the application of sol gel technique on Aluminum substrate resulted in absorptivity 0.83 and emissivity of 0.01 [13]. In 2005 Bostrom used sol-gel spin coating, [19] to obtain competitive properties for multilayered coatings with nitrogen annealing of Al_2O_3: Ni multilayered coating absorbing 97% of the incoming solar energy and with a thermal emissivity lower than 5%. In year 2008 and 2010 [20,21] highly selective coating based on Cu-Mn-Si-O oxides were obtained showing excellent optical performance with absorptivity of 0.95 and emissivity of 0.035 on Aluminum substrates. Lately in 2013 [8] the optimization of the sol gel process of $CoCuMnO_x$ led to a solar absorption of 0.95 and emission of 0.11 on stainless steel substrates. The surface preparation was just cleaning the surface with ethanol and water. Recently in (2014) [1] excellent selective optical properties were obtained (0.9/0.011) for copper and 0.9/0.029 for Aluminum using the $CoCuMnO_x$ as a selective coat.

This paper aims to coat stainless steel substrate with CuCoMnOx coating using dip coat sol gel technique. The effect of process parameters including different concentrations of the solution, different number of dips and different withdrawal rates on the optical properties and coat characteristics are studied.

2. Experimental Work:

Solution preparation:

Precursor solution was prepared with Mn (II) acetate, Cu (II) nitrate and Co (II) acetate. The molar ratio of Co:Cu:Mn was 1:3:3. First Cu (II) nitrate was dissolved in ethylene glycol (50 ml) at room temperature and then Mn (II) acetate was dissolved in absolute ethanol (60 ml) at room temperature. The two solutions were then mixed together. This was followed by additions of Co (II) acetate and ethyl acetoacetate (EAA) (12 ml). The thermal hydrolysis was performed at 60-70°C until the volume of the solution decreased to half of its initial value. The precursor was added with different concentration in molar weight (divided by 50, 60 and 70) to a fixed amount of solvent in order to study the effect of solution concentration.

Substrate preparation:

Stainless steel:

The substrate samples were cut from stainless steel sheet to dimensions of 100x20x0.5 mm. The samples were treated by sandblasting machine GREAT SHOT Abrasive blasting Equipment using sand with grain size 410 mesh and a pressure of 3~5 bar. The samples were cleaned in acetone using ultrasonic vibrations. The samples were then rinsed by distilled water and dried.

Coating:

For the coating process, the samples were dipped in the sol and withdrawn at a predetermined rate. The solution concentration was varied by dividing molar weight by /50, 60 and 70 and adding it to a fixed amount of solvent. Different withdrawal rates (0.5, 1 and 2 cm /min) were applied. The number of dips was 1, 2 and 3 dips. For each condition three samples were prepared and studied. The samples were then heat treated at 450 ˚ C for 30 minutes based on previous work as in reference [1] and [13]. For each condition three samples were prepared and studied.

Characterization techniques:

Some of the physical attributes, thickness and surface roughness of the coatings were determined using Scanning microscope (Jeol JSM-5410) and Qualitest (TR100/TR101) respectively. At least 5 points were measured on each sample and the average used for the data interpretation. For thickness measurements the samples were mounted and the cross section was investigated as in figure 1.

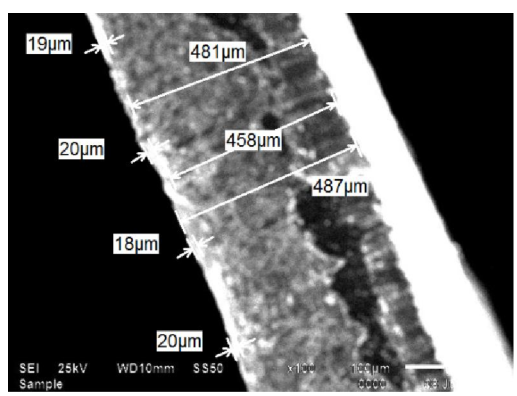

Fig. 1: Thickness of the samples measured by the SEM microscope

Testing:

The absorptivity of the coat was determined using the UV spectrometer PG instruments 90 +with integrating sphere. The average reflectance (R) was evaluated for wavelength between 230 nm and 700 nm. The absorptivity (α) was obtained using the equation: α

+ R + t = 1; Where α is the absorptivity, r is the reflectance and t is the transmittance of the surface. Since t=0 for opaque surfaces, then α = 1 – R.

For the emissivity measurements, the IR JASCO spectrometer was used. The emissivity (Ɛ) by (1-reflectance) was calculated from the reflectance measurements in the IR range (from 3000 to 25000 nm). The optical properties were measured on three positions on each sample and the average values were used for the data interpretation. Using the ratio of the absorptivity and emissivity (α / Ɛ) it was possible to estimate the selectivity.

3. Results and discussion:

Effect of different solution concentration on optical properties.

The stainless steel substrates were used to study the effect of the different solution concentration on the coat properties at 1 cm/min withdrawal speed and only 1 dip in the sol-gel. In general, visual observation revealed poor coat adhesion which was improved by sandblasting the surface which increased the roughness resulting in an adequate coat adhesion to the substrate. The reflectance curves for absorptivity and emissivity for the stainless steel samples prepared by dipping in solutions obtained for precursor molar ratios 50, 60, and 70 are shown in Figure 2 and 3. The average absorptivity and emissivity are listed in Table 1. The results indicate that the maximum absorptivity is obtained for the solutions with molar ratio /60 where the absorptivity reached 0.91 ± 0.01 and the lowest emissivity 0.09 ± 0.001 resulting in a best selectivity of 10.11, which is considered a good value. Therefore, the molar ratio /60 was selected for the rest of the work.

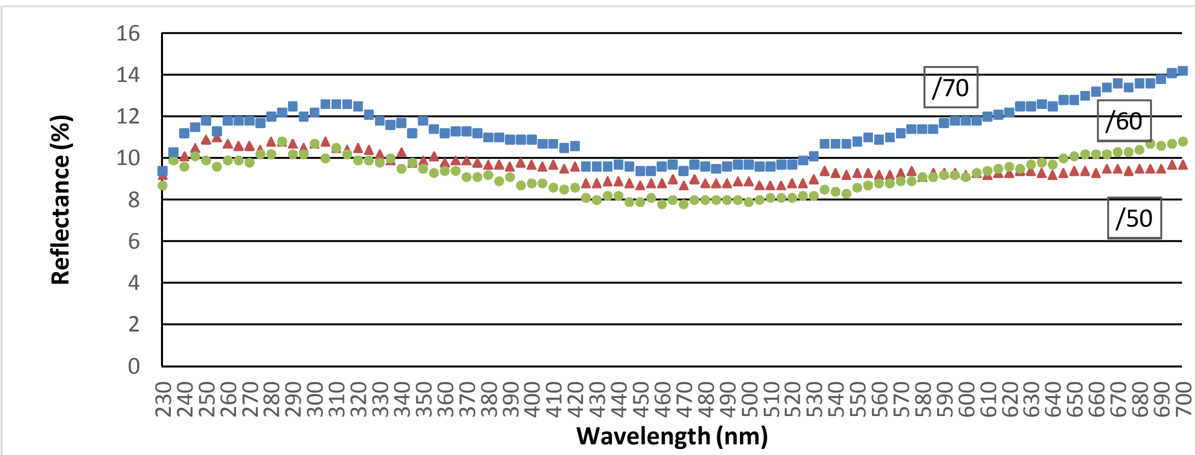

Fig. 2: Reflectance measurements in UV range for measuring absorptivity of Stainless steel samples after the dipping-heat treatment cycle, in three different solutions: with molar ratio /50 (molar 50), /60 (molar 60) and /70 (molar 70).

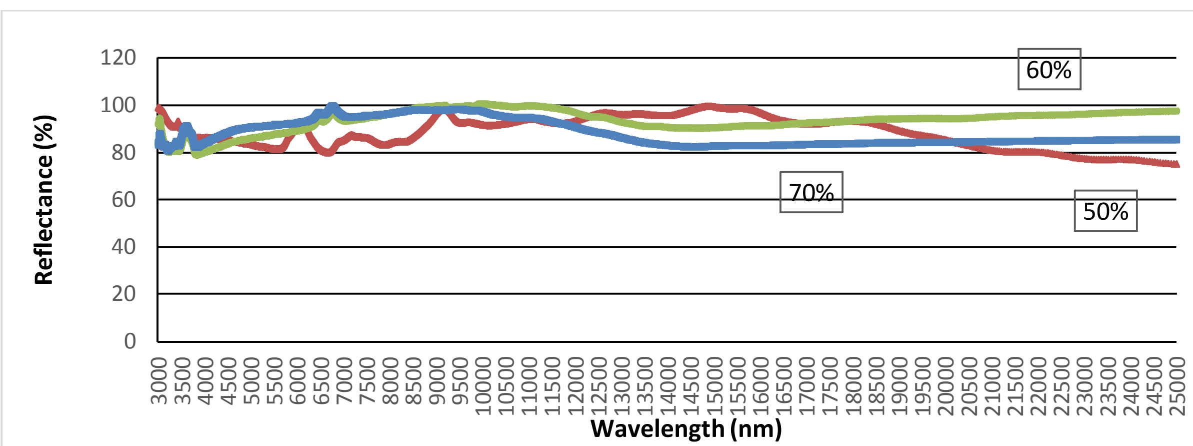

Fig. 3: Reflectance measurements in IR range for measuring emissivity of Stainless steel samples after the dipping-heat treatment cycle, in three different solutions with molar ratio of chemicals /50 (molar 50), /60 (molar 60) and /70 (molar 70).

Table 1: Effect of different molar ratio of the solution on coat characteristics of coated stainless steel samples.

Molar ratio/ x	Thickness (µm) (average)	Roughness Ra (µm) (average)	Absorptivity (α) (average)	Emissivity (Ɛ) (average)	Selectivity (α/ Ɛ)
Molar ratio/ 50	19.33	1.14	0.90	0.11	8.18
Molar ratio/ 60	17.3	1.37	0.91	0.09	10.11
Molar ratio/ 70	15.5	0.9	0.88	0.10	8.8

The thickness of the coatings is also given in Table 1 where it can be observed that the thickness of the coatings decreases with decreasing concentration of the precursors in the solution. This is due to the decrease in viscosity of the solution. Table 1 indicates that the highest roughness 1.37 µm was obtained with molar ratio /60 and this corresponds to the highest absorptivity 0.91 compared to the other molar ratios. It is also noticed from the results in table 1 that the absorptivity increases with increase in surface roughness. As the roughness of the surface increases the pits and groves of the surface increase that facilitates trapping the radiation as shown in Fig. 4 and increases the absorptivity as well. This is in agreement with previous work [12] where the higher the absorptivity was related to higher roughness.

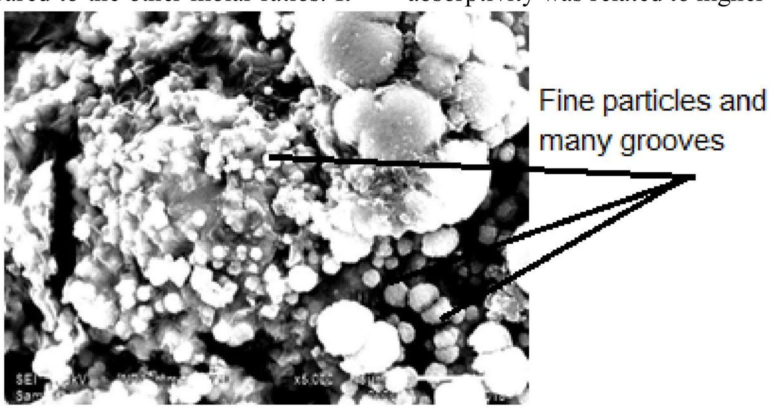

Fig. 4: SEM of Stainless steel sample coated with $CuCoMnO_x$ with highest selectivity 10.11, absorptivity 0.91 and emissivity 0.09. Preparation conditions: molar ratio /60 and withdrawal rate is 1 cm/min and only one dip in the coat. Magnification X 5000

Effect of withdrawal rate on optical properties.

Different withdrawal rates were used in coating stainless steel substrates followed by heat treatment. Figure 5 indicates that with increasing the withdrawal rate, the thickness of the coating increased. This is in agreement with previous work as it has been reported in 2013 and 2014 [1] and [8] that the deposited film thickness on the substrates by sol gel technique depends on the liquid viscosity, the substrate speed, the density of the liquid and the liquid-vapor surface tension based on Landau and Levich law and that the thickness is proportional to (the withdrawal rate) $^{2/3}$.

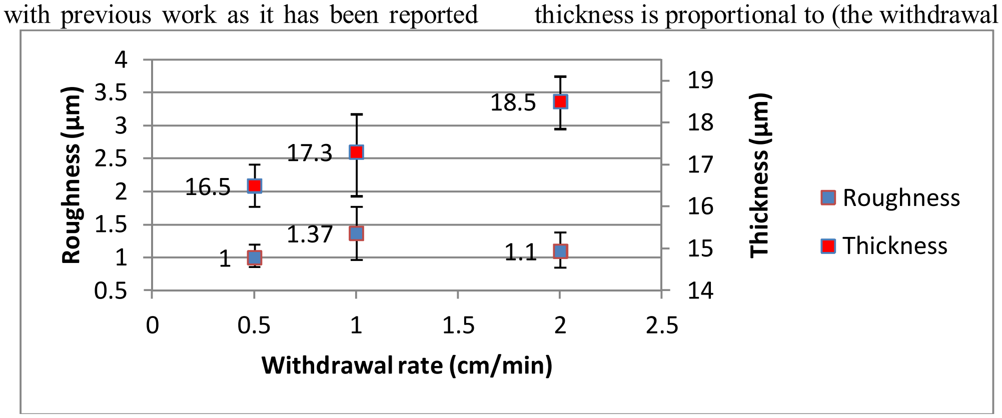

Fig. 5: Effect of withdrawal rate on the thickness and roughness of the coated samples.

By measuring the surface roughness of the substrates after coating (average of 5 readings) it was found that it falls in the range of 1 µm to 1.37 µm shown in Fig. 5. Considering the roughness of the surface before coating (average 5 readings) it was found to fall between 1.33 µm and 1.7 µm with an average of 1.5 µm indicating that after coating, the roughness decreased to reach from 1 µm to 1.37 µm due to smoothening of the surface. It can be noticed from the results that the withdrawal rate has no sensible effect on the surface roughness.

Previous work [1] reported that with increasing the withdrawal rate from 1 to 7cm/min using aluminum substrate, the thickness of the coat increased from 11.6µm to 14.8 µm in agreement with the present work. On the other hand it was found that the roughness decreased from 1.3 µm to 0.51µ m, which is different from the present findings, however the initial substrate roughness was not mentioned in the previous work. Regarding the roughness, it is also reasonable that the higher the roughness of the substrate, the higher the roughness of the deposited layer especially when only a few microns are deposited. It could be reasonable to say that as the thickness increases the roughness decreases too.

Effect of number of dips on optical properties.

Keeping the withdrawal rate 1 cm/min, multiple dipping also has a great effect on the absorptivity and emissivity.

Table 2. Effect of withdrawal rate on coat thickness, roughness and optical properties

Withdrawal rate (cm/min)	Thickness (µm) (average)	Roughness Ra (µm) (average)	Absorptivity (α) (average)	Emissivity (ϵ) (average)	Selectivity (α/ϵ)
0.5	16.5	1.0	0.88	0.11?	8
1	17.3	1.37	0.91	0.09	10.1
2	18.5	1.1	0.91	0.13	7

Table 3. Effect of number of dips on the coat thickness, roughness and optical properties

Number of dips	Thickness (µm) (average)	Roughness (µm) (average)	Absorptivity (α) average)	Emissivity (Ɛ) (average)	Selectivity (α/ Ɛ)
1	17.3	1.37	0.91	0.09	10.11
2	19.4	1.1	0.89	0.11	8.9
3	20.6	0.73	0.87	0.13	6.69

Table 3 and Fig.6 show that with increasing the number of dips the coat thickness obviously increases and the surface roughness decreases due to smoothening of the irregularities of the surface with more deposits and filling all the pits. This is reflected on the decrease in absorptivity as discussed previously. As the emissivity also increased with more coat layers, the selectivity decreased. The best selectivity is obtained with one dip that having a molar ratio/60 and withdrawal rate 1 cm /min.

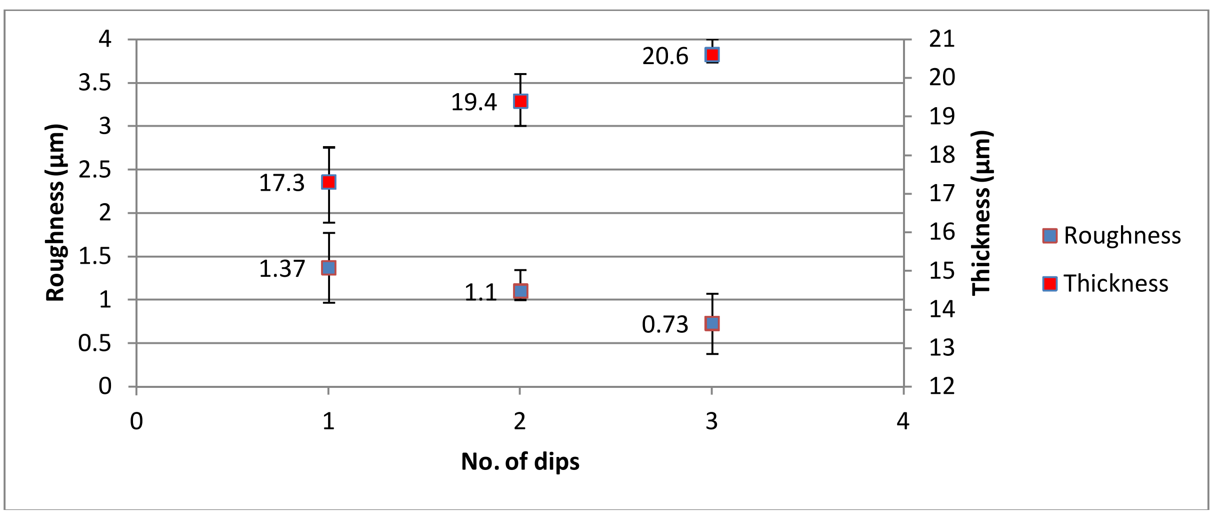

Figure 6: Thickness and roughness versus number of dips relation for stainless steel samples coated

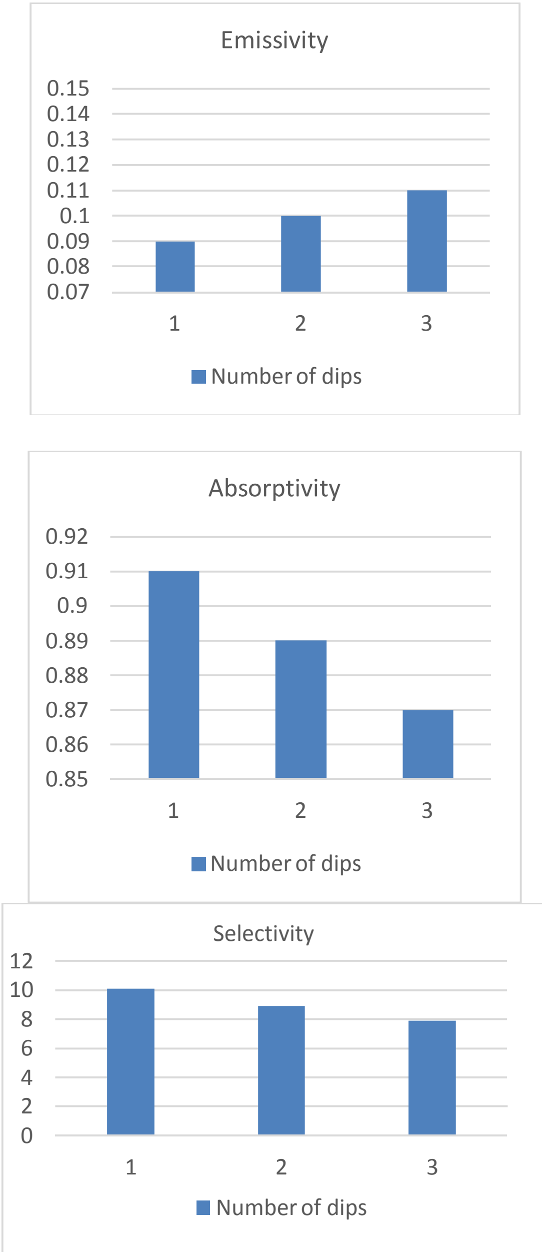

Fig.7: Effect of number of dips on optical properties

Figure 7 shows the more the number of dips, the lower absorptivity and higher emissivity which resulted in lower selectivity. As we can see there is a trend that by increasing the layers of coating, the selectivity decreases in return. To sum up; the solution concentration, the withdrawal rate, and number of dips affected the coat thickness and roughness. All the previous results were plotted together to study the effect of coat thickness and roughness on the optical properties; absorptivity, emissivity and selectivity. The results are shown in Fig. 8.

It is perceived that the roughness plays an important role on the absorptivity of the coated stainless steel substrates; whenever it increased, the absorptivity increased. This leads to a high selectivity. This is in agreement of reference [1]. As for the emissivity, a slight increase with thickness is noticed from Fig. 8 c. From Fig. 8 e and f, it could be observed that there is a trend to increase the selectivity with decrease in thickness and increase in roughness.

It is known that stainless steel is not as a good conductor as the aluminum and copper; however, it is proven in this paper that it can be a good selective coat and has better selectivity.

In a recent report using aluminum substrate [1], and depositing $CuCoMnO_x$ by sol-gel with molar ratio /50, 1 cm/min withdrawal rate , only one dip and surface was treated chemically; the results were α/ Ɛ =0.9/0.12=7.5 .Nonetheless, copper gave α/ Ɛ 0.91/0.2 =4.55 using the same deposited coat and conditions. In another report [2], it is indicated that using stainless steel with the same sol gel coat without any surface treatment except cleaning with ethanol and water , constant withdrawal rate and one dip only ; resulted in α/ Ɛ =0.86/0.11 =7.81. In the present work α/ Ɛ = 0.9/0.11 =8.18 using sol-gel with molar ratio /50 which indicate that higher selectivity can be obtained due to sandblasting process since it increased the surface roughness from 0.02 to 1.50 µm.

To find the most promising conditions, the molar ratios / 60, withdrawal rate 1 cm / min and only a single layer of the coat, resulted in the highest selectivity among all the samples prepared with different conditions where α/ Ɛ =0.91/ 0.09=10.1 was obtained as shown in Table 1, indicating that the concentration of the solution has also a great effect on the optical properties in addition to the withdrawal rate and the number of layers.

Conclusions

1. Applying $CuCoMnO_x$ coat on stainless steel using sol gel dipping technique was successful specially after the increasing the surface roughness by sandblasting. The best optical properties which is maximum absorptivity and minimum emissivity are obtained by using a precursor molar ration /60 and a withdrawal rate of 1 cm/ min and only 1 dip followed by heat treatment at 450 °C for 30 minutes where α/Ɛ = 0.91/0.09=10.11which are good results.
2. By increasing the surface roughness of the stainless steel the absorptivity increased while the emissivity is less affected by the roughness.
3. As the coat thickness increases the selectivity decreases due to the increase in emissivity.

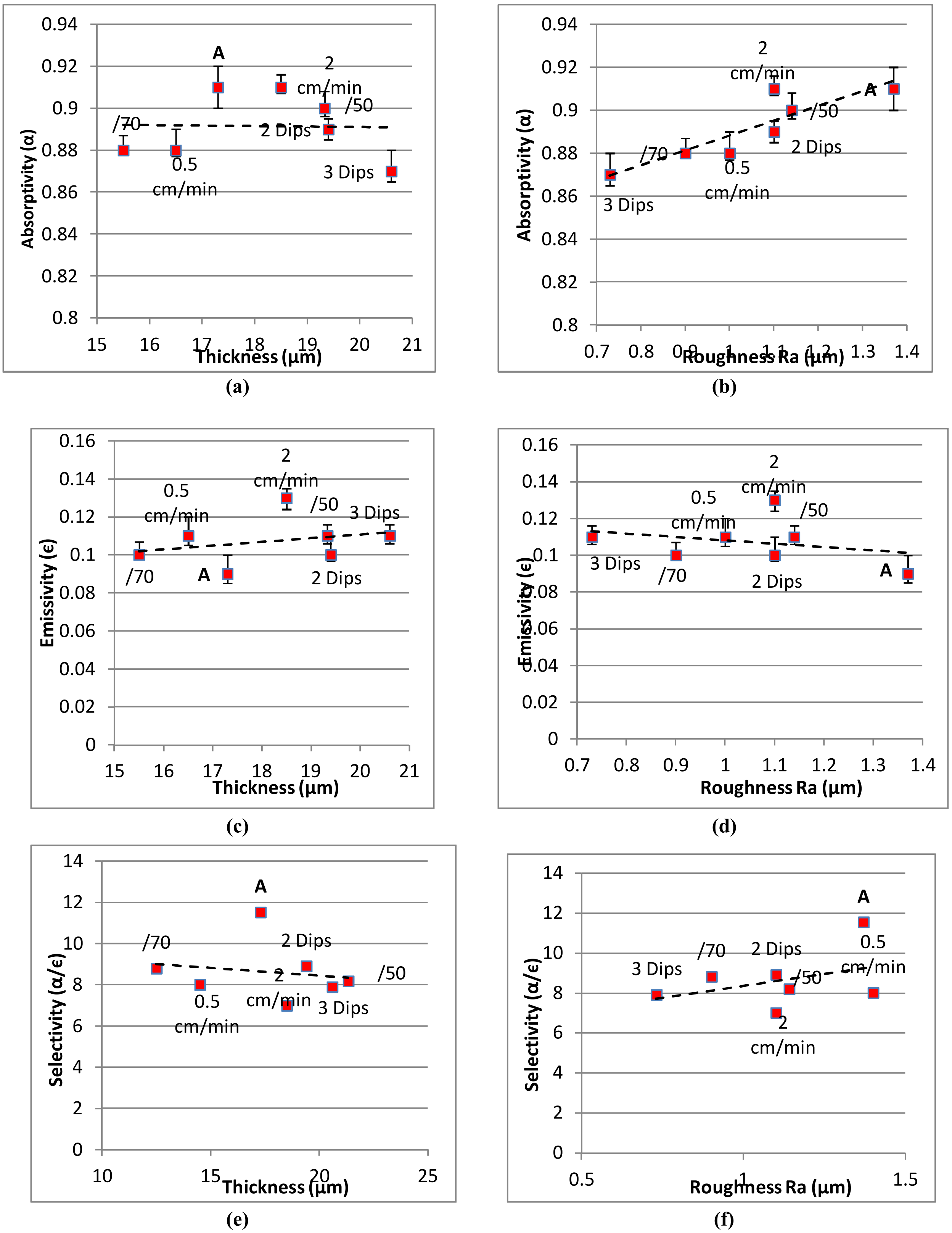

Fig. 8: Effect of thickness and roughness on (a), (b) absorptivity, (c), (d) emissivity, (e), (f) Selectivity, where A is the best selectivity of molar ratio /60 1 cm / min and 1 dip.

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