

## Research Journal of Pharmaceutical, Biological and Chemical Sciences

### Characterization of Black Ni and Sn as Optically Selective Absorber Coatings in Thermal Solar Collectors Mainly (Part I).

**MF Shaffei, N Khattab, AM Awad, and HS Hussein\***

Chemical Engineering and Pilot Plant Department, National Research Centre, Dokki, Cairo, Egypt.

#### ABSTRACT

This investigation has been directed towards the improvement of the light absorption efficiency of black coated solar panels, infrared instruments and detectors. Tin and nickel based coatings were the most commercially popular. The technique of electrolytic coloring of anodized aluminum has been adapted. Residence time for anodizing was the main process variable experimented from 10 to 60 minute. Comparison of the instrumental analysis measurements for optical, environmental aspects protection, and thickness proved that tin based coatings characteristics show more enhancements. Optimum anodization residence time for tin and nickel found to be 45 and 30 minutes respectively.

**Keywords:** solar energy, collectors, solar panels, heating, electrolytic coloring

*\*Corresponding author*

## INTRODUCTION

Black Solar energy collectors are the main component of the solar water heater system. Spectrally selective, anodic coating and electrolytically colored aluminum surface is promised to absorb solar radiation in the visible region and near infrared, where heat gain is transferred to water flow and stored in isolated tank [1, 2].

Using tin and nickel particles, in the range of nano and micron size, are widely spread for filling the porous anodic coatings. This approach was undertaken to color aluminum or other metal surface with black tones of deeper degree [3, 4]. It is considered a suitable substitute for the conventional organic black painting method. Many previous investigations, for coloration with the forementioned elements have been conducted [5, 6].

However, the difference of characteristics between them has not detected. In this research, the coloration in two stages was chosen. In the first one, a porous thin aluminum oxide layer was formed [7-10]. The second one involves the filling of that formed pores with either of those metallic species by the influence of an electromotive force [11-15]. This work is divided into two parts. Varying the anodizing time before coloring is the role of the first part, Moreover, instrumental analysis for characteristic evaluation and comparison in the second part.

## EXPERIMENTAL

### Materials

Sulfuric acid (98%) was diluted to 170 g/l and used as the electrolytic solution in the anodizing step. In the coloring bath 25 g/l tin (II) sulfate was used for tin coloring and nickel (II) sulfate, magnesium sulfate and boric acid were used for nickel coloring. In both coloring bathes the solution was acidified by addition of a few drops of diluted sulfuric acid until the optimum pH.

### Apparatus components

- A magnetic stirrer (PMC-BARNSTEAD/THERMOLYNE-USA) was used for continuous agitation of the solution in the anodizing and coloring steps.
- GW Lab DC Power Supply GPR-3030 was used as the source of direct electric current between both electrodes the working electrode (aluminum) and counter electrode (lead) in the anodization cell.
- Main AC electric current was used of 220 volt potential and adjusted to the experimental value by an electric transformer in the coloring cell.
- Spectrophotometer V-570 UV/VIS/NIR serial number CO296357 was used for the measurements of the reflection. SEM analysis was measured by using JEOL, JXA-840 A: ELECTRON PROB. Polarization resistance and corrosion rate was measured by using potentiostate Metrohm Autolab, NOVA 1.8 Model AUT 85335 FRA 32M.

**Procedures**

- Primary treatments: The aluminum sheet (Al 98.5%, Si 1.5%) was cut to the required dimensions 7 x 2.5 cm, and degreased by acetone and then distilled water. It was etched in a solution of NaOH (12%) for 10 min, then rinsed by tap water and distilled water. The sample was then immersed in a solution of nitric acid 20% for 30 s , then rinsed by distilled water for 3 min.
- Anodizing Step: The sample was taken directly to the anodizing bath containing sulfuric acid, and the temperature was controlled at  $18 \pm 2$  °C. Stirring of the solution was kept continuous for 10 to 60 min. then the anodized sample was rinsed well by distilled water for 3 min.
- Coloring step: the anodized sample was transferred directly to the coloring bath containing tin or nickel ions with gently stirring at room temperature for 10 min. then the colored sample was taken and rinsed with distilled water .Assessment of the colored surface by measuring reflection of the surface, corrosion resistance and morphology of the surface by SEM. The following flow chart shows the whole steps of the experiments Fig.1.

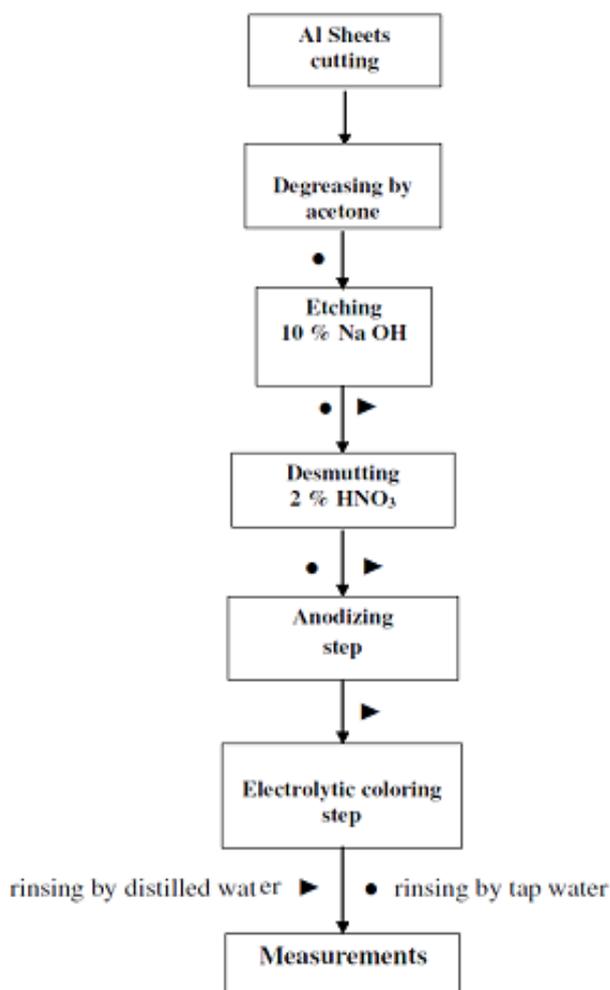


Fig.1 Flow chart of the steps of the electrolytic coloring process.

## RESULTS AND DISCUSSION

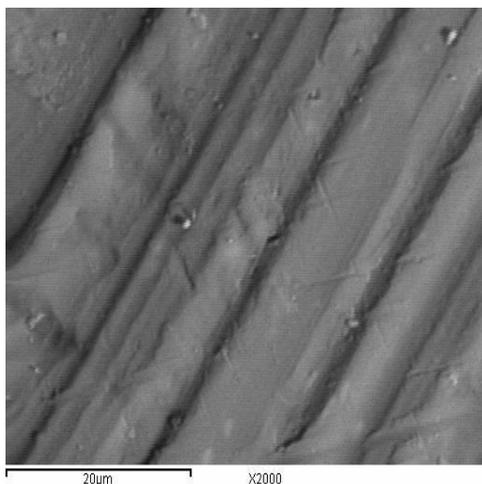
### Scanning Electron Microscope Analysis (SEM)

The image of aluminum surface substrate Fig.2a revealed highly rough and different lines due to mechanical machining and rolling of the surface. While, after anodic oxidation (anodization) of the surface, the morphology of the surface was varied, as shown in image Fig. 2b, it depicts the presence of dense porous film and high number of columns with open pores over the surface.

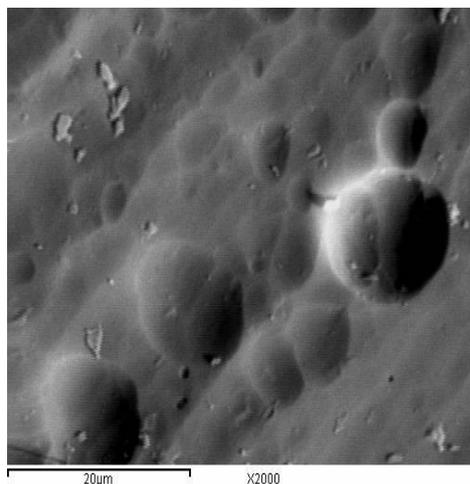
The presence of huge number of empty pores and hexagonal open holes of columns are obviously appeared over the surface, where metal ions are deposited and fill all empty pores.

The number of pores was more increased after the electrolytic coloring, where the anodic oxidation was continued by the anodic cycle of alternating current applied (AC). However, at cathodic cycle of AC current, open and empty columns were totally filled with Sn as shown in Fig.2c and filled with Ni as shown in Fig.2d by electro-deposition, imparting a uniform black color over the surface. Both amounts  $\text{Sn}^{2+}$  and  $\text{Ni}^{2+}$  were electrolytically deposited and neutralized into columns until filling of the porous film according to the conditions of anodization and coloring.

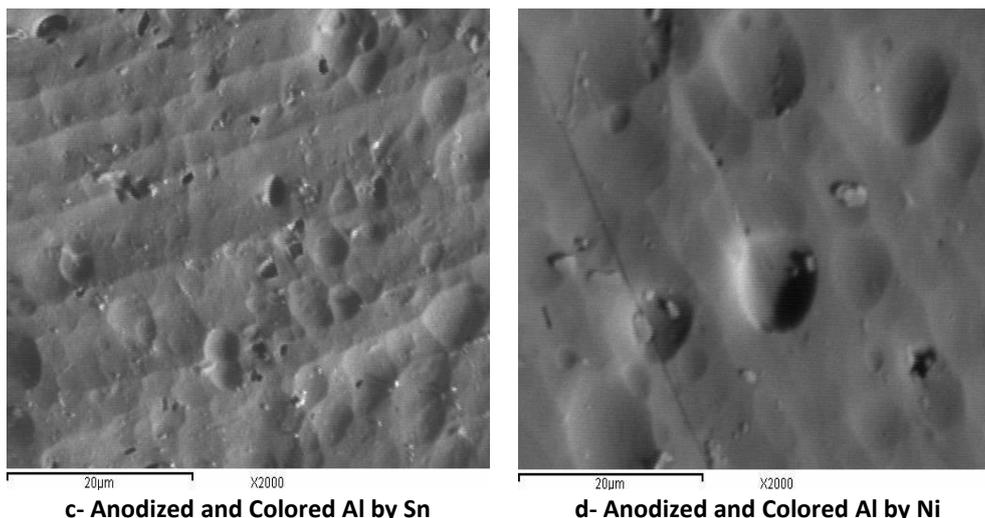
SEM image of the anodized aluminum sample colored by Sn showed a dense tin filling the columns of anodic film more than the amount of nickel filling the porous film. This may be attributed to the difference of atomic radius of both Ni 149 pm and Sn 145 pm.



**a- Aluminum substrate surface**



**b- Anodized aluminum surface**

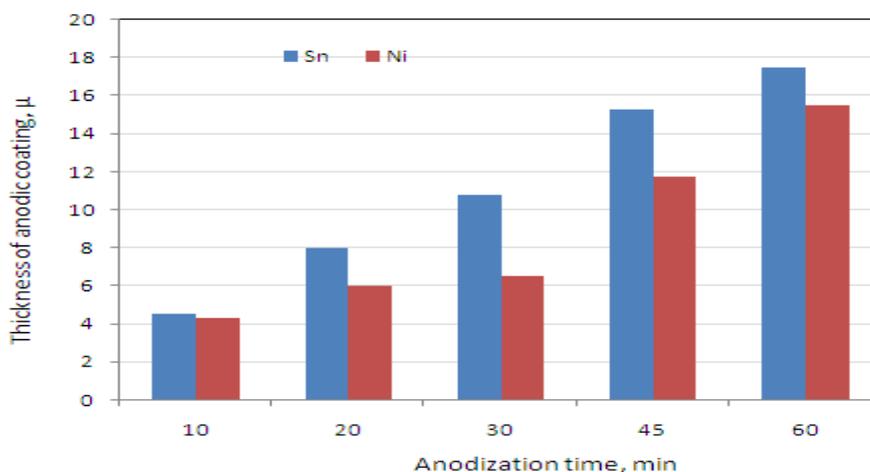


**Fig.2 SEM images and morphology details of the surface of different samples**  
**a) Substrate, b) anodized, c) anodized and colored by Sn and**  
**d) anodized and colored by Ni**

During the investigation of the morphological characteristics of the sample after anodization step, pores diameter was measured overall the surface. The results revealed that the pore size diameter varied between 200 nm and 450 nm according to the conditions applied of anodic oxidation. This scale is appropriate for the deposition and penetration of some types of metal ions such as Sn of atomic radius 145 pm and Ni of atomic radius 149 pm to fill and encapsulated into the empty huge columns number of anodic film.

**Measurements of colored coating thickness**

The thickness of anodic coating was increased as an adequate time of anodic oxidation was used, where thin non porous barrier layer and thick porous layer are built-up on the surface of Al substrate. As shown in Fig.3, at low anodization time 10 min., both tin and nickel colored samples showed thin oxide layer 4.5 and 4.25 µ, respectively. Hence, low color uniformity was formed over the surface due to low columns height of anodic layer.



**Fig.3 Measured thickness of anodic coating (µ) of both tin and nickel colored samples at constant coloring time 5 min and different anodization time.**

The thickness of porous film was gradually increased with more of anodization time, where the diameter was widened and the column height raised. So, thickness of Sn and Ni colored samples was increased to 17.5 and 15.5  $\mu$ , respectively corresponding to 60 min. anodizing time. The anodic oxide film thickness at 30 min. residence time was about 10.4  $\mu$ , 6.2  $\mu$  for tin coating and nickel coating respectively. Thickness reduction occurs during the coloring step.

### Optical properties

Specular reflection percent of the black colored samples have been represented in Figs 4 to 7. Results in Figs. 4 and 5 show a comparison between the absorption efficiency trend for the aluminum and anodized aluminum from a side, and the group of colored samples in the other, along the ultraviolet and visible zones of light spectra. Reflection percent for aluminum surface before processing is the highest as a result of its luster. When tin was anodized the reflection reduces markedly and the curve takes a steady state. This behavior may be due to the light scattering at the outline surface of the opaque pores.

Most anodized samples colored with tin show a linear relationship for the reflection percent versus light wave length. However, the sample, with residence anodization time 10 minute, has some oscillatory from. Anodized samples colored with nickel behave mostly in an oscillatory form as indicated in Fig. 6, with deeper peaks for exception the sample that anodized at 30 min. has a linear relation.

Figs. 6 and 7 involve the scaling up of the reflection results axis in addition to the infrared zone of light. For tin colored samples in Fig. 6, an increase in the absorption efficiency is observed proportional to the anodization time. However for 45 and 60 time the efficiency is identical and time 45 can be chosen as economically wise reason. For nickel colored samples, in Fig. 7, continuous increase is found with time for the absorption efficiency untill 30 minutes anodizing time. There after a marked reduction in absorption efficiency occurs. Moreover the relation is oscillatory for the various conditions. For finding a qualitative measure for their comparison, the numerical results are presented in Table 1.

**Table 1 Reflection percent (R%) for nickel and tin colored samples anodized at 30 and 45 min. respectively at wave length,  $\lambda$  , range 200-2500 nm.**

$\lambda$ ,nm	200	500	1000	1500	2000	2500
Nickel , R%	0.360	0.465	1.334	3.539	3.392	6.403
Tin, R%	0.456	0.504	0.658	0.927	1.497	1.668

Reflection percent, from Table 1, indicates that it is identical for the two samples in the narrow ultraviolet zone. Hence, it becomes two fold for nickel in the visible region. Then, it reaches about three to four fold in the near infrared zone. This means that, light absorption for tin shows much enhancement in a wider region. Consequently, tin colored

coatings anodized at 45 min. can be recommended strongly for higher thermal efficiency solar collectors and other devices as infrared instruments and detectors.

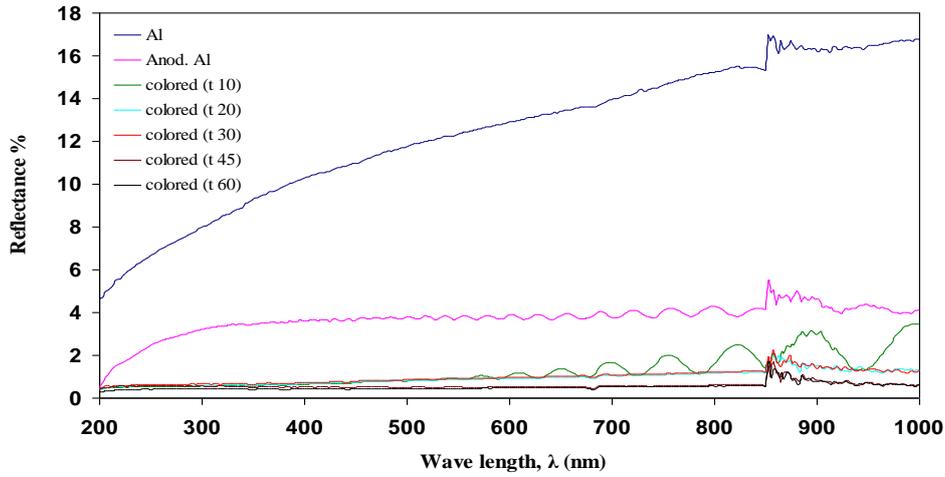


Fig.4 Reflectance spectra for various electrolytically colored Al samples by Sn deposition at different anodizing time 10-60 min.

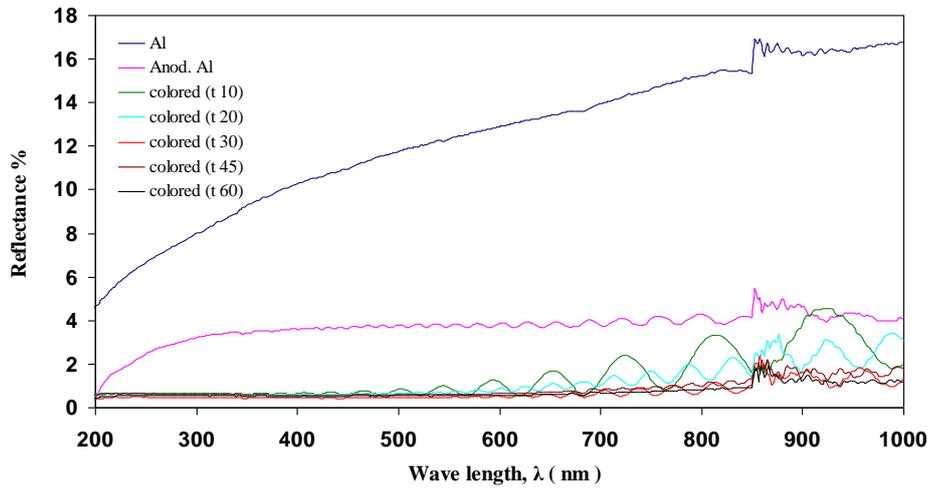


Fig.5 Reflectance spectra for various electrolytically colored Al samples by Ni deposition at different anodizing time 10-60 min.

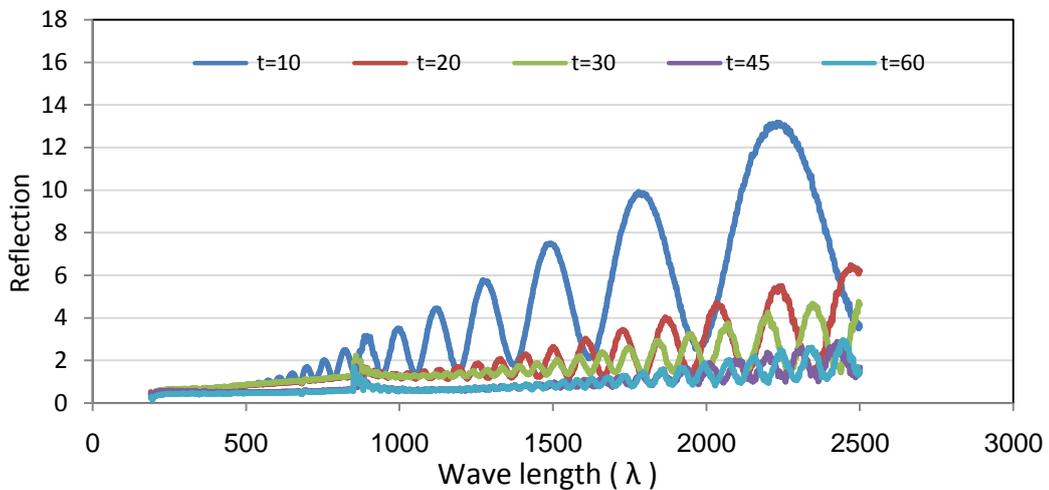


Fig.6 Reflection diagram of tin colored Anodized aluminum.

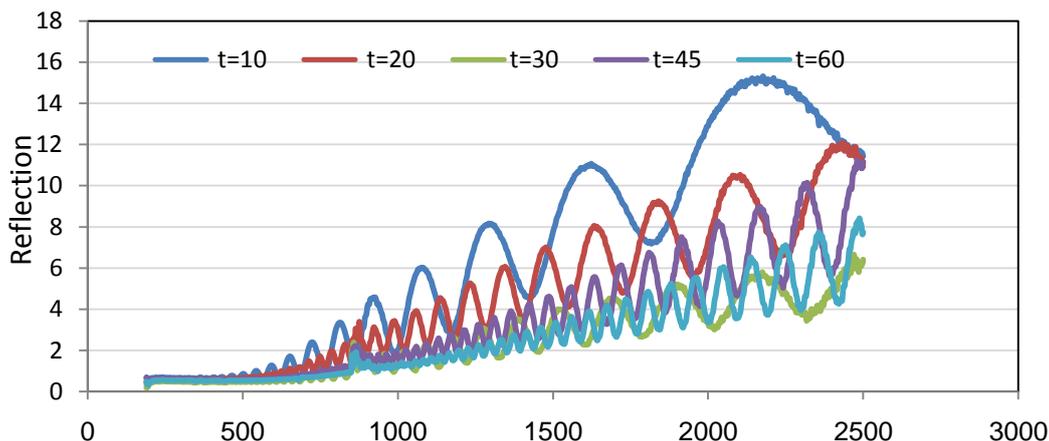


Fig.7 Reflection diagram of nickel colored anodized aluminum.

### Corrosion characteristics

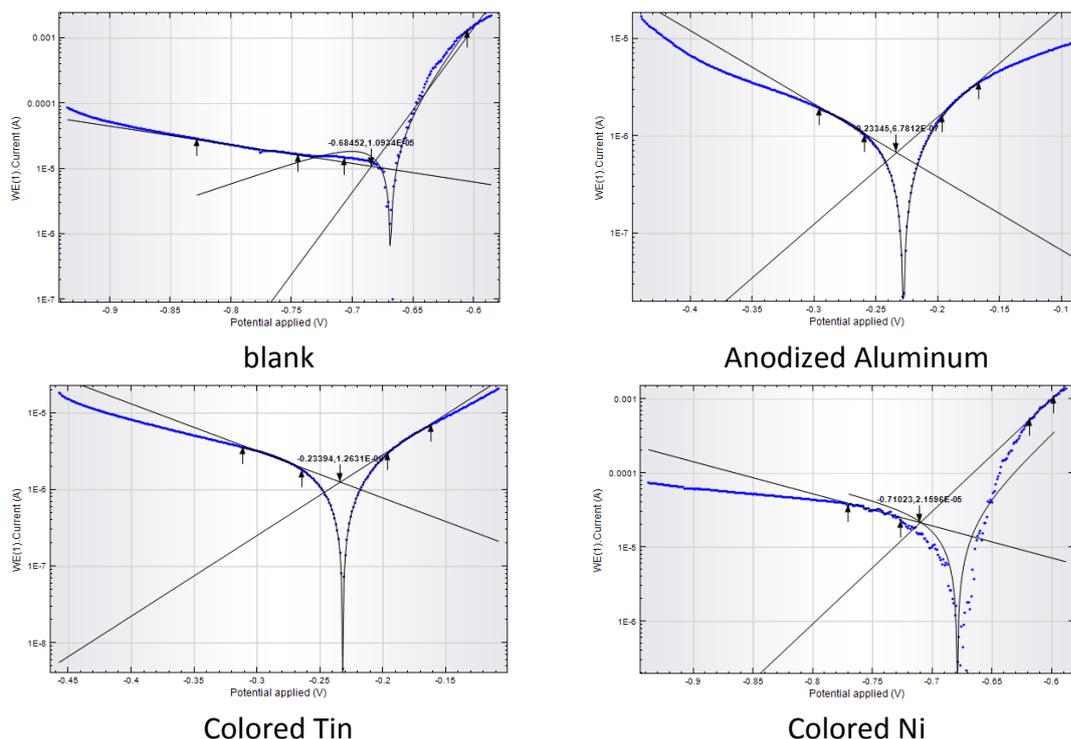
The surface is highly influenced by the nature of coating and metal deposition. Corrosion resistance and corrosion rate were measured. As shown in Table.2, the results revealed that the corrosion resistance of aluminum substrate showed low corrosion resistance 0.5953 KΩ and high corrosion rate 0.4284 mm/y at corrosion current 130.86 μA.

The corrosion resistance was improved after anodization to 24.216 Ω at corrosion current 7.494 μA, where a protective passive layer of porous film was build over the surface. So, the corrosion rate was sharply reduced to 0.0817 mm/y.

Table 2 Corrosion characteristics of the surface before and after anodization and coloring

Item	Corrosion Rate , mm/y	Corrosion Resistance , KΩ	Corrosion current , μA
Aluminum	0.4284	0.5953	130.86
Anodized Aluminum	0.0817	24.216	7.494
Coloring by Tin	0.1593	11.190	14.607
Coloring by Nickel	0.2354	1.031	21.596

After electrolytic deposition of Sn and Ni ions then neutralized into the porous film, the surface revealed lower corrosion resistance than the anodized sample but remain higher than the corrosion resistance of the substrate, where the corrosion resistance was slightly decreased to 11.190 and 1.031 KΩ at corrosion current 14.607 and 21.596 μA for both samples colored by tin and nickel, respectively. Moreover, the measured corrosion rate of samples colored by Sn (0.1593 mm/y) and Ni (0.2354 mm/y) were higher than the anodized sample. The results are summarized in Table 2 and polarization curves of four samples are shown in Fig. 8. These results are matched with the results of Shih and Huang [10] that the resistance of anodized aluminum is higher than the colored sample when coloring temperature >20 °C.



**Fig.8 Polarization curve of different samples blank, Anodized , Colored by Sn and colored by Ni in constant concentration 0.5 M NaCl**

The sample colored by Ni revealed a corrosion resistance 1.031 KΩ lower than the sample colored by Sn 11.190 KΩ, this result can be attributed to the difference in electrode potential and galvanic corrosion of tin = -0.14 V and nickel = -0.24 V. This indicates that Ni colored sample is rapidly subjected to corrosion more than Sn colored sample.

The performance of electrolytic coloring was highly influenced by the anodizing conditions, the duration time govern the thickness and porosity of sensitive anodic film. The type of metal deposited was highly influenced the uniformity of black color and hence, the characteristics of selective coating can be achieved by high absorbitivity and low emissivity coefficients. This technique revealed a corrosion resistance due to passivation.

### CONCLUSION

The study revealed that the anodization time is essential factor for producing a uniform and highly absorbed black coating of aluminum surface. Anodization time 10 and 20 min was insufficient and showed thickness 4 and 6 μ in case of Ni coloring and 4.2 and 8 μ in case of Sn coloring respectively. While, the thickness was increased to 6.2 μ for Ni coloring and 10.4 μ for Sn coloring by elongation of time to 30 min. More increase to 15.4 μ for Ni coloring and 17.6 μ for Sn coloring was achieved at 60 min. the results of thickness reflected the dense of metal deposition, where 1.7 and 2.9 mg/ cm<sup>2</sup> of Ni were filled the micro tubes of anodic film at anodization time 10 and 60 min, respectively.

Optical measurements proved that tin based coatings have improved absorption in the visible range. Moreover, they are promising for infrared instruments and detectors for their reduced reflection values in the near infrared region. Referring to their corrosion resistance, there is marked improvement. However, the anodic coating acquires higher resistance for its passive nature. Objects using tin coating can be used in a variety of applications where infrared absorption, environmental or spectral reflectance are important. Some of these applications include radiometers and solar panels.

#### REFERENCES

- [1] Ghasempour Z, Rozati SM, World Renewable Energy Congress , Solar thermal applications, 8-13 May, Linkoping Sweden, 2011.
- [2] Kil Dong Lee, Journal of the Korean Physical Society, Vol. 57, No. 1, July 2010; pp. 111-119
- [3] Granqvist C G, Materials Science for Solar Energy Conversion Systems (Pergamon Press, Oxford), 1991.
- [4] Niklasson G A and Granqvist CG, Materials Science for Solar Energy Conversion Systems, edited by Granqvist CG Pergamon Press, Oxford 1991, p. 70.
- [5] Tuquabo Tesfamichael, PhD, Characterization of Selective Solar Absorbers, the Faculty of science and Technology, Acta universitatis upsaliensis, Uppsala, 2000.
- [6] McCroskey DM, Abell GC, Chidester MH, The International Society for Optical Engineering (Ed.), vol. 4096, 2000 ; pp. 119–128.
- [7] Magdy A, Ibrahim M, J. Appl. Electrochem. 2006; 36:295–301.
- [8] Shrestha S, Shashkov P, Dunn BD, Microstructural and thermo-optical properties of black Keronite PEO coating on aluminium alloy AA7075 for spacecraft materials applications. In: Proceedings of ISMSE & ICPMSE, SP-616, ESA Publication Division, Collioure, France, 2006 pp. s1.5.1–9.
- [9] LeVesque R, Ho M, Vickers B, Babel H, Pard A, Black anodize as a thermal control coating for space station freedom. AIAA-92-2160-CP. AIAA Technical Papers (A92-31285 12- 23), Washington, USA, 1992 pp. 56–65.
- [10] Shih HH, Huang YC. J Mater Process Technol 2008; 12 : 119.
- [11] Saxena V, Uma Rani R, Sharma AK. Sur Coat Technol 2006; 201 : 855.
- [12] Shaffei MF, Abd El-Rehim SS, Shaaban NA, Hussein HS. Renew Energy 2001;23:489.
- [13] Liana Anicai. Corrosion Reviews 2007; 25(5-6):607- 620.
- [14] Cantu ML, Sabio AM, Brustenga A , Romero PG. Sol Energy Mater Sol Cell 2005; 87: 685.
- [15] Ibrahim MAM. J Appl Electrochem 2006;36:295.