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Research Article

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Characterization and comparison between porous anodized aluminum colored by nickel and tin deposition

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ABSTRACT

Anodic oxidation and electrolytic coloring of aluminum surface are continuously studied due to their versatile applications. In this work, aluminum surface was anodically anodized in H_2SO_4 for different time 10, 20, 30, 45 and 60 min. and colored by two types of metals Sn and Ni. Electrodeposition of Sn and Ni ions was carried out from sulphate salts based electrolyte using a cell of working electrode and stainless steel auxiliary electrode. The bath of Sn composed of $SnSO_4$, 5-sulfosalysilic acid, while the bath of Ni composed of $NiSO_4$, $MgSO_4$, H_3BO_3 and $MgCl_2$. Also, a co-deposition of both Sn and Ni was carried out at different ratios of electrodeposition time (t_{Sn}/t_{Ni}) 2/8, 3/7, 5/5, 7/3, and 8/2. XRD, EDX and atomic absorption analysis were used to reveal the composition of oxide layer, contents of deposited metals and metal density per surface area. Linear polarization was studied in 0.5 M HCl and Tafel plots were plotted. Optical characteristic of each surface was measured using spectrophotometer, where the absorbance of Sn colored surface was detected at 1.3 within the range of visible region.

Key words: Al surface, anodization, porous film, electrodeposition, metal content, absorbance,

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INTRODUCTION

Applications of electrodeposition of metal ions into nano porous anodized aluminum oxide (AAO) by either one step or two steps anodization are widely studied [1, 2]. The application fields of electrodeposited Sn-Ni alloys were paid attention due to their appearance and corrosion resistance; they are of great interest for the metal finishing industry [3]. Electronic industry also used electrodeposited Ni-Sn alloys for printed circuit boards as protective and etch-resistant coatings**.** Electrodeposited Ni-Sn alloys show properties, e.g. hardness, chemical and tarnish resistance that actually are better than features of pure nickel and tin.[4]. Nowadays, tin has become an interesting material for incorporation into a nickel matrix. In most of the previous studies, tin particles had an average grain size of 14-50 nm [5]. So, Sn-Ni alloys are used usually as corrosion protective [6, 7] and alternative to decorative chromium coatings [8], a partial substitute of gold in the printed circuit board manufacturing industry or as oil retaining surfaces in automotive industry [9]. Lastly, the alloys have found new application areas, especially as anode material in lithium ion batteries or cathode substrate for hydrogen evolution [10-12]. Electrodeposition of Ni-Sn alloys was firstly described over seventy five years ago [13] and the process was introduced to the industrial practice relatively fast. Initially, the alloys were obtained from alkaline cyanide–stannate baths, but then acidic fluoride–chloride electrolytes were patented and adopted successfully for the commercial plating [14]. Fluoride–chloride solutions are still predominantly used for electrodeposition of Ni–Sn alloys, since stable tin (II)-fluoride complexes are formed in such conditions [15]. However, hot fluoride baths are rather hard to operate due to corrosion problems caused by free hydrogen fluoride as well as the requirement to use separate nickel and tin anodes working at different current

densities [16]. Shaffei *et al.* studied the electrodeposition of Ni and Sn in separately baths [17]. They concluded that tin coating showed an enhancement in light absorption and improvement of corrosion resistance.
This work aimed to prepare Ni-Sn coating by low cost method and examine the composition, structure and morphology of coating to be applied in solar purposes.

In the present study the electrodeposition of Sn and Ni was carried out and the surface was investigated to reveal the disparity of both metals. X-ray diffraction was used to reveal the qualitative screening and examine the atomic structure into the porous film. In addition, EDX measurement was used for the quantitative analysis of deposited metals. Corrosion resistance of each sample anodically coated at different time and electrolytically colored by Sn or Ni was measured using linear polarization. Optical characterization of black surfaces was investigated and the surface absorbance was measured after deposition of both Sn and Ni.

EXPERIMENTAL SECTION

2.1 Materials

Samples of dimensions 10 x 3 cm were cut from aluminum sheet 99.5 %. Lead plate was used as counter electrode in the anodization process. For pretreatment of aluminum surface, acetone, sodium hydroxide and nitric acid were used in appropriate concentrations. Sulfuric acid 170 g/l was prepared and used as the electrolyte for anodic oxidation.

2.2 Set-up, Procedures and Measurements

Cooling system was used for controlling temperature of electrolytic solution during anodization. The system consists of thermostat, compressor and copper serpentine for Freon circulation immersed in water bath. DC Power Supply GW Lab GPR-3030 was used as the source of DC current during anodization.

Aluminum samples were firstly degreased by acetone for the disposal of grease and oils which may remain over the surface, etching by immersion the sample in a solution of sodium hydroxide 12 %, and then dismutting was done by immersion into a solution of nitric acid. Anodization step was carried out using electrolytic cell of

two electrodes system connected to DC power supply and both electrodes were immersed into electrolytic solution of prepared H_2SO_4 170 g/l. Electric potential 15V was applied and the solution was cooled to 17˚C before starting anodization step for 30 min. Finally, the sample was fixed in the electrolytic coloring bath of $SnSO_4$ or $NiSO_4$ at pH 2, where Sn^{2+} or Ni^{2+} ions were reduced and deposited within the nano porous film. Then, a homogeneous black color was formed.

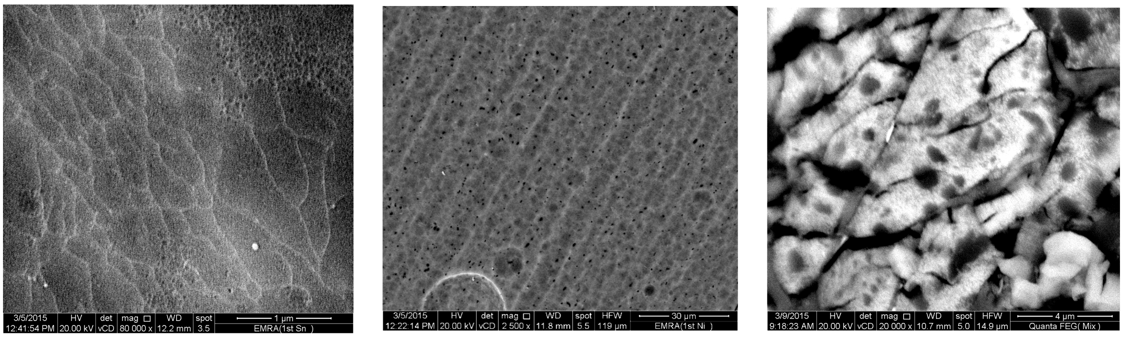
Philips X-Ray Diffraction equipment model X ′Pert PRO with Monochromator, Cu radiation (λ=1.542Å) at 50 K.V., 40 M.A. and scanning speed 0.02o/sec were used. The reflection peaks between $2\theta = 2^o$ and 60^o, corresponding spacing (d, Å) and relative intensities (I/Io) were obtained. The diffraction charts and relative intensities were obtained and compared with ICDD files. EDX analysis was used by QUANTA FEG 250 (FEI). Absorbance was measured using spectrophotometer UV/VIS/NIR Lambda 19 Perkin Elmer spectrophotometer with integrating sphere which was used to measure the total reflection of the coatings in the range of 250 –2500 nm wave length. The light absorbed has been given as a function of the incident light wave length. The data of the absorption of the colored aluminum samples were represented as curves.

RESULTS AND DISCUSSION

3-1 Surface morphology

The morphology of porous anodic film formed after anodic oxidation and electrolytic coloring of aluminum surfcae was investigated using FESEM . The top image shown in Fig.1 of the sample colored by Sn revealed the presence of arrays of porous film of aluminum oxide surrounded by the grain boundaries of origion aluminum surface. The appearance of Al grains indicates the thin anodic fim present. The top image of the surface colored by Ni shows the distribution of tremendous number of fine pores over the anodic film and the grains of Al surface. The grains of Al are not obviously appeared and the anodized film looks as a texture of aluminum oxide film.

Moreover, the sample colored by deposition of both Sn and then Ni for 5 min depicts the presence of Al grains around the fine porosity.



AAO layer colored by Sn **AAO layer colored by Ni** **AAO layer colored by Sn and Ni**

Fig.1: Top images FESEM of anodized and and colored porous anodic film by Sn, Ni and mix of Sn and Ni

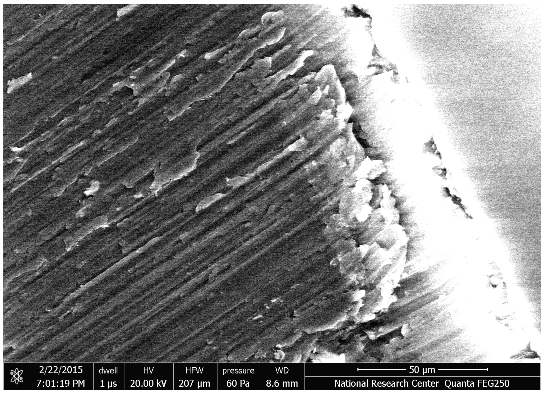


Fig.2: FESEM of cross section of 1st anodized Al

In addition, investigation of cross section of anodic porous Al oxide film by FESEM reveals the presence of thin film of huge number of fine pillars of Al oxide on the outer surface stems from the origin aluminum surface, as shown in Fig.2.

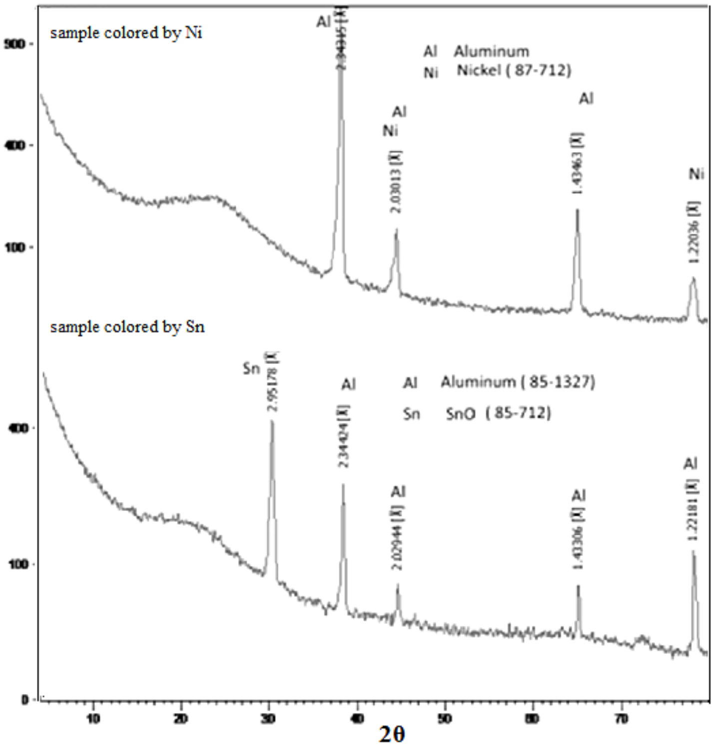


Fig.3: X-ray diffraction chart of two samples anodized aluminum and electrolytically colored by Sn and Ni

3-2 X-ray diffraction analysis (XRD)

Precipitation of Ni and Sn from their salts on the aluminum surface was detected by XRD. The electrodeposition is based on the time, electric potential and consequently coloring material. X-ray diffraction patterns of different colored surfaces by Sn, Ni or both Sn and Ni are shown in Fig 3 and 4.

The patterns indicated the presence of tin oxide SnO and native Sn through the indexed d-spacing line (2.956 and 2.92 Å- ICCD85-712 and 89-4898), however other lines was hidden. Precipitation of native Ni is identified in the pattern at d-spacing line (2.03Å – ICCD 4-0850) as clear shoulder accompanied Al line at 2.02 Å. A clear hump was detected in all patterns, especially in case of the precipitation of both Sn and Ni at 2θ~ 25 (d-spacing line ~ 3.50 Å). A Diffused peaks of amorphous layer are present and the small hump indicates the new formation but not complete. It may be influenced by the phase transition of aluminum oxide from sol phase to gel phase.

Precipitation of both metals in a weak line of Sn and Al was observed, however Ni was not appeared in the pattern. Other lines in the patterns are belonging to native aluminum of d-spacing lines (2.33, 2.02 and 1.43 Å- ICCD 89-3657).

Precipitation of both Ni and Sn together shows different patterns that may detect the behavior of both elements. The lines of SnO or Sn were obviously appeared more than Ni. This is may refer to the volume of both SnO and Sn into the porous film which are heavier than Ni.

X-ray diffraction analysis showed that SnO and Sn were precipitated which mean that the dissolved Sn is removed from the electrochemical cell explaining oxide state was detected (< 1%) to appear in the x-ray diffraction patterns. The presence of amorphous patterns depicted in Fig.4 may render to the electrolytic coloring intercept for a few seconds for transfer from Sn bath to the Ni bath, which may allow the outer oxide film to convert to bohimite form of Al oxide and incomplete crystallization.

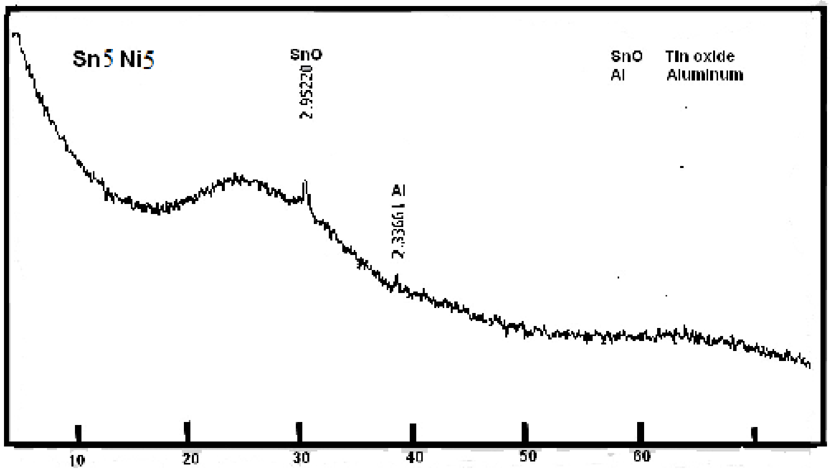


Fig 4: X ray diffraction patterns of aluminum surface containing precipitation of either Ni or Sn or both Ni and Sn

The X-ray diffraction of samples of black colored by the electrodeposition of different ratios of Sn/Ni is shown in Fig.5. It reveals the presence of peaks of Ni, Sn and SnO in case of ratio 2/8, while, Ni peak was ceased in case of 8/2 ratio, where the peaks of Sn and SnO were only predominated.

3-3 EDX Analysis

The charts of EDX analysis of the surfaces of anodized aluminum after electrodeposition of Ni, Sn and both Sn/Ni are shown in Fig.6. Table.1 shows the percentage of elements content by EDX analysis of each sample.

The EDX charts of each sample revealed the contents of the outer surface after anodization and electrolytic coloring. The high peaks of Al and O indicates the major presence of porous oxide film. According to the type of metal deposited either Sn or Ni, a small peaks of Sn and Ni were appeared. A trace of sulfur was obviously appeared may due to the reduction of sulfur deposition into porous layer by the usage of H_2SO_4 in both anodization and coloring steps.

The contents of Sn and Ni are shown in Table-1, where the surface colored by Sn deposition into porous film contains 10.22 % by weight. Also, 9.69 % by weight of Ni was detected in the surface colored by Ni deposition.

While, in the surface colored by mixture deposition of Sn and Ni revealed the presence of 9.98 and 7.34 % of Sn and Ni by weight, respectively.

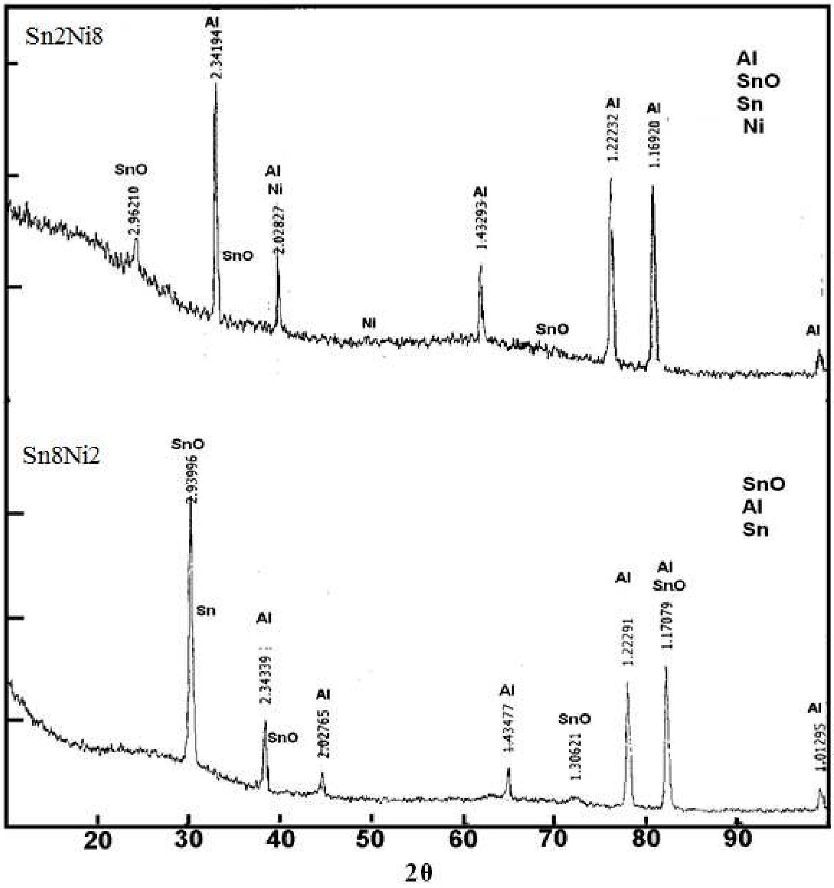


Fig 5. Comparison of X ray diffraction patterns of aluminum surface after deposition of mixture of both Sn/Ni

3-4 Measurements of Sn and Ni density (mg/cm^2)

The measurements of Sn and Ni density per 1cm^2 of the surface revealed the presence of Sn content ranged from 2.1 to 5.7 mg/cm^2, while, Ni content was vacillated between 0.8 and 1.2 mg/cm^2 as the anodization time increased from 10 to 60 min, as shown in Fig.7.

In addition, Fig.8 shows the effect of variation of time of electrodeposition of Sn and Ni, where Sn content was increased from 1.1 to 5.2 mg/cm^2, while Ni content was detected between 1.1 1and 1.3 (low variation), as the time ratio t_{Sn}/t_{Ni} increased from 2/8 to 8/2. This indicates that the ions of tin are capable of penetration and filling the nano pores diameter of Al_2O_3 layer more than nickel ions. This may renders to the variation of atomic size and electrode potential of each element.

Table.1: Element content of the surface of each sample after EDX analysis

Process	Al % wt	O % wt	S % wt	Sn % wt	Ni % wt
1st anodized + colored Sn	49.56	31.91	8.31	10.22	-
1st anodized + colored Ni	50.08	33.89	6.34	-	9.69
1st anodized + colored both Sn/Ni	52.79	23.99	5.91	9.98	7.34

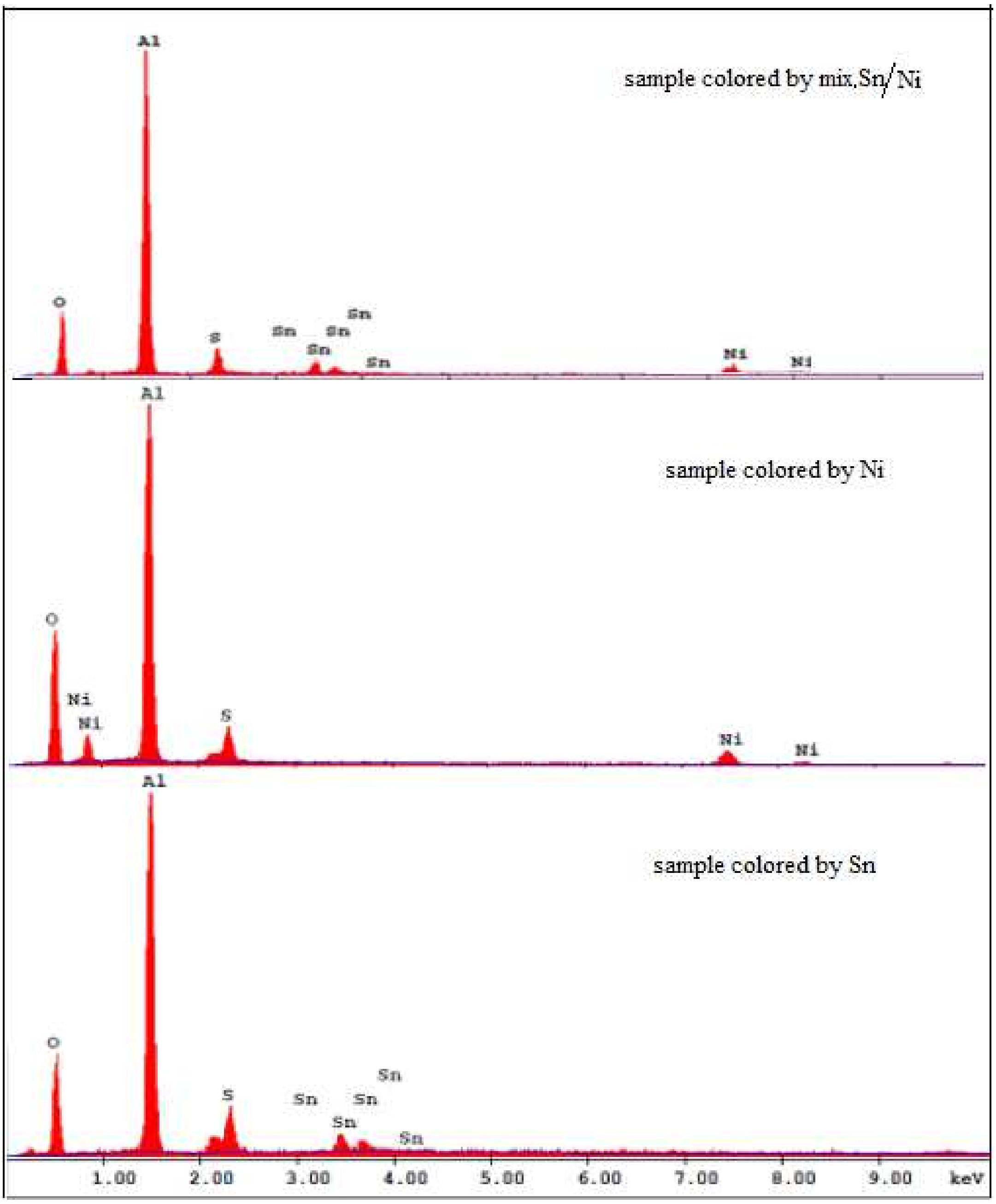


Fig.6: EDX analysis of samples anodized and electrolytically colored by Sn, Ni and mix. of Sn/Ni

3-5 Corrosion results

The Tafel plot of linear polarization of both samples colored by tin after different anodization time shown in Fig.9, it indicates that the corrosion potential was detected at - 0.8 and - 1.2 V for samples anodized at 10 and 60 min, respectively. The higher metal content led to lower corrosion resistance of the surface. So, the sample anodized for 60 min showed lower corrosion resistance due to higher Sn content.

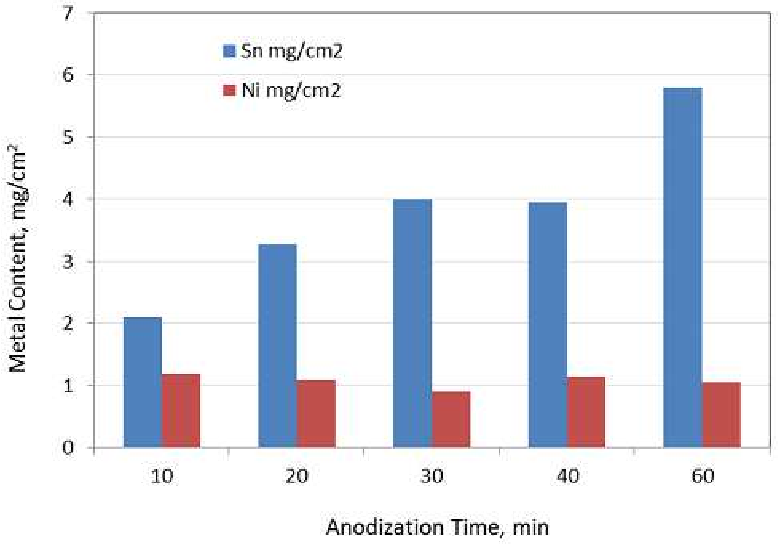


Fig.7: The measured Sn and Ni content after electrodeposition for constant time 10 min measured by Atomic Absorption

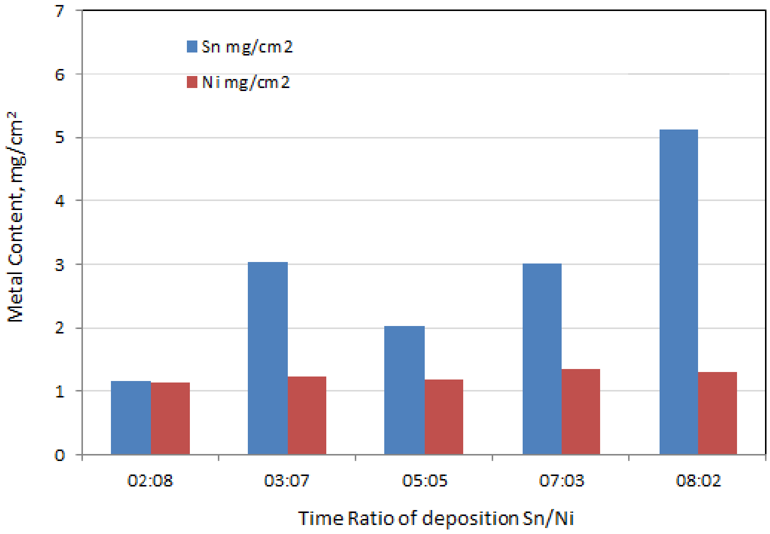


Fig.8: The measured Mixture Sn and Ni content of different time of electrodeposition ratio (t_{Sn}/t_{Ni}) measured by Atomic Absorption

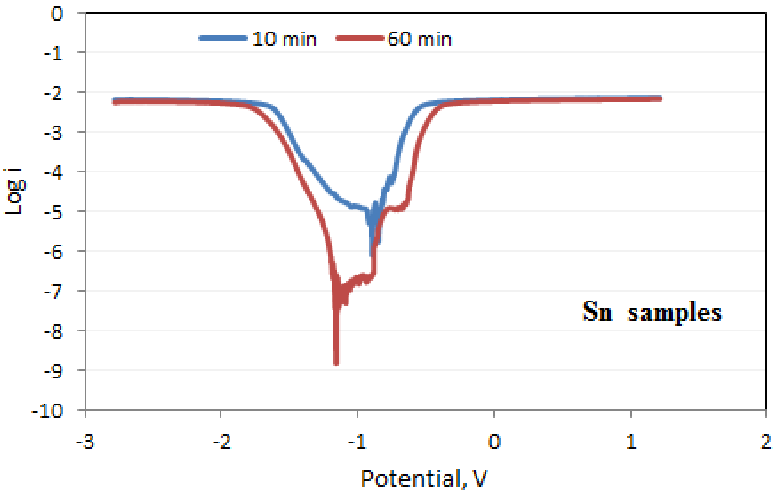


Fig.9: Tafel plot of samples anodized for 10 and 60 min and colored by Sn deposition

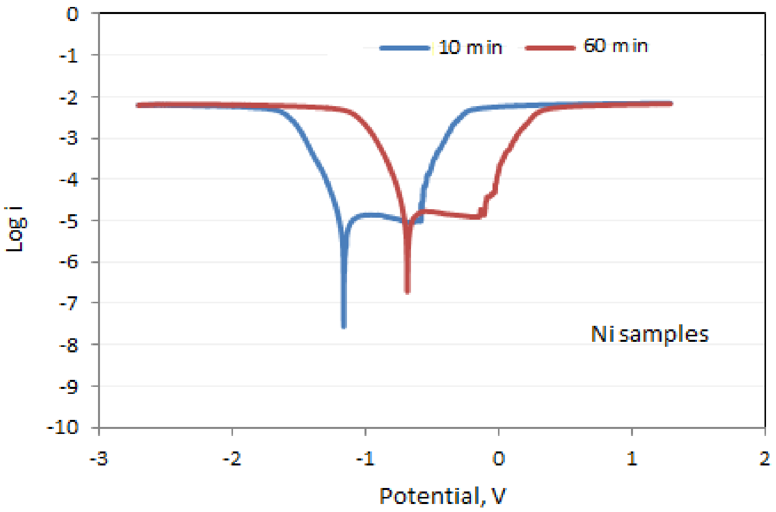


Fig.10: Tafel plot of samples anodized for 10 and 60 min and colored by Ni deposition

On the other hand, the low Ni content in spit of using high anodizing time 60 min showed higher corrosion resistance and corrosion potential at - 0.7 V as shown in Fig.10, while the sample anodized for 10 min and colored by Ni showed lower corrosion resistance and corrosion potential at - 1.1 V. The corrosion resistance of colored surfcae either by Sn or Ni are ascribed to the metal content. These results are matched with those obtained in Figs.7 and 8.

3-6 Optical Characteristics

The optical measurements of the sample surface colored by Sn after different anodization time from 10 to 60 min are shown in Fig.11. The absorbance measurements revealed that all samples colored by Sn showed a high absorbance of light (A= 1.3) in the range of visible region from 350 to 850 nm. This indicates the presence of adequate content of Sn after electrodeposition step and a uniform color was achieved in spite of variation of anodization time as a consequence of pore size disparities.

In contrast as shown in Fig.12, the absorbance measurements of samples colored by Ni showed also high absobance of light in the range of visible region. But, slightly the samples showed absorbance values less than samples colored by tin due to the difference of metal density. This indicates the presence of low content of Ni after electrodeposition.

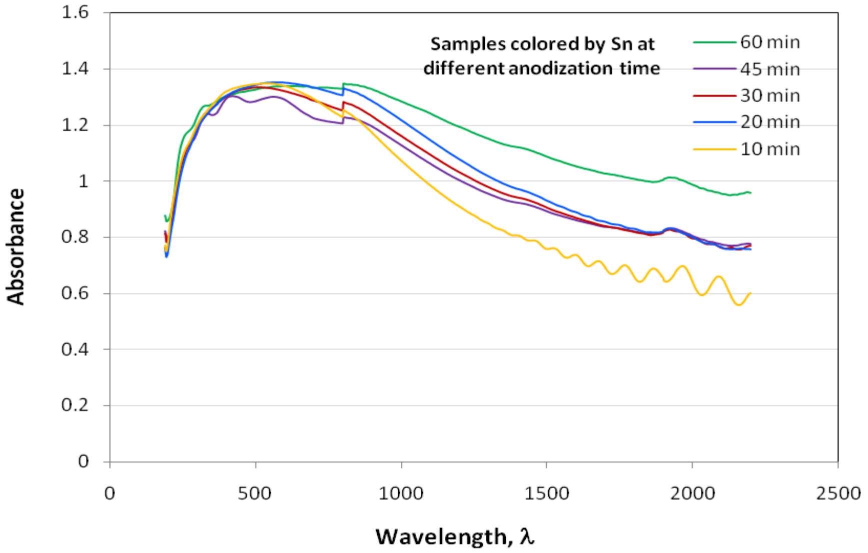


Fig.11: Spectrophotometer measurements of samples colored by Sn and anodized for 10- 60 min

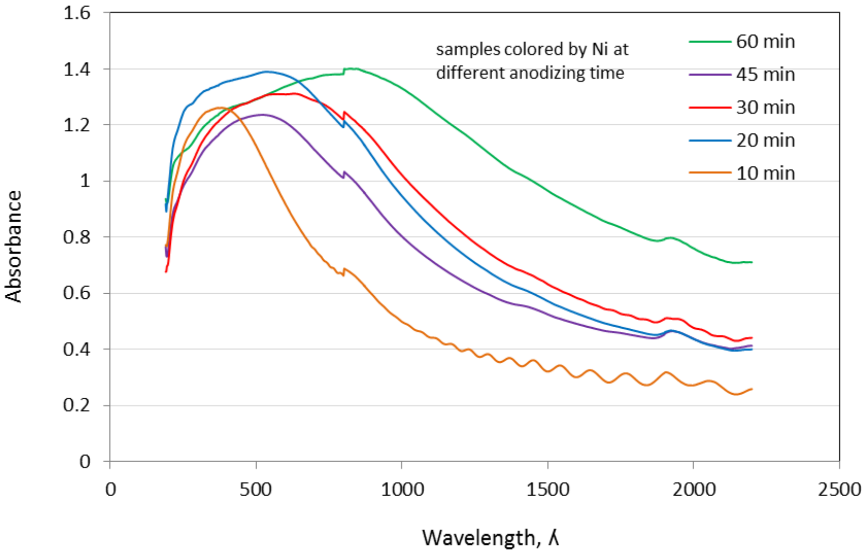


Fig.12: Spectrophotometer measurements of samples colored by Ni and anodized for 10- 60 min

From these findings, the content of Sn and Ni showed covariance of their behavior in spite of using the same time of anodization. This appeared in the surface characteristic such as corrosion resistance, metal density, EDX, XRD analysis and absorbance measurements. The presence of SnO found by X-ray diffraction may due to the high content of Sn into the nano pores of anodic film. The exposure of Sn atoms to continuous anodic oxidation during the anodic cycle of AC current may lead to oxidation of a few atoms of Sn to SnO. While, there was no detection to the presence of nickel oxide, where low density of nickel content was measured and higher potential required for nickel oxidation The high absorbance of colored samples perceived as a promised surfaces for applications of highly absorber plates and solar water heaters.

CONCLUSION

The study revealed the variation of samples colored by Sn and Ni at the same anodizing conditions. XRD showed the presence of peaks of Sn , Ni and low content of SnO. EDX analysis showed the presence of 10.22, 9.69 % by weight for the samples colored by Sn and Ni, respectively. Sn 9.98 % and Ni 7.34 % by wt. were detected in the samples after co-deposition of Sn and Ni. The measurements of metal density per surface area revealed the presence of Sn ranged from 2.1 to 5.7 mg/cm^2, while, Ni content was vacillated between 0.8 and 1.2 mg/cm^2 as the anodization time increased from 10 to 60 min. Also, the Sn content was increased from 1.1 to 5.2 mg/cm^2, while Ni content was detected between 1.1 1and 1.3 mg/cm^2 (low variation), as the time ratio t_{Sn}/t_{Ni} increased from 2/8 to 8/2. The sample anodized for 60 min showed lower corrosion resistance due to higher Sn content. While, the sample anodized for 60 min and colored by Ni showed higher corrosion resistance. The samples colored by Sn showed a higher absorbance A=1.3 in the range visible region.

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