

ELECTRODEPOSITION OF CHROMIUM IN ALUMINUM ALLOY AA6060

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Abstract

Chromium electrodeposits improve the hardness, wear resistance, and corrosion resistance of engineering components. These properties made chromium very acceptable for electroplating. Aluminum alloy AA6060 is used for enclosing constructions such as windows, facade construction, winter gardens, internal partitions, stairs, fences, rail, heating and cooling pipes, furniture, etc. These applications make this alloy extremely interesting for electroplating technology. This paper studies mass of electrodeposited chromium and its thickness in different five samples of aluminum alloy AA6060 which have undergone the galvanizing process. The galvanizing process is performed for different time intervals 20 min, 40 min, 60 min, 80 min and 100 min, respectively. Masses of the samples of aluminum alloy were measured before and after galvanizing with a technical scale. The thickness of electrodeposited chromium in different samples was defined from photographs obtained with metallurgical optical microscope with a magnification of 60500X. For the electrolysis process samples were prepared with abrasive papers while for optical microscope observation was used a polishing machine. The solution used for the electrolysis process was potassium dichromate. The methods used during work of this paper have been: electroplating, metallographic specimen preparation and optical microscopy. The key process of this work is galvanizing process while the main law in accordance with which galvanizing process takes place is Faraday's first law of electrolysis.

Keywords: Aluminum Alloy 6060, Electroplating, Mass of electrodeposited chromium, Thickness of electrodeposited chromium

1. Introduction

The properties of AA6XXX alloys like high strength-to-weight ratio, plasticity, capacity for crucial shape forming along with their ease for joining, and good corrosion resistance have become increasingly focused for versatile applications such as the design of armor structures, rocket, missile casing, light-weight defense vehicle, cars, and marine structure (Mukhopadhyay, 2012). AA6060 is an excellent nonferrous extrusion alloy. Very complex shapes are possible and press quenching (T5) can be achieved. This alloy has excellent anodizing properties (Vargel, 2020). AA6060 is used for windows and doors, utility vehicles, conductors, housings, furniture, space frames, bumpers, bent tubing, etc. (Totten et al., 2019).

Electrodeposition is the process of forming a film or a bulk material using an electrochemical process where the electrons are supplied by an external power supply (Bard et al., 2008). Key impacts on physical properties of coatings during electrodeposition have current density, electrolyte concentration, electrolyte temperature, hydrogen embrittlement, substrate morphology, surface pretreatment, additives, porosity, adhesion, diffusion, amount of impurities, the nature of the substrate upon which the plating occurs (Plener, 1950) (Đorđević, 1970). Electrodeposition on aluminum alloy substrates often is difficult in producing a coating with good adhesion when compared to other metals (Othman, 2016). The aluminum alloy substrate usually needs pretreatment to minimize, stabilize or convert the surface oxide to achieve adequate coating adhesion (Wang et al., 2021).

Electroplated chromium deposits rank among the most important plated metals and are used almost exclusively as the final deposit on parts. Without the physical properties offered by electroplated chromium deposits, the service life of most parts would be much shorter due to wear, corrosion, and the like. Parts would have to be replaced or repaired more frequently, or they would have to be made from more expensive materials, thus wasting valuable resources. The thickness of electroplated chromium deposits falls into two classifications: decorative and functional. Decorative deposits are usually under in thickness. They offer a pleasing, reflective, lubricity, and durability. Decorative chromium deposits are typically plated over nickel but are occasionally plated directly over the substrate of the part. Functional “hard chrome” deposits have a thickness customarily greater than $0.80 \mu m$ and are used for industrial, not decorative, applications. Functional chromium is usually plated directly on the substrate and only occasionally over other electrodeposits, such as nickel. Industrial coatings take advantage of the special properties of chromium, including resistance to heat, hardness, wear, corrosion, and erosion, and a low coefficient of friction. Functional chromium deposits also are decorative in appearance. They are used on parts such as cutting tools and strip steel and are even thinner than decorative deposits (Shlesinger & Paunovic, 2010).

It is well known by Faraday’s law that the mass of substance liberated at an electrode during electrolysis m is proportional to electrochemical coefficient, the current flowing through the electrolyte, and current flow time (Δt):

$$m = k_e I \Delta t \quad (1)$$

For other geometrical considerations we find that thickness of electrodeposited chromium is in direct proportion to electrochemical coefficient, the current flowing through the electrolyte (I) and current flow time (Δt), while it is in inverse proportion with the density of the deposited layer material (ρ) and its surface area (S):

$$d = \frac{k_e I \Delta t}{\rho S} \quad (2)$$

The two basic tasks of this paper are the measure of the electrodeposited mass and the determination of electrodeposited layer thickness.

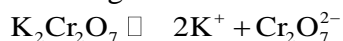
2. Experimental procedure

2.1. The determination of the chemical composition of the aluminum alloys: In the laboratory of TEAL factory in Tetovo with help of spectrometer SPECTROMAXx, we have made a chemical analysis of aluminum alloy 6060 expressed in wt.%. The composition of aluminum alloy 6060 is 0.476 % Si, 0.334% Fe, 0.045 % Cu, 0.052 % Mn, 0.497 % Mg, 0.0038 % Cr, 0.0076 % Ni, 0.101 % Zn, <0.0020 % Ti, <0.0001 % Ag, <0.0002 % B, <0.0001 % Be, <0.0010 % Bi, 0.0028 % Ca, < 0.0010 % Co, < 0.0002 % Li, 0.0012 % Na, 0.0057 % Pb, <0.0010 % Sn, 0.0001 % Sr, 0.0060 % V, < 0.0003 % Zr, <98.5 % Al, <0.0001 % Cd. SPECTROMAXx works with the so-called principle of optical emission spectroscopy (arc spark OES). Atoms and ions, contained in the vaporized sample material, are stimulated into the emission of radiation. The emitted radiation is dispersed into its spectral components and emitted wavelengths of each element are measured. The intensity of the radiation is proportional to the concentration of the element in the sample. The calculation is made internally from a set of calibration curves and can be shown directly as a per cent concentration (Spectral Analysis with SPECTROMAXx, 2018).

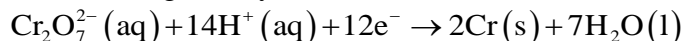
2.2. *Preparation of aluminum alloys samples for the electrolysis process:* Initially we have performed cutting of five samples of aluminum alloy 6060 in pieces with rectangular geometry. After this we have performed surface cleaning. The most important requirement in electroplating technology is cleanliness of the surface to which coatings are applied. The presence of grease, oil, corrosion products, dirt, or other extraneous material affects the adherence, appearance, composition, corrosion resistance, continuity, and general durability of plated deposits. Metal cleaning is usually accomplished by six general methods of handling the work in relation to the cleaning media. These methods are (a) soak tank, (b) electrocleaning tank, (c) spray washer, (d) solvent vapor degreaser, (e) steam gun, and (f) abrasion with grit, shot blast, or tumbling. (Mandich, 2002) In our case we have applied method of abrasive grinding with abrasive papers smirdex P1000 in time interval 3 min each part. After grinding each sample is washed with water and detergent.

2.3. *Preparation of the potassium dichromate solution for galvanizing with chromium:* The most used baths for galvanizing with chromium are: chromium (III) oxide, sodium dichromate, potassium dichromate, etc. In our case to take part in electrolysis, we have prepared a potassium dichromate solution with molar concentration $C(K_2Cr_2O_7) = 0,0083 \text{ mol/dm}^3$ and volume $V = 300 \text{ ml}$. In each 300 ml solution of potassium dichromate, we have added three drops of sulphuric acid 95-97%. Molar concentration of potassium dichromate solutions during electrolysis of five samples of aluminum alloy 6060 are kept being constant.

2.4. *Preparation of electrolysis circuit:* To ensure electrical flow in electrolytes we have used a DC power supply with a voltage range of 0-24 V. Carbon is the most commonly used electrode material in electroanalytical chemistry and it is available in a variety of microstructures: graphite, glassy, carbon fiber, nanotube, amorphous powders, and diamond. During our experimental procedure, we have used graphite as a reference electrode. The reference electrode is that electrode that can maintain a constant potential under changing experimental conditions (Cynthia, 2007). Graphite is used as an electrode material because it can undergo insertion electrochemical reaction (Bard et al., 2008). As a working electrode in two cases, we have used samples of aluminum alloys. We connected the reference electrode of graphite with a positive pole. The aluminum samples as working electrodes we have connected with the negative pole of the power supply. The distance between the reference and the working electrode (2,2 cm) in both cases is kept constant. The current during the galvanizing process with chromium has been $I = 0,55 \text{ A}$ and its value was kept constant. Dissociation of potassium dichromate in water is given:



Cathodic reduction of dichromate ion is given by this reaction:



2.5. *Preparation of galvanized aluminum alloy samples for optical microscope observation:* To extract important microstructure details of samples surface is required careful surface preparation. For this reason, the surface of each sample is grounded and polished to a smooth mirror-like finish. This is accomplished by using successively finer abrasive papers and powders (Callister & Rethwisch, 2014). In our case, we have used a polishing machine Knuth-Rotor 2 Struers. The basic polishing machine has a rotating turntable on which an interchangeable disk, covered with a polishing cloth, is placed. Normally the polishing process will consist of two to four steps, including rough polishing, polishing, and final polishing. Most models have one turntable for 200 mm, 230 mm, 250 mm, or 300 mm disks, one/two speeds or continuously variable speed, a water supply, and a drain (Geels et al., 2007). During polishing, we have used different abrasive paper with different grit numbers. On such abrasive papers, we have cast aluminum oxide suspension Al_2O_3 99.98% (3000Å). We positioned the samples with areas we wanted to observe with an optical microscope on the rotating abrasive

papers in the polishing machine. During this, we have rotated samples for 90° after every 2 min treatment of the part which we have examined. By changing the abrasive papers and using abrasive papers with increasingly lower granulation we have obtained flat and suitable surfaces to observe with an optical microscope.

2.6. Determination of deposited layer thickness in galvanized aluminum alloy samples: The thickness influences many aspects of the coating such as electrical, mechanical, corrosion protection, and even aesthetic properties. Methods for measuring deposited layer thickness could be classified into two different categories: destructive and non-destructive techniques. Destructive techniques are Mechanical Cross-Sectioning, Ion Beam Cross-Sectioning, Angle Lapping, Calo Tester, TEM Lamella Preparation. Non-destructive techniques are: X-ray fluorescence spectroscopy (XRF), Electron Probe Microanalysis (EPMA), X-ray reflectivity (XRR), X-ray Photoemission Spectroscopy (XPS) (Giurlani et al., 2020). In our case, we have used mechanical cross-sectioning for the preparation of samples. To measure the thickness of electrodeposited layers in galvanized samples, we used optical microscopy or Meiji IM7200 metallurgical optical microscope with a magnification of 500X. For data processing, we have used the Corel Draw software package. During this, we photographed five chromium galvanized samples of 6060 aluminum alloy, respectively, and we determined the electrodeposited layer thickness of each sample.

3. Results

In this paper, we measured the mass of each 6060 aluminum alloy sample before and after the galvanizing process. We found the mass of the deposited chromium layer by calculating the difference between the sample mass after galvanizing and the sample mass before galvanizing. We repeated the calculation for each of the 6060 galvanized aluminum alloy samples for time intervals of 20 min, 40 min, 60 min, 80 min, and 100 min. The data are presented in tabular form in Table 1 and graphically in Figure 2.

Table 1. The mass of chromium deposited in 6060 aluminum alloy samples for different current flow time intervals

Sample number	Current flow time t (min)	Deposited mass m (g)
1	20	0,0142
2	40	0,0191
3	60	0,0224
4	80	0,0282
5	100	0,0306

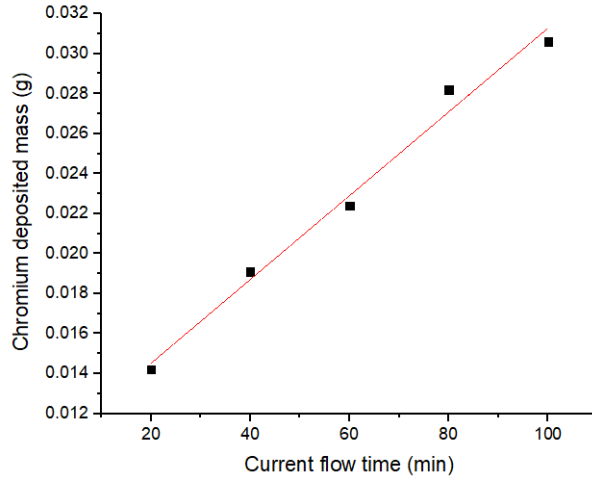


Fig 1. The mass of chromium deposited on 6060 aluminum alloy samples with current flow time through the electrolyte

The results of the measurements of Table 1 and the graph of the dependence of the deposited mass of chromium with the time of current flow through the electrolyte of Figure 1 show that the deposited mass of chromium in the 6060 aluminum alloy samples increases with increasing current flow time through the electrolyte. This is in line with Faraday's first law of electrolysis.

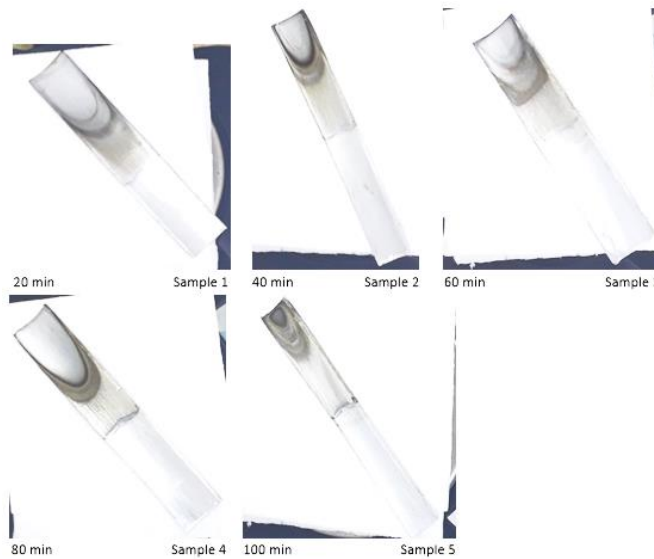


Fig 2. Visual observation of the chromium coatings on the 6060 aluminum alloy samples for 20 min, 40 min, 60 min, 80 min, and 100 min

Figure 2 shows the visual observation of chromium coatings electrodeposited in 6060 aluminum alloy samples at different deposition times. It can be seen obviously that the 6060 aluminum alloy samples surface exposed during the electrodeposition process was covered with smooth coatings with dark grayish-blue color. The first sample is galvanized for time interval 20 min, the second sample for time interval 40 min, the third sample for time interval 60 min, the fourth sample for 80 min, and the fifth sample for the time interval 100 min.

During this work, we measured the thickness value of the deposited copper layer using the Meiji IM7200 metallurgical optical microscope with a magnification of 500X and Corel Draw software package. The

thickness values of the deposited layers are shown in Figure 7. The dark grayish-blue area is the chromium deposition area while the gray area is the 6060 aluminum alloy area.

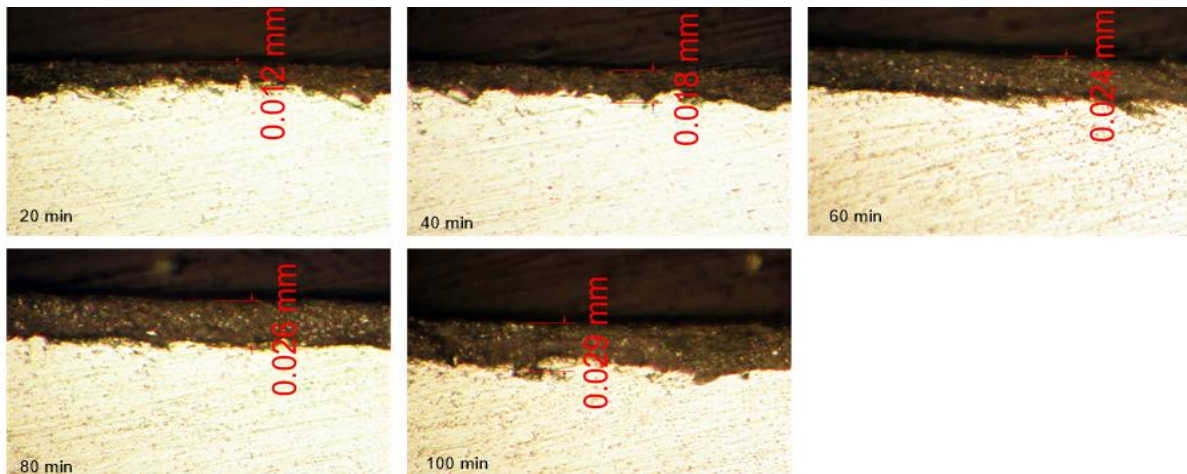


Fig 3. Cross-section microstructure of electroplated chromium in 6060 aluminum alloy samples for thickness measurements during electrodeposition for 20 min, 40 min, 60 min, 80 min, and 100 min

Table 2. The thickness of electrodeposited chromium layer in 6060 aluminum alloy samples for different current flow time intervals

Sample number	Current flow time t (min)	Layer thickness d (mm)
1	20	0,012
2	40	0,018
3	60	0,024
4	80	0,026
5	100	0,029

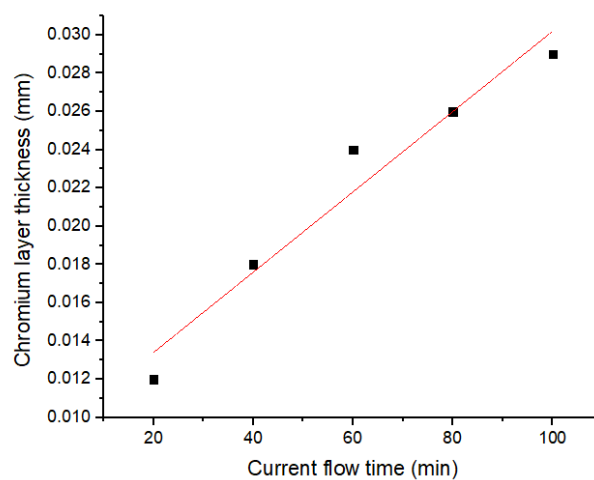


Fig 4. The thickness of electrodeposited chromium layer in 6060 aluminum alloy samples with current flow time through the electrolyte

From Figure 3, Table 2, and Figure 4 we note that the thickness of the electrodeposited chromium with current flow time increases. Such a conclusion is consistent with the theoretical prediction of Faraday's first law on electrolysis.

4. Discussion

The chromium coatings were successfully deposited on 6060 aluminum alloy samples using potassium dichromate solution. Before electrodeposition, surface pre-treatment was done to remove contamination and oxide layer on aluminum alloy substrate. Scout Pro electronic balance was applied to measure the mass of electrodeposited chromium in different 6060 aluminum alloy samples for different current flow times through the electrolyte. Based on measurements we see that the increase of the flow time of the current through the electrolyte also increases the deposited mass of chromium in the samples of 6060 aluminum alloy. Meiji IM7200 metallurgical optical microscope with a magnification of 500X and Corel Draw software package were used to study the thickness of the electrodeposited layer of chromium in 6060 aluminum alloy samples. From the measurements presented above, we see that with the increase of the current flow time through electrolyte the thickness of electrodeposited chromium in 6060 aluminum alloy samples also increases.

References

- [1]. Bard, A. ., Inzelt, G., & Scholz, F. (2008). *Electrochemical Dictionary*. Springer. <https://bit.ly/3lITza0>
- [2]. Callister, W. D., & Rethwisch, D. G. (2014). *Materials science and engineering An Introduction* (9th ed.). Wiley. <https://bit.ly/3qRHJWb>
- [3]. Cynthia, Z. (2007). *Handbook of Electrochemistry*. Elsevier Science. <https://bit.ly/3bMS1T9>
- [4]. Đorđević, S. (1970). *Metalne prevlake*. Tehnička knjiga.
- [5]. Geels, K., Fowler, D., Kopp, W.-U., & Ruckert, M. (2007). *Metallographic and Materialographic Specimen Preparation, Light Microscopy, Image Analysis and Hardness Testing*. ASTM International. <https://bit.ly/3liR1cq>
- [6]. Giurlani, W., Berretti, E., Lavacchi, A., & Innocenti, M. (2020). Measuring the Thickness of Metal Films: A Selection Guide to the Most Suitable Technique. *MI*, 6823. <https://doi.org/10.3390/ciwc2020-06823>
- [7]. Mandich, N. . (2002). Surface Preparation of Metals Prior To Plating: Part 1. In *Cleaning and Pretreatment* (pp. 761–828). American Electroplaters and Surface Finishers Society. <https://bit.ly/3eH4fOW>
- [8]. Mukhopadhyay, P. (2012). Alloy Designation, Processing, and Use of AA6XXX Series Aluminum Alloys. *ISRN Metallurgy*, 2012(Table 1), 1–15. <https://doi.org/10.5402/2012/165082>
- [9]. Othman, I. S. (2016). Electrodeposition of nickel coatings on aluminum alloy 7075 through a modified single zincating process | Request PDF. <https://bit.ly/3nQfxUY>
- [10]. Plener, A. J. (1950). *Galvaniziranje u teoriji i praksi*. RAD.
- [11]. Shlesinger, M., & Paunovic, M. (2010). *Modern Electroplating*. Wiley. <https://cutt.ly/tzVEcg2>
- [12]. *Spectral analysis with SPECTROMAXx*. (2018). <https://bit.ly/3brM8cF>
- [13]. Totten, G. E., Tiryakioglu, M., & Kessler, O. (2019). *Encyclopedia of Aluminum and its Alloys*. CRC Press. <https://bit.ly/3vM4BK7>
- [14]. Vargel, C. (2020). *Corrosion of Aluminum 2nd Edition*. <https://bit.ly/3frm6Zq>
- [15]. Wang, Y., Guan, L., He, Z., Zhang, S., Singh, H., Hayat, M. D., & Yao, C. (2021). Influence of pretreatments on physicochemical properties of Ni-P coatings electrodeposited on aluminum alloy. *Materials and Design*, 197, 1. <https://doi.org/10.1016/j.matdes.2020.109233>