

STUDY OF COPPER GALVANIZATION PROCESS IN ALUMINUM ALLOY 6063

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Abstract

Electrical conductivity, resistance to thermal expansion, metallic brightness and electrodeposition efficiency makes copper very suitable and beneficial for electroplating. Extensive industrial application of aluminium alloy 6063 is a serious reason for studying the galvanizing process of this alloy with copper. In this work, we have studied the mass of electrodeposited copper and its thickness in five samples of aluminium alloy 6063 which have undergone the galvanizing process. The galvanizing process is performed for different time intervals 20 min, 40 min, 50 min, 60 min and 80 min, respectively. Masses of the samples of aluminium alloy were measured before and after galvanizing with a technical scale. The thickness of electrodeposited copper in different samples was defined from photographs obtained with a metallurgical optical microscope with magnification 500X. 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 copper (II) sulfate pentahydrate. The methods used during the work of this paper have been: electroplating, metallographic specimen preparation and optical microscopy. The key process of this work is a galvanizing process while the main law by which galvanizing process takes place is Faraday's first law of electrolysis. We expect that copper deposition in aluminium alloy samples will take place according to Faraday's law respectively the mass and the thickness of copper deposits will be in direct proportion with current flow time.

Keywords: Aluminium Alloy 6063, Copper, Electroplating, Mass of electrodeposited copper, Thickness of electrodeposited copper

1. Introduction

Copper, the red metal, apart from gold the only metallic element with a colour different from a grey tone, has been known since the early days of humans. The utility of pure copper is based on its physical and chemical properties, above all, its electrical and thermal conductivity (exceed only by silver), its outstanding ductility and thus excellent workability, and its corrosion resistance (Habashi, 1997). Copper is the most common metal plated, exclusive of continuous strip plating and nickel (Flott, 2000). The major uses of electroplated copper are plating on plastics, printed wiring boards, zinc dye casting, automotive bumpers, rotogravure rolls, electrorefining, and electroforming (Sard, 1986). Copper is electrodeposited for numerous engineering and decorative application requiring a wide range of mechanical and physical properties (Safranek, 1986). Copper is an excellent choice for an underplate since it often covers minor imperfections in the base metal. It is easy to buff or polish copper, giving it a high gloss. This gloss greatly enhances the appearance

of any subsequent over plate. The copper plate is relatively inert in most plating solutions of other common metals; it has very high plating efficiency, resulting in excellent coverage even on difficult-to-plate parts. Copper is less environmentally hazardous than many other common metals and can, under some circumstances, be recycled. Copper is highly conductive, making it an excellent coating for printed wiring boards or as a coating on steel wire used to conduct electricity (Flott, 2000). The copper deposit also acts as thermal expansion barriers by absorbing the stress produced when metals with different thermal expansion coefficients undergo temperature changes, and this is particularly helpful with plastic substrates. The levelling and brightness properties of copper deposits can be further enhanced by buffing, and since is much softer than steel or nickel, it is easy and relatively inexpensive to buff (Shlesinger & Paunovic, 2010). Copper plating is used extensively in a variety of manufacturing procedures. It is used to prevent corrosion on various surfaces, as a binding layer for additional metal layers, to increase thermal conductivity and to provide conducting paths in many electrical applications. Indeed, much of the recent increase in the activity in copper electroplating is in the manufacture of electrical devices such as circuit boards, integrated circuits, electrical contact surfaces etc (Patent No. 4,469,564, 1984). Typically, copper will be applied in 2.5 to 5 μm and finish coatings for “commercial” copper plate will run 5 to 10 μm . The upper limit of 10 μm applies generally to externally threaded parts, but is common to most applications as well. Some automotive applications require 12 μm minimum (Flott, 2000). In our case, we made a layer of copper in aluminium alloy 6063 that run from 13 to 37 μm .

On the other hand aluminium alloy 6063 is used in pipe railing, furniture, architectural extrusions, appliance parts and trim, automotive parts, building products, electrical and electronic parts, highway signs, hospital and medical equipment, kitchen equipment, marine applications, machine parts, pipe, railroad cars, recreation equipment, recreation vehicles, trucks and trailers (Davis, 2001), (Izairi, Ajredini, Ristova, & Vevecka-Priftaj, 2013). Our study takes part in the subject of electrochemistry. Electrochemistry is the study of the formation and behaviour of ions in solutions. It includes electrolysis and the generation of electricity by a chemical reaction in cells. The crucial concept of electrochemistry is electrolysis. Electrolysis is the production of chemical change bypassing charge through certain conducting liquids (electrolytes). The current is conducted by migration of ions – positive ones (cations) to the cathode (negative electrode), and negative ones (anions) to the anode (positive electrode). The reaction takes place at the electrode by transfer of electrons to or from them (Dainthith & Rennie, 2005). 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. Electroplating bath is a commonly used term describing a solution used for electrodeposition of galvanic layers (Bard, Inzelt, & Scholz, 2008). 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 (k_e), the current flowing through the electrolyte (I) and current flow time (Δt):

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

For other geometrical consideration we find that thickness of electrodeposited copper is in direct proportion to electrochemical coefficient (k_e), 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):

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

The two basic tasks of this paper are the measure of the electrodeposited mass of the copper and the determination of copper thickness in aluminium alloy 6063 samples for different current flow time intervals in the electrolyte.

2. Methods

2.1 The determination of the chemical composition of the aluminium alloy 6063

In the laboratory of TEAL factory in Tetovo with help of spectrometer SPECTROMAXx we have made a chemical analysis of aluminium alloy 6063 expressed in wt.%. The composition of this alloy is 0.476 % Si, 0.329 Fe, 0.045 % Cu, 0.051 % Mn, 0.487 % Mg, 0.0034 % Cr, 0.0055 % Ni, 0.100 % Zn, <0.0020 % Ti, <0.0001 % Ag, <0.0002 % B, <0.0001 % Be, <0.0010 % Bi, 0.0030 % Ca, <0.0010 % Co, <0.0002 % Li, 0.0012 % Na, 0.0051 % Pb, <0.0010 % Sn, <0.0001 % Sr, 0.0053 % 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 the aluminium alloy 6063 samples for the electrolysis process

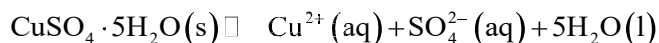
Initially, we have performed a cutting of five samples of aluminium alloy 6063 in pieces with rectangular geometry. After this, we have performed surface cleaning. Electrodeposition onto aluminium poses a several number of fundamental problems to the electroplater. Aluminium has a great affinity for oxygen and when it is exposed to air, direct oxidation causes the spontaneous formation of thin, compact, tough and inert film of oxide. Therefore, special pretreatment sequences are essential to enable aluminium substrates to be electroplated with adherent coatings (Oduoza, Khan, & Sihra, 2014). The most important requirement in electroplating technology is the cleanliness of the surface on 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 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) electro cleaning tank, (c) spray washer, (d) solvent vapour degreaser, (e) steam gun, and (f) abrasion with grit, shot blast, or tumbling (Mandich, 2002). In our case, we have applied the 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 copper sulfate solution for galvanising with copper

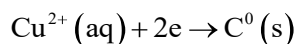
The most used baths for galvanising with copper are copper cyanide baths, copper pyrophosphate plating baths and copper sulfate baths. Copper sulfate solution is economical to prepare, operate, and waste treatment. They are used in printed circuits, electronics, semiconductor, rotogravure, electroforming, decorative, and plating-on-plastics applications (Murphy, 2000). In our case to takes part in electrolysis, we have prepared a solution of copper (II) sulfate pentahydrate with molar concentration $C(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}) = 0.5 \text{ mol/dm}^3$ and volume $V = 200 \text{ ml}$. In each 200 ml solution of copper (II) sulfate pentahydrate, we have added three drops of sulphuric acid 95-97%. Molar concentration of copper (II) sulfate pentahydrate solutions during electrolysis of five samples of aluminium alloy 6063 are kept being constant.

2.4 Preparation of the electrolysis circuit

To ensure the electrical flow in electrolyte we have used power supply AC/DC with a voltage range of 0-24 V. Carbon is the most used electrode material in electroanalytical chemistry and it is available in a variety of microstructures: graphite, glassy, carbon fibre, nanotube, amorphous powders, and diamond. During our experimental procedure, we have used graphite as the reference electrode. The reference electrode is that electrode which can maintain a constant potential under changing experimental condition (Cynthia, 2007). Graphite is used as the electrode material because it can undergo an insertion electrochemical reaction (Bard et al., 2008). As a working electrode, we have used samples of aluminium alloys 6063. We have connected the reference electrode of graphite with the positive pole while the aluminium samples as were working electrodes, we have connected them with the negative pole of the power supply. The distance of $d = 2,2 \text{ cm}$ between reference and working electrode is kept constant. Current during galvanising process with copper was $I = 0,20 \text{ A}$ and its value was kept constant. Dissociation of copper (II) sulfate pentahydrate in water is given:



Cathodic reduction of copper is given by this reaction:



2.5 The determination of the deposited mass of copper in aluminium alloy 6063 samples

During the deposition mass study, we have measured the mass of each 6063 aluminium alloy sample before and after the electrolysis process. After the electrolysis, each sample before the measurement was subjected to the drying process with a hairdryer at time intervals of 2-3 min. After drying, the measurement was not performed until the samples were cooled to room temperature 25°C . The measurements we have made with technical scale.

2.6 The preparation of 6063 aluminium samples galvanized with copper for optical microscope observation

We started the study of the thickness of the deposited copper layer in 6063 aluminium alloy samples with the preparation of galvanized samples for microscopic observation. All greases, oils, and other residues on the specimen should be removed by water with a detergent or a suitable organic solvent. Also, oxidation should be removed (Geels, Fowler, Kopp, & Ruckert, 2007). To extract important microstructure details of samples surface is required careful and meticulous 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. The basic polishing machine has a rotating turntable on which an interchangeable disk, covered with a polishing cloth, is placed. Usually, 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 pieces of paper with different grit number. On such abrasive papers, we have cast aluminium oxide suspension Al_2O_3 99.98% (3000 Å). We positioned the samples with the areas we want to observe with an optical microscope on the rotating abrasive papers in the polishing machine. During this, we have rotated samples by 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 a flat and suitable surface to observe with an optical microscope.

2.7 The determination of deposited copper layer thickness in 6063 aluminium alloy samples

After preparing the samples, utilizing the Meiji IM7200 metallurgical optical microscope with magnification 500X and Corel Draw software package, we photographed five copper galvanized samples of 6063 aluminium alloy, respectively, we have determined the thickness of the deposited copper layer in each sample, separately.

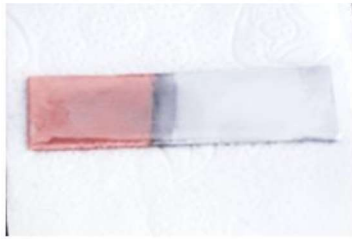
3. Results

In this paper, we have measured the mass of each 6063 aluminium alloy sample before and after the galvanising process. We found the mass of the deposited copper layer by calculating the difference between the sample mass after galvanising and the sample mass before galvanizing. We repeated the calculation for each of the 6063 galvanized aluminium alloy samples for time intervals of 20 min, 40 min, 50 min, 60 min and 80 min. The data are presented in tabular form in **Table 1** and graphically in **Figure 1**.

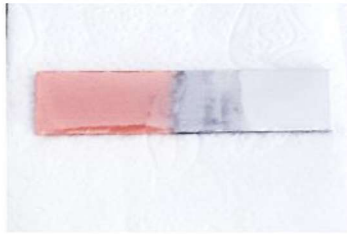
Table 1. The mass of copper deposited in 6063 aluminium alloy samples for different time intervals

Sample number	Deposited mass m [g]	Current flow time t [min]
1	0,09	20
2	0,17	40

3	0,23	50
4	0,25	60
5	0,34	80



Sample 1



Sample 2



Sample 3



Sample 4



Sample 5

Figure 1. Five samples of 6063 aluminium galvanized copper alloy for time intervals 20 min, 40 min, 50 min, 60 min and 80 min

From **Figure 1** the pink-coloured areas of the 6063 aluminium alloy samples are the galvanized copper areas. The first sample is galvanized for time interval 20 min, the second sample for time interval 40 min, the third sample for time interval 50 min, the fourth sample for 60 min and the fifth sample for time interval 80 min.

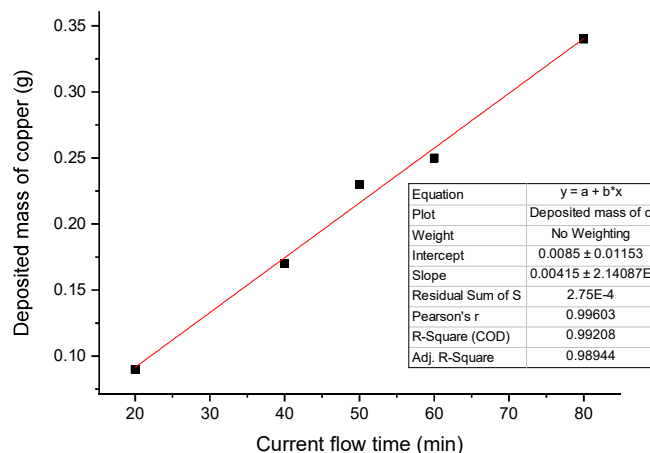


Figure 2. The mass of copper deposited on 6063 aluminium alloy samples with the time of current flow through the electrolyte

The results of the measurements of **Table 1** and the graph of the dependence of the deposited mass of copper with the flow time of **Figure 2** show that the deposited mass of copper in the 6063 aluminium alloy samples increases with increasing current flow time through the electrolyte. This is in line with Faraday's first law of electrolysis.

During this work, we measured the thickness value of the deposited copper layer using the Meiji IM7200 metallurgical optical microscope with 500X magnification and Corel Draw software package. The thickness values of the deposited layers are shown in **Figure 3-7**. The orange area is the copper deposition area while the grey area is the 6063 aluminium alloy area.

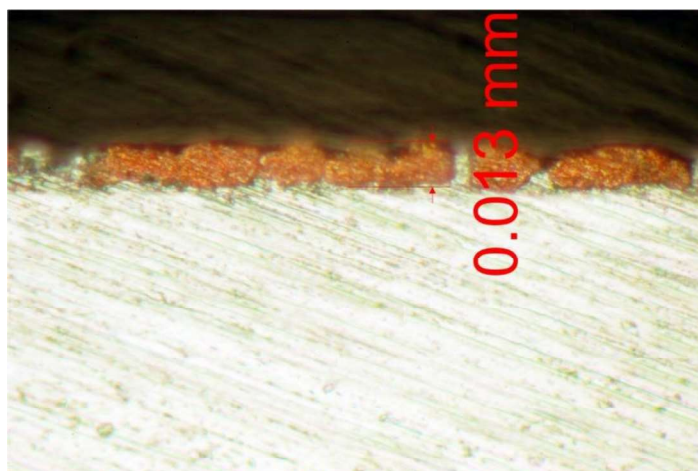


Figure 3. Micrograph of the deposited copper layer in the first 6063 aluminium alloy sample for 20 min current flow time

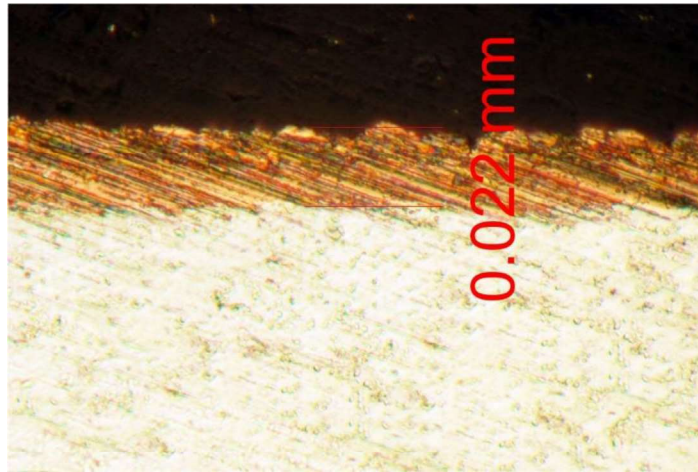


Figure 4. Micrograph of the deposited copper layer in the second 6063 aluminium alloy sample for 40 min current flow time

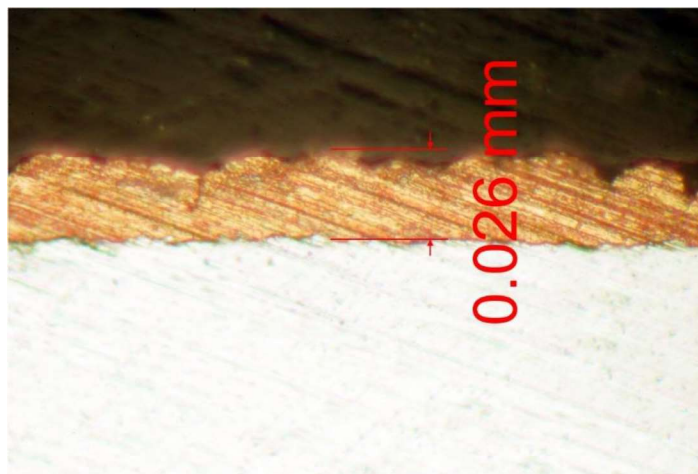


Figure 5. Micrograph of the deposited copper layer in the third 6063 aluminium alloy sample for 50 min current flow time

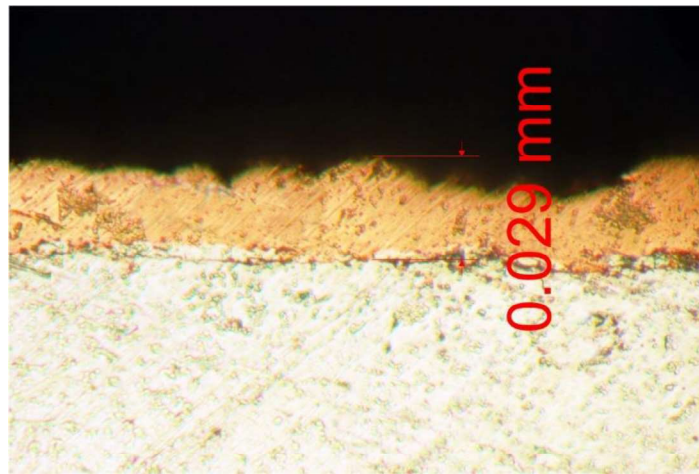


Figure 6. Micrograph of the deposited copper layer in the fourth 6063 aluminium alloy sample for 60 min current flow time

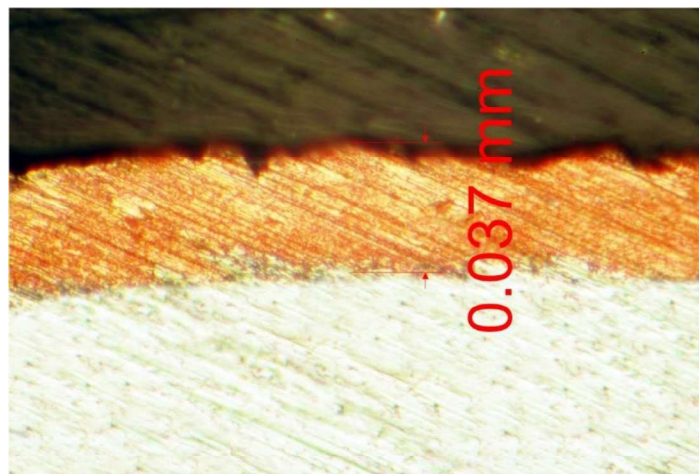


Figure 7. Micrograph of the deposited copper layer in the fifth 6063 aluminium alloy sample for 80 min current flow time

Table 2. The thickness of deposited copper layer in 6063 aluminium alloy samples for different current flow time intervals

Sample number	Current flow time t [min]	Layer thickness d [mm]
1	20	0,013
2	40	0,022
3	50	0,026
4	60	0,029
5	80	0,037

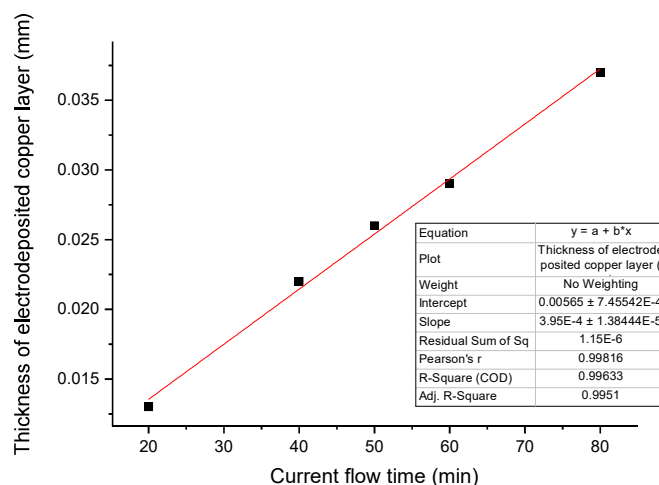


Figure 8. The thickness of electrodeposited copper layer in aluminium alloy 6063 with current flow time through the electrolyte

From **Figure 3-7**, **Table 2** and the graph of the dependence of the thickness of the deposited copper layer for different current flow time through the electrolyte of **Figure 8** we note that the thickness of the deposited copper layer increases with increasing current flow time through the electrolyte. Such a conclusion is consistent with the theoretical prediction of Faraday's first law on electrolysis.

4. Discussion and conclusions

- (1) Spectroscopy, electrochemistry and optical microscopy offer good experimental possibilities for determining the chemical composition of 6063 aluminium alloy, the electrodeposition process in samples of this alloy with copper and the study of the microstructural properties of the copper deposits in the respective samples.
- (2) From the results presented above we see that the increase of the flow time of the current through the electrolyte also increases the deposited mass of copper in the samples of aluminium alloy 6063.
- (3) From the measurements presented above we see that with the increase of the current flow time through electrolyte the thickness of electrodeposited copper in 6063 aluminium alloy samples also increases.
- (5) The deposited mass of copper in 6063 aluminium alloy samples for time intervals from 20 min to 80 min varies from 0,09 g to 0,34 g.
- (6) The thickness of the electrodeposited copper layer in the 6063 aluminium alloy samples for the time intervals from 20 min to 80 min varies from 0,013 mm to 0,037 mm.
- (7) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution with molar concentration $0,5 \text{ mol/dm}^3$, for the value of electric current 0,20 A through the electrolyte at electrolysis time intervals of 20 min to 80 min in 6063 aluminium alloy samples gives a pink copper coating.

5. References

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