

The Effect of Pulsed Electrodeposition Parameters on the Percentage of Gold and Thickness of the Gold-Copper Layers

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ABSTRACT

The results of this study indicated the optimization of the effective parameters in fixing the percentage of gold and thickness of Au-Cu alloy on the pure silver electrode. This method included specific parameters such as the average current density, duty cycle percentage, bath temperature, concentration of gold and cyanide ions in electrolyte, pH, stirring of electrolyte and the wetting agent additive for obtaining gold percentage with standard 18K standard carat (75% gold and 25% Copper) which have been optimized effectively using "one-factor-at-a-time" method. Under optimum conditions and fixing up the percentage of gold in the alloy, along with changes in the duty cycles (20% to 90%), the thickness of the layers was also optimized. The thickness of the cross sections of the co-deposited samples and the percentage of gold in the deposits were investigated by SEM-EDX, XRF, and ICP-OES. Optimum conditions were determined regarding the amount of gold co-deposited with copper and the thickness of deposits. The results showed that the Au-Cu alloy electro-deposited layer in the 30% duty cycle and the average current density by $0.6 \left(\frac{\text{mA}}{\text{cm}^2}\right)$ was as the layer formed in optimal conditions with 74.4 wt. % gold and with 202 μm electro-deposit thickness.

Keywords: Electro-deposition, Average current density, One-factor-at-a-time method, Optimization of Au-Cu alloys, Duty cycle, Electro-deposit thickness, Percentage of gold

1-Introduction

The electrodeposition facilitates the control of experimental parameters including the electrolytic composition, deposition temperature, applied current density, load to be deposited and pH of the solution [1]. It is a highly suitable method for fabricating such structures as it allows deposition of metals with much larger thickness and better morphology than that achieved by physical deposition. The electrochemical deposition of gold is one of the methods for producing hollow gold jewelry with various karats [2]. The microstructure in electrodeposited metals can be controlled by different deposition parameters like bath temperature, solution pH and applied current density [3]. Gold alloy layers with standard karats of 9K to 22K, which are formed by the electrochemical deposition method, are characterized by a specific gold percentage, mechanical properties, hardness and flexibility for making hollow gold jewelry. Initially, the Au-Cu-Cd baths were created because cadmium was used as a brightening agent in a solution of Au-Cu alloying electrolytes. The bath was widely used in the production of hollow artifacts of gold and watch cases with different percentages of gold in the alloy. These layers were very shiny, uniform, ductile and also, they were capable of creating high thicknesses about 300-500 μm [4-5]. The color of the layers resulting from the electrochemical deposition of gold and copper is often the same as the color of the alloy produced by the metallurgical method. The addition of the third element is considered as the main problem, because, the brightening and uniformity of the surface layer should be maintained in addition to the color and gold percentage in the alloy. In creating thick gold and alloys in the production of hollow gold jewelry [6-7], due to cadmium toxicity, this element is removed from the Au-Cu of the basic things gradually.

One of the goals regarding the use of pulse current is to reach the desired thickness by maintaining the percentage of alloying elements as well as its mechanical properties. Electrochemical deposition with pulsed current has provided a great opportunity for extensive research not only in the industry of producing hollow artifacts, but also in the electronics, aerospace and automotive industries [8-9]. Some of the most important advantages of electrochemical deposition using pulsed current, especially in forming the thick layers, include increasing the deposition efficiency, creating higher density and fine-grained layers. The changes are much less in the thickness of the layers at different points of the surface which indicates the less need for organic additives rather than direct current [10]. The use of pulsed current provides the basis for creating a denser layer rather than direct current, which results in an increase in nucleation and formation of fine-grained layers [11-12]. Furthermore, increasing

the current results in the surface roughness [13-14]. In deposition by direct current, the current density is the only variable parameter, but in pulsed electrochemical deposition, there are at least three parameters including the pulse height (I_p), off-time and on-time time, which can be found in various electro-chemical deposition processes for optimization. Typically, the pulse illumination time can vary from 1.0 to 9.9 milliseconds and the pulse power off time may vary from 1 to 99 milliseconds. The average current density is obtained using an ammeter. In order to have the same deposition rate using pulse current instead of direct current, the average current density should be equal to direct current [15].

Given the pulse current at any moment, the current density and the pulse duration can be adjusted. By selecting the pulse parameters for the electrochemical deposition of metals and alloys carefully, the physical and chemical properties of the deposited layers can be controlled very carefully. Having adjusted the pulse current parameters, a significant increase would be achieved in the thickness of the layer compared to the direct current at the same values of electricity from the electrolyte [7]. During pulse electro-deposition, the percentage of duty cycle (% θ) represents the percentage of total pulse cycle time [7] and it is calculated by the following equation:

$$\% \text{ Duty Cycle} = \frac{t_{on}}{t_{on}+t_{off}} \times 100 \quad (1)$$

In the pulsed electrochemical deposition process, the average flow density (I_{avg}) is :

$$I_{avg} = I_p \frac{t_{on}}{t_{on}+t_{off}} \quad (2)$$

Which I_{avg} and I_p are the mean values of the average current density and pulse current density [7].

The theory thickness (T_{theory}), in micrometers, also follows from the relation

$$T_{th} = \frac{m_a \times 10^4}{A \times \rho_{alloy}} \quad (3)$$

It is calculated that m_a is the mass of the deposited layer in grams; A is the cathode surface area in cm^2 and ρ_{alloy} , is the density of the deposited layer in grams per cubic centimeter [16]. ρ_{alloy} Is obtained from the following relationship :

$$\frac{1}{\rho_{alloy}} = \frac{f_{Au}}{\rho_{Au}} + \frac{f_{Cu}}{\rho_{Cu}} \quad (4)$$

In the above relation, ρ_{Au} and ρ_{Cu} are the density of gold and copper whose value are equal to $\rho_{Au}=19.3 \frac{gr}{cm^3}$ and $\rho_{Cu}=8.96 \frac{gr}{cm^3}$, as well as f_{Au} and ρ_{Cu} that are the components of weighted gold and copper deposited in the layer [2]. Using the results obtained by scanning emission microscopy (SEM), the average thickness of the layers obtained in experimental study was compared with theoretical values, and the percentage of the formation of the layers (% ϵ) was calculated by the following equation :

$$\% \epsilon = \frac{T_{avg}}{T_{th}} \times 100 \quad (5)$$

T_{avg} and T_{th} are the average thicknesses of the layer obtained and calculated regarding thickness of the theory in micrometers [16].

In electro-deposition with the same values of electricity, the pulse current would be thicker than direct current. By applying the specified potential value during a pulse cycle, at the Off-time of pulse, the potential decreases slightly. Hence, electrochemical reduction is observed over the period of Off-time [9].

In this research, firstly, the parameters of direct and pulsed current density (with 10% duty cycle), bath temperature, concentration of gold and cyanide in solution, pH, agitation speed and additive effect were optimized by the "one- factor- at- a- time" method [17], in order to reach the standard percentage of gold in the sample (Wt.75% Au and wt.% 25 Cu). After fixing the percentage of gold in the layers, changes in the percentage of duty cycle (20% to 90%) were investigated in order to achieve the optimal thickness of the alloy layer.

The analysis and determination of the exact amount of Au in alloys of gold artifacts were carried out using the standard method called copulation. New developments in the field of ICP spectrometry, which were more specific for precious metals, suggested that the mentioned technique could be regarded as a suitable alternative to copulation. The precision, speed and the possibility of simultaneous analysis of several metals in alloys of gold artifacts were the advantages of this method compared to copulation. The use of ICP to determine the values of precious metals in gold artifacts could be confirmed only if the results of this method had an error rate of less than 0.1%. In particular, in order to determine the amount of gold in alloys of gold artifacts, the amount of gold should be focused more than all other alloying elements [18].

2-Materials and Methodology

Potassium Cyanide, Copper (I) cyanide, Lauryl dimethyl amine oxide (LDAO), Sodium hydroxide and Sulfuric acid were purchased from Merck and Potassium gold cyanide was purchased from Umicore GmbH.

An electro-deposition bath was a Pyrex beaker with a diameter of 110 mm and a height of 140 mm in the volume of 1 liter. The temperature control in the bath was performed using an IKA C-MAG HS7 heater with an accuracy of ± 0.1 . The anodes were platinum-titanium mesh beads with dimensions of 80×100 millimeter, which were fixed in the beaker wall. Pure silver was prepared by casting as a cathode in the dimensions of 1cm^2 and thickness of 1mm, and then the finishing and polishing operations were done [4]. The bath agitation was carried out by a magnetic stirrer. The pH of the bath was also adjusted by the HANNA HI 98107 pH meter.

All experiments were performed by the pulsed power supply of the SL20 PRC switch mode, made in Iran. The current density (pulse and direct) in the range of $2\text{-}12 \frac{\text{mA}}{\text{cm}^2}$ was used to create the layers with a specific gold percentage and also to investigate the thickness of the layers. Weighing the samples was carried out using the Sartorius GK1203 analytical balance with a precision of 0.0001 g before and after electro-deposition.

The Au-Cu alloy bath was prepared by the composition listed in Table 1 [19-20].

Table 1. Electrodeposition bath composition of Au-Cu

Electrolyte concentration range (g/l)	Components
18-25	KCN
5-10	$\text{KAu}(\text{CN})_2$. 68.2 wt. %
55	CuCN
0.5 1.75	$\text{C}_{14}\text{H}_{31}\text{NO}$

Before the electrodeposition, the samples were degreased out by special silver degreasing chemical, and were rinsed by ion-free water. They were neutralized using 5% sulfuric acid solution and finally were washed by double rinsed ion-free water [4]. After this step, the samples were electro-deposited under the conditions listed in Table 2.

Table 2. Conditions for the Au-Cu electro-deposition

Used range	Parameter
2-12 (mA/cm^2)	Current density (mA/cm^2)
60-70 ($^{\circ}\text{C}$)	Bath Temperature
11.5-12.5	pH
50-175 (rpm)	Agitation

The pH of the solution was adjusted using 10% NaOH and 5% H_2SO_4 . In this study, firstly, the parameters of direct and pulsed current density (with a working cycle of 10%), the concentration of gold and cyanide ions, the bath temperature, pH, agitation and the amount of additive for creating the Au-Cu alloy layers containing wt.% 75 gold standard value were optimized by one-factor-at-a-time method. Then, using a constant Au percentage in the alloy, the thickness of the layers was optimized by changing the different duty cycle parameters. Pulse on and off time parameters were set at 0.01 seconds [15]. Thickness measurement of formed layers was done by the SEM CamScan MV2300 scanning electron microscope equipped with EDXBruker XFlash6110 in order to determine the percentage of elements in the alloy accurately. The exact amount of gold in Au-Cu alloy deposits was investigated by inducing the coupler plasma spectrometry by ICP-OES, Varian 710, and X-ray fluorescence XRF Fischer scope® X-RAY XAN® 220 diffraction compared

3-Results and Discussion

The values of the parameters obtained in the optimization of direct and pulsed current deposition are summarized in Table 4 in order to create the deposited layers with the value of 75% wt. Au in alloy.

Table 3. Optimized conditions electrochemical deposition of Au-Cu alloy with direct current and pulse with 10% working cycle for stabilization of wt. % 75 gold per alloy

C.D ($\frac{\text{mA}}{\text{cm}^2}$)	C _{Au⁺} ($\frac{\text{gr}}{\text{l}}$)	C _{Cu⁺} ($\frac{\text{gr}}{\text{l}}$)	C _{CN⁻} ($\frac{\text{gr}}{\text{l}}$)	Agitation (rpm)	Temp (°C)	pH	Additive ($\frac{\text{ml}}{\text{l}}$)
6	66	55	24	100	66	22	1

In the electro-deposition of Au-Cu, the percentage of alloying elements and the thickness of the formed layer were influenced by various parameters, and in particular they were influenced by the current density. In fixed deposition conditions, if the same amount of current density was used, the pulse current would be increased significantly compared to direct current [7].

Figures 1 and 2 show the SEM image and EDS analysis of the cross section of Au-Cu deposited layers with direct and pulsed currents, both of which were identical in terms of optimal conditions and with a direct current density of 6 $\frac{\text{mA}}{\text{cm}^2}$ and the average thickness of the alloying layer which was about 82 μm and also with the 73.3 wt. % of gold. However, the average thickness of the layer produced by the pulse current was about 151 micrometers and with 74.4 wt. % of gold.

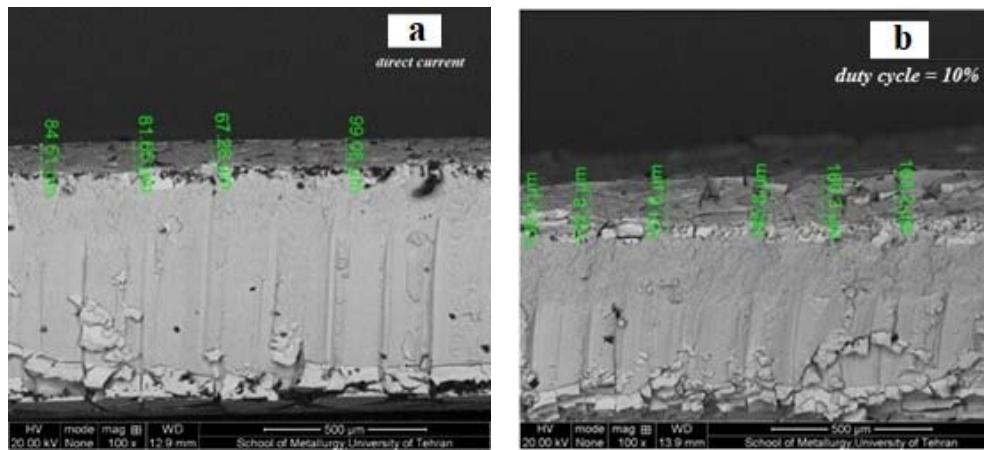


Fig. 1 SEM image of the cross-section of deposited samples to measure the average thickness of the layers, 82 μm with direct current (a), 151 μm with pulse current and 10% cyclic cycle (b).

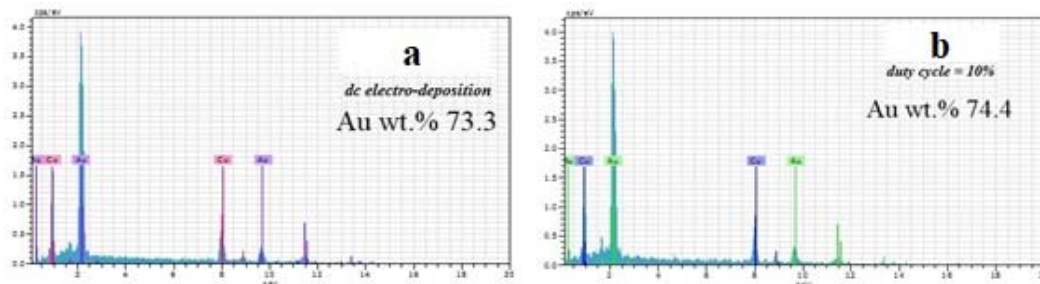


Fig. 2 EDS analysis of cross section of deposited samples to measure the amount of gold in the layers, wt. 73.3% by direct current (a) w / w% 74.44 with pulse current and 10% (b).

Tables 5 and 6 show the effect of direct and pulse current on the mass of the layers, the percentage of gold, the current efficiency and thickness of the Au-Cu layers formed in the 240 minute period under optimum conditions.

Table 4. The effect of direct current density on mass, gold percent and thickness of layer in 240 minute under optimum conditions

C. D ($\frac{\text{mA}}{\text{cm}^2}$)	m _{alloy} (mgr)	Alloy (%)		A (cm^2)	ρ_{alloy} ($\frac{\text{gr}}{\text{cm}^3}$)	T _{th} (μm)	T _{avg} (μm)	τ (min)
		Au	Cu					
6	82.327	733	267	1	14.49	88	82	240

Table 5. The effect of average pulse current density on mass, gold percent and thickness of layer in 240 minutes under optimum conditions

θ (%)	I_{avg} ($\frac{mA}{cm^2}$)	m_{alloy} (gr)	Alloy(%)		A (cm^2)	ρ_{alloy} ($\frac{gr}{cm^3}$)	τ (min)	T_{th} (μm)	T_{avg} (μm)
			Au	Cu					
10	0.6	153.211	744	256	1	14.92	240	160	151

The Au-Cu formed layers in the duty cycle of 30%, had a thickness of 0.841 μm and also contained 74.4 wt. % of gold in the alloy, which was more than the amount of alloy gold obtained in some of the commercial processes of the jewelry and watch case electroforming [21]. In duty cycles more than 30%, a significant decrease was observed in the thickness of the Au-Cu alloy that was formed in the same conditions. Increasing the duty cycle meant reducing the off-time. If the pulse time was too short, the electrical double layer wouldn't have enough growth opportunity, it would be very thin and in fact, there would be no difference using the mode of direct current [7]. Figure 4 and 5 show microanalysis of SEM-EDX of all the electro-depositions with various duty cycles ranging 20-90% of the samples cross sections that were at the same values of operation condition.

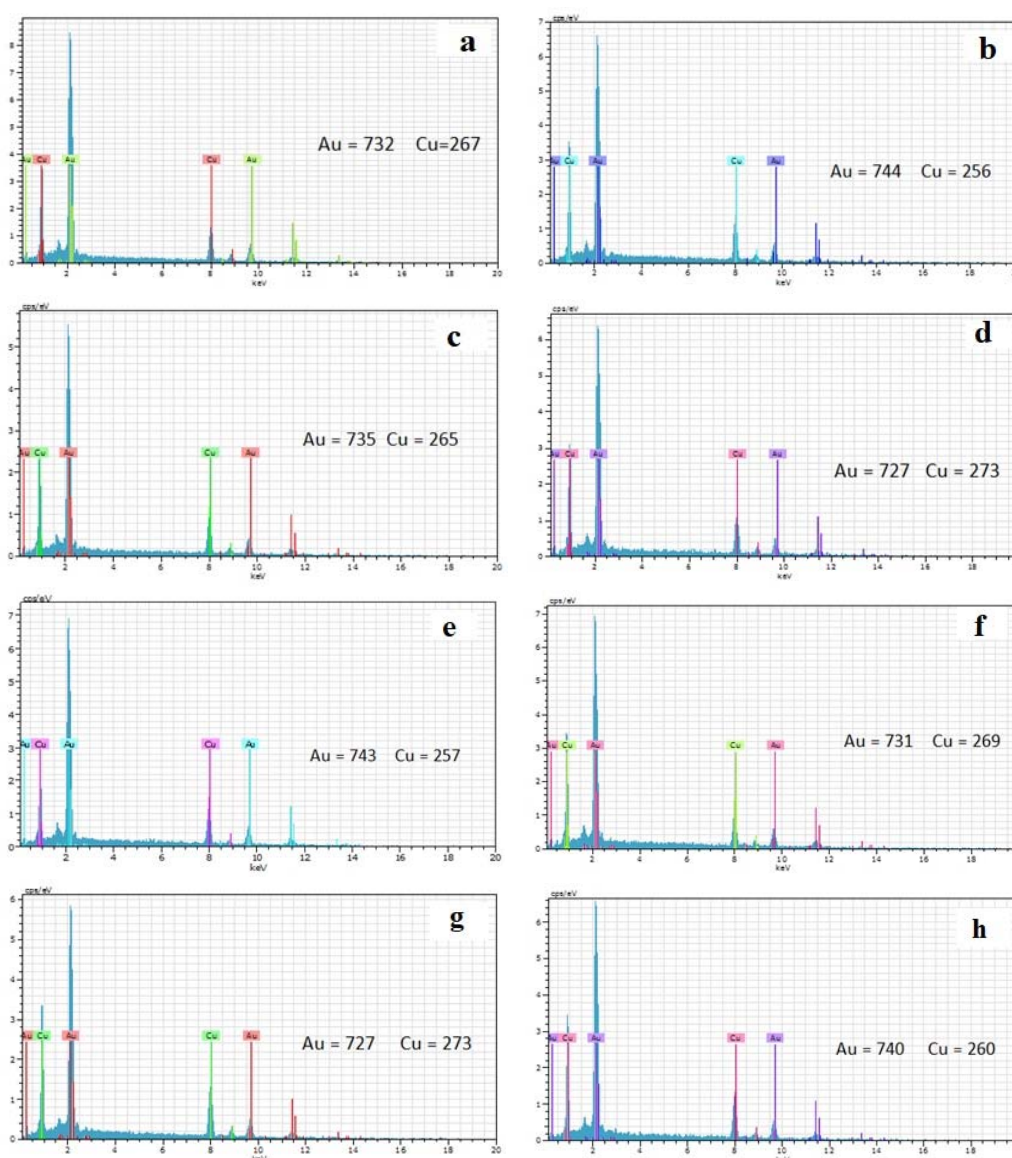


Fig.4. EDS micrographs of Au-Cu alloy analysis in the electro-deposits (a to h) at same operation condition, at 20% duty cycle contents 73.2% Au(a) 30% duty cycle contents 74.4% Au (b) 40% duty cycle contents 73.5% Au (c). 50% duty cycle contents 72.7% Au (d) and 60% duty cycle contents 74.3% Au (e) 70% duty cycle contents 73.1% Au (f) 80% duty cycle contents 72.7% Au (g) and 90% duty cycle contents 74.0% Au (h).

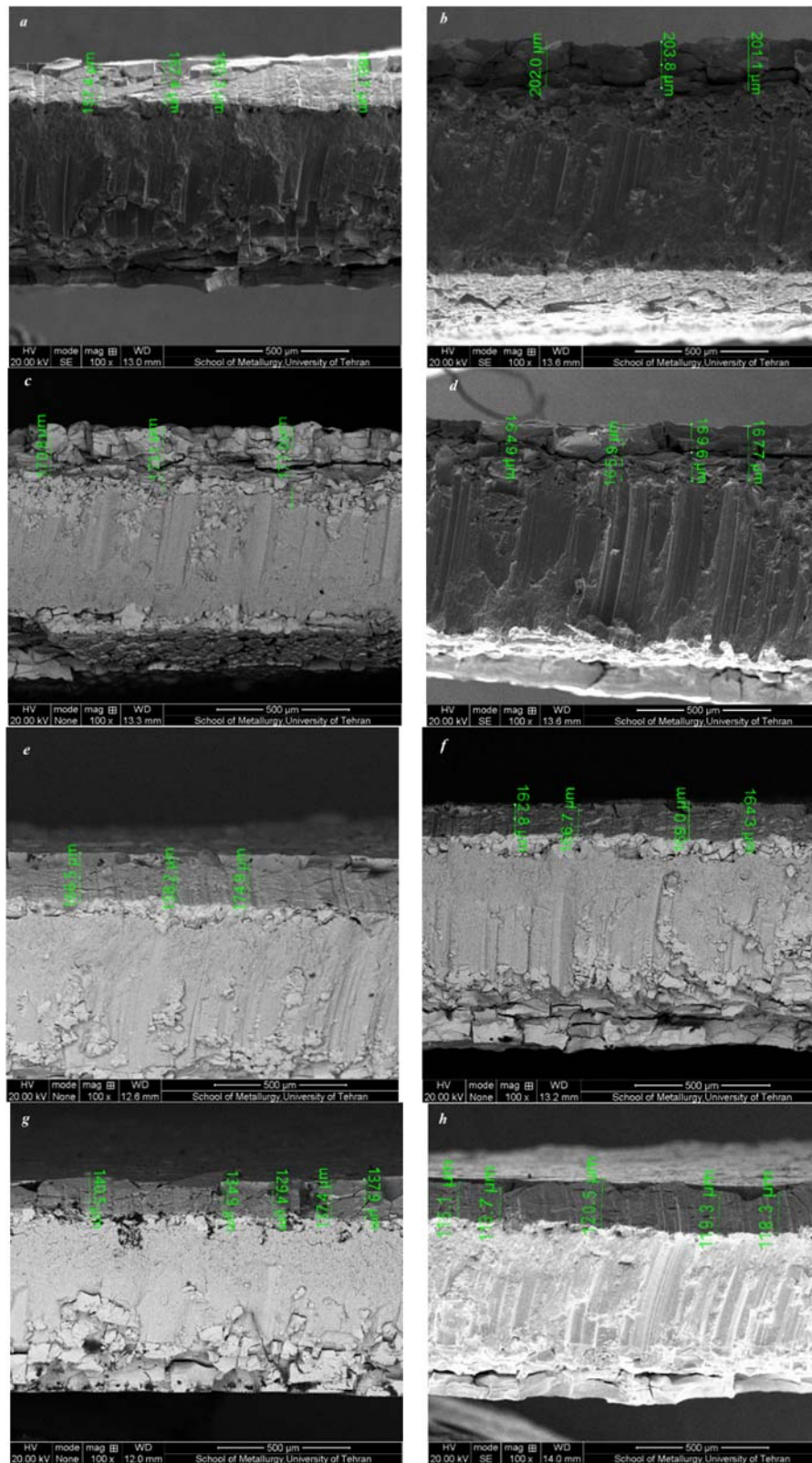


Fig.5. SEM cross section images of Au-Cu alloy (a to h) at same operation condition, at 20% duty cycle contents 162 μ m (a) 30% duty cycle contents 202 μ m (b) 40% duty cycle contents 174 μ m (c). 50% duty cycle contents 167 μ m (d) and 60% duty cycle contents 166 μ m (e) 70% duty cycle contents 165 μ m (f) 80% duty cycle contents 136 μ m (g) and 90 % duty cycle contents 117 μ m (h).

As the data shown in Table.7, the influence of pulse duty cycle variation was investigated on the metals percentage, deposits mass, thickness and current efficiency of the gold-copper heavy electrodeposition with current density of 6 mA /cm². Table.7 shows that the percentage of gold-copper alloy (74.4% Au and 25.6% Cu) in the layer was acceptable and heavy electro-deposition rate increased significantly in the optimum duty cycle

($\theta=30\%$). This was confirmed by the results of influence of pulse duty cycle on the deposition rate compared to the calculated ones (Table.7). As duty cycle increased, deposition rate decreased. This was attributed to less amount of off-time at higher duty cycle [16]. Therefore, less time is provided for atoms to transfer to a stable position during off-time [22].

Table 6. Influence of duty cycle (%) variation on pulse electro-deposition mass, deposition rate and composition of gold-copper alloy, and comparison of experimental values of the deposition thickness with calculated values.

θ %	m_{alloy} (gr)	I_{avg} ($\frac{\text{mA}}{\text{cm}^2}$)	Alloy (%)		A (cm^2)	ρ_{alloy} ($\frac{\text{gr}}{\text{cm}^3}$)	T_{th} (μm)	T_{avg} (μm)	τ (min)	R_{avg} ($\frac{\mu\text{m}}{\text{min}}$)
			Au	Cu						
10	0.127	6	733	267	1	14.49	88	82	240	0.363
20	0.255	0.6	732	267	1	14.74	173	163	240	0.679
30	0.313	0.6	744	256	1	14.90	210	202	240	0.841
40	0.272	0.6	735	265	1	14.79	184	174	240	0.725
50	0.254	0.6	727	273	1	14.65	174	167	240	0.695
60	0.258	0.6	743	257	1	14.90	173	166	240	0.687
70	0.254	0.6	731	269	1	14.74	172	165	240	0.683
80	0.211	0.6	727	273	1	14.65	144	136	240	0.566
90	0.185	0.6	740	260	1	14.91	124	117	240	0.487

Electro-deposition with 30% duty cycle was selected as the optimal duty cycle due to the highest percentage of gold (74.4% wt.) and its closeness to 75 wt.%. Figure 5 shows the variations in the values of the various duty cycles with the percentage of gold in the treated layers.

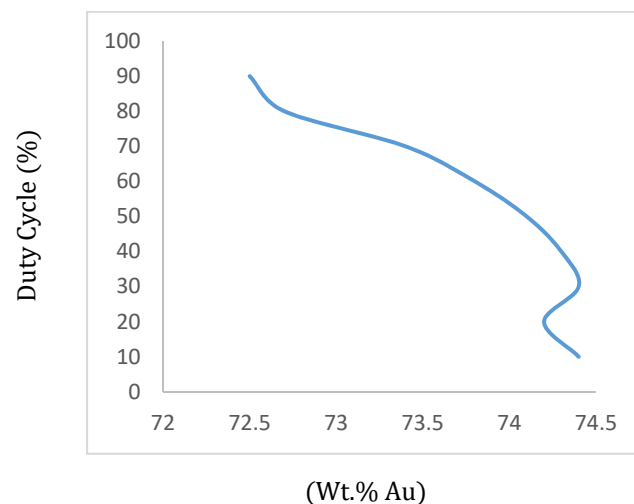


Fig. 5 The variations of various duty cycles on the percentage of gold in the Au-Cu layer

Figure 6 shows the variation of different values of the duty cycle with the deposition rate of the Au-Cu alloy in the deposited layers.

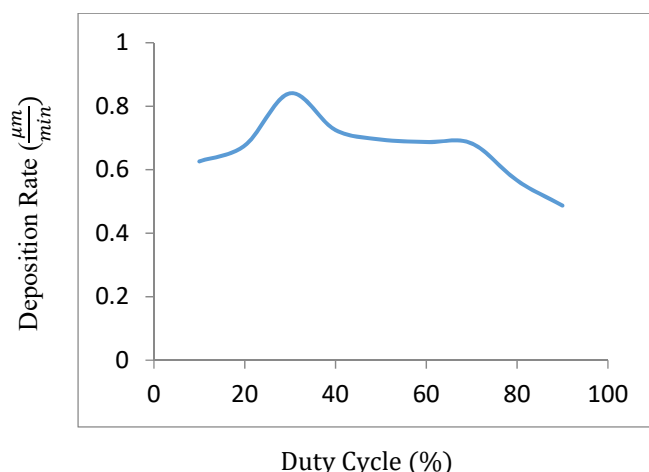


Fig. 6 The variations of different values of the duty cycles on the of Au-Cu electro-deposition rate.

As can be seen in Table 8, there were differences among the Au values in each sample. In case of the comparison of analytical techniques (ICP-OES and XRF), there was no statistical difference between the two methods regarding Au content, This means that using both equipment was possible to analyze the Au in gold alloys, but the ICP-OES apparatus was more accurate and precise than XRF method [23].

Table 7. Paired-data test between the results of ICP-OES and XRF techniques for Au content.

% Duty Cycle	Au (part per thousand)		Paired Test ICP-OES and XRF Differences
	ICP-OES	XRF	
Direct Current	744.1	742.0	1.7
10	739.9	739.7	0.2
20	732.3	729.9	2.4
30	744.8	749.6	- 4.8
40	735.4	741.4	- 6.0
50	726.9	740.0	- 13.1
60	743.6	740.3	3.3
70	731.2	746.1	- 14.9
80	726.6	735.0	8.4
90	739.8	745.1	5.3

4. CONCLUSIONS

According to the results of this study, obtaining the necessary thickness of gold-copper electro-deposited layers for making gold alloy artifacts was possible to be faster rather than conventional D.C. electro-deposition by using pulse current. Pulse electrodeposition of gold-copper was a repeatable and controllable technique to prepare a layer with a certain composition of gold and copper. In this method, the pulse parameters (duty cycle percentage and average current density) and operation condition (gold and cyanide concentration, temperature, pH and agitation of the alloy gold bath) variations' effects were investigated. In heavy electro-deposition of gold-copper, LDAO could be used as a suitable surfactant to provide a thick gold alloys deposit at acceptable karat and deposition rates. It was found that at pulse current density by the constant value of $6 \frac{\text{mA}}{\text{cm}^2}$ and 30% duty cycle, the best amount of gold was obtained and highest rate of deposited layer was observed on the silver cathodes.

Duty cycles above 30% led to lower rates of the depositions. Also, it has been observed that the experimental deposition rate and current efficiency of D.C. electrodepositions were lower than those of pulse electro-deposition. In order to improve the %weight of gold in deposited layers, it was recommended to apply this method with gold-silver.

5. ACKNOWLEDGEMENTS

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