Rare Metal Materials and Engineering
Volume 48, Issue 6, June 2019
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Rare Metal Materials and Engineering, 2019, 48(6): 1797-1802.

ARTICLE

Influence of Pulse Period of Bidirectional Pulse Electrodeposition Process on the Properties of Electroformed Layer of Gold

Zheng Lishan[1], Yuan Xinqiang[1], Lei Ting[2]

[1] China University of Geosciences, Wuhan 430074, China; [2] Wuhan University of Engineering Science, Wuhan 430200, China

Abstract: Electroformed gold layers were prepared by bidirectional pulse electrodeposition process, with thickness up to 150 μm in 20 h from cyanide-free bath. Through a single variable experiment, in which the pulse period was treated as a single variable, we studied the effect of pulse period on the properties of electroformed layer of gold using bidirectional pulse power. Scanning electron microscopy, X-ray diffraction, and Vickers hardness test were used to research the surface morphology, average crystal size and hardness of electroformed gold layers. Results show that the microhardness of electroformed layer of gold is higher when pulse period changes between 45 and 75 ms, which can reach to 1170 MPa. Strong (111) preferred orientation can result in flatter micro surface and higher microhardness of electroformed gold layers.

Key words: bidirectional pulse; pulse period; gold; Vickers hardness; non-cyanide electrodeposition

Electroformed gold layers have many applications because of their excellent mechanical capabilities. And they possess higher hardness in the premise of high purity. Cyanide bath is highly toxic, and more and more gold complex ion has been discovered. At present, electrodeposition process of gold has high pollution and cannot get enough thickness with high efficiency. Pulse electrodeposition technology for gold in non-cyanide plating bath can always catch people's interest. But it is also puzzling.

Properties of gold plating obtained by pulse current and bidirectional pulse current are better than those obtained by simple direct current. The application of technique of pulse-reverse current can better improve the quality and properties of the electrodeposition than pulse current[1-3].

Liu et al[4] found that reverse current density and pulse width have a significant impact on the morphology, roughness, current efficiency, and porosity of cobalt hard gold obtained by pulse reverse plating process. Frade et al[5] also found that the anodic pulse current density exerts a remarkable influence on the plating morphology and zinc crystallite size in the experiment of pulsed-reverse current electrolysis. Cheng et al[6] investigated spontaneous microstructural evolution in electroplated Cu films and found that the PR plating waveform produces plating with lower impurity. In brief, electroplating technology using bidirectional pulse plating produced plating with finer grain size, smaller size, and lower porosity than that using DC plating or on-off pulse plating.

Most researches were focused on electroplating, with thickness of 10 μm to 20 μm. Our research is based on electroformed thick gold layer, whose thickness can reach to 150 μm, prepared by pulse-reverse electrodeposition progress.

In this paper, single variable experiments were conducted using pulse period as the single variable. Different electroformed gold layers were gained after 20 h. Scanning electron microscope was used to study the surface morphology of the samples. We also had a contrastive analysis of crystal orientation of different electroformed gold layers by X-ray diffraction method. Different deposition conditions resulted in different microhardness of electroformed gold layers, which were measured by Vickers Indenter.

Received date: June 23, 2018
Foundation item: Gemmological Institute China University of Geosciences (Wuhan) Open Fund（CJHIXM-S201615）
Corresponding author: Zheng Lishan, Candidate for Ph. D., Gemmological Institute, China University of Geosciences (Wuhan), Wuhan 430074, P. R. China, E-mail: zhenglishan901113@163.com

1 Experiment

1.1 Experimental environment

The electrodeposition process was conducted in a 50 mL beaker as the electrolytic cell, which was washed clean with distilled water. 30 mL non-cyanide electrolytic solution consisted of 20 g/L gold ions ($AuClO_4$), 100 g/L potassium chloride (KCl), 10 g/L potassium dihydrogen phosphate (KH_2PO_4), and 10 mg/L additive. The pH of electrolytic solution was adjusted to 5~6. All reagents were prepared by distilled water.

There was a PTFE cap with two perforations with diameter of 6 mm and distance of 20 mm. The two electrodes were fixed on two copper bars, which perforated through the PTFE cover and linked with the bidirectional pulse current power. The cathode was high purity (99.9% metal basis) titanium (Ti) plate (15 mm×10 mm×2 mm); and anode was gold plate (about 30 mm×20 mm×1mm) with a purity of 99.9%. Pulse reverse voltage was provided by Nanjing Hope Technology power supply model HP-MCB25. The experiment setup is shown in Fig.1. The gold plate was used as the anode in the electrodepositing technology, and the weight of the gold plate was found to decrease by comparing the weight of the anode plate before and after the experiment. Using a three-electrode system and using the gold plate as the working electrode, the volt-ampere curve of the gold anode in the range of 0~1V was tested (Fig.2). It is found that a gold oxidation peak appears near 0.65V. Therefore, the gold plate exists as a soluble anode in this system.

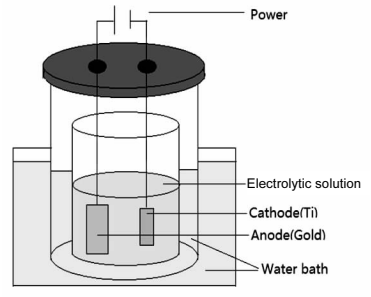

Fig.1 Experiment setup

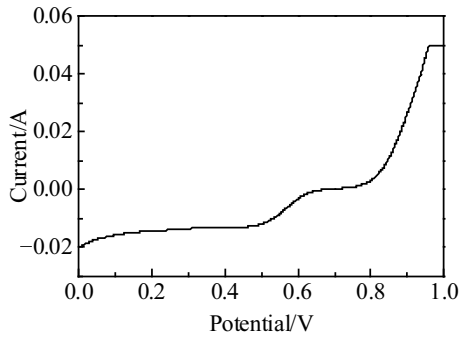

Fig.2 Cyclic voltammogram of the gold anode

Firstly, cathode plate was polished by abrasive paper of different number (from small to big number) in order to get a smooth and bright surface. Then cathode and anode were both put into the degreasing solution for about 30 min to remove grease from surface. Thirdly, the electrodes were put into 10% hydrochloric acid for 10 min for activation. The electrodes were washed completely by distilled water for 2 min at the end of each step. While putting the PTFE cap on the beaker, cathode and anode were immersed into electrolytic solution. The temperature of electrodeposition was controlled at 35 °C by water bath.

The electrodeposition current was supplied by bidirectional pulse power, which provided a square waveform shown in Fig.3. Parameters of bidirectional pulse power were complex. The main power parameters are shown in Table 1. On the basis of cyanide-free electrodeposition process, we had a study on the influence of pulse period on the properties of electrodeposited gold layers using pulse reverse voltage power. We took pulse period as a single variable; other experiment parameters were shown in Table 1. Through changing the whole pulse period, we maintained the pulse period of positive impulse always being twice of negative pulse period. As shown in Fig.3, a set of positive pulse current was followed by a set of negative pulse current in one cycle.

The pulse period T varied from 15 ms to 120 ms. We made a set of contrast experiments. Test number and parameters of variable are listed in Table 2. The period of gold electrodeposition lasted 20 h per experiment. After 20 h, the cathode was took down, washed thoroughly by distilled water for 2 min, and then dried at 50 °C. Finally, 8 samples were obtained to be tested.

1.2 Test experiment

The microhardness of electroformed gold layers was measured by HVS-1000B type Vickers hardness tester, and the loading and holding time were 9.8 N and 15 s, respectively. The

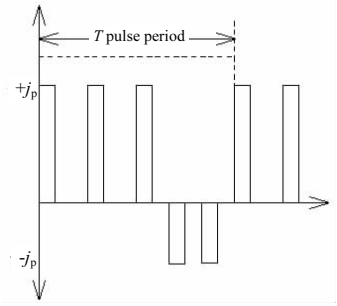

Fig.3 Pulse waveform of experiment

Table 1 Fixed experimental parameters

Positive/Negative Current density/A·dm^{-2}	Positive/Negative Duty cycle/%	Positive/Negative Pulse frequency/Hz
0.8/0.4	40/60	333/1000

Table 2 Pulse period of each experiment

Test number	Pulse period/ms
1	15
2	30
3	45
4	60
5	75
6	90
7	105
8	120

mean value of microhardness was calculated from five micro-areas per sample.

The grain size and preferential orientation were analyzed using Bruker D8-FOCUS X-ray diffractometer. The crystallites size perpendicular to the (*hkl*) crystalline plane can be calculated through Scherrer equation $D(hkl)=k\lambda/(\beta\cos\theta)-1$. In the equation, k is the Scherrer constant (k=0.89); $D(hkl)$ is the crystallites size perpendicular to the crystalline plane (nm); β is the full width at half maximum of the strongest diffraction reflection of the (*hkl*) crystalline plane (°); λ is the length of X-ray wave (nm). Typically the electrodeposited metal is nanocrystalline, so its grain size can be measured by the X-ray diffraction method. Preferential orientation of different samples can be measured by texture coefficient (TC). For (*hkl*) crystal plane, $TC_{(hkl)}$ can be written as:

$$TC_{(hkl)}=\frac{I_{(hkl)}/I_{0(hkl)}}{\sum_{i=1}^{n} I_{(h_ik_il_i)}/I_{0(h_ik_il_i)}} \quad (1)$$

where $I_{(hkl)}$ and $I_{0(hkl)}$ are the diffraction intensities of (*hkl*) crystal plane of the electrodeposited sample and the standard powder sample, respectively; n is the number of crystalline planes with relatively high diffraction intensity. If TC values of the crystalline planes are tantamount, preferred orientation is not evident.

2 Results and Discussion

The appearances of electroformed gold layers prepared at different pulse period are shown in Fig.4. We find these samples at different pulse periods are all qualified samples, with highly smooth and bright golden surfaces, in which obvious difference could not be found by naked eyes.

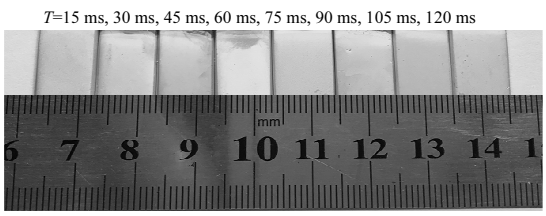

Fig.4 Appearance of samples taken at different pulse period

2.1 Hardness test

We got experimental Vickers hardness data of eight samples at the same test condition. To get a relatively specific and accurate value, each sample was tested five times at different areas. The average value of Vickers hardness of these five data was regarded as the Vickers hardness of the sample. The experiment data of Vickers hardness are shown in Table 3.

As shown in Table 3, different samples have different average Vickers hardness values. Fig.5 shows the relationship between pulse period and the Vickers hardness of electrodeposited gold layers. With the increase of pulse period, the Vickers hardness of gold layers originally increases and then decreases. Vickers hardness of different samples vary from 752 MPa to 1170 MPa. The highest Vickers hardness could reach to 1170 MPa when the pulse period is 60 ms.

2.2 Grain size

The XRD patterns of gold layers prepared at different pulse periods are shown in Fig.6. Compared with mineral PDF standard cards, these samples prepared at different conditions are all high purity gold. The strongest diffraction reflection appears at 2θ of about 38°, which corresponds to the (111) gold crystalline plane. Based on Fig.4, the gold layer prepared at different pulse periods has relatively higher X-ray diffraction peak intensity.

The grain sizes of the gold layers were calculated using Scherrer equation, and data were taken from the strongest

Table 3 Average values of Vickers hardness ($HV_{0.1}$) of different samples

Pulse period/ms	Five measurement of different micro-area at one sample/×10 MPa					
	No.1	No.2	No.3	No.4	No.5	Average value
15	95.7	86.9	88.8	84.0	89.2	88.9
30	92.9	90.0	83.6	91.2	99.4	91.4
45	117.7	114.8	109.8	111.4	108.7	112.5
60	111.4	117.1	128.4	110.3	117.7	117.0
75	129.1	111.4	109.3	107.7	112.5	114.0
90	92.4	96.7	90.8	92.4	101.2	94.7
105	77.6	81.6	72.4	72.7	78.2	76.5
120	69.1	76.0	87.6	76.0	67.5	75.2

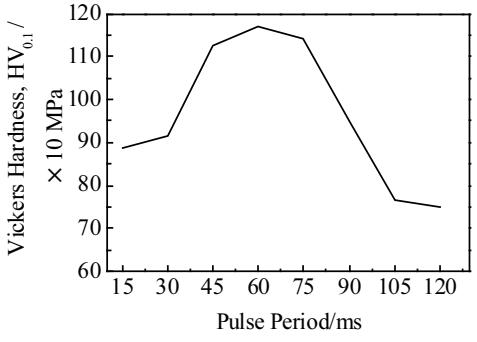

Fig.5 Relationship between pulse period and Vickers hardness

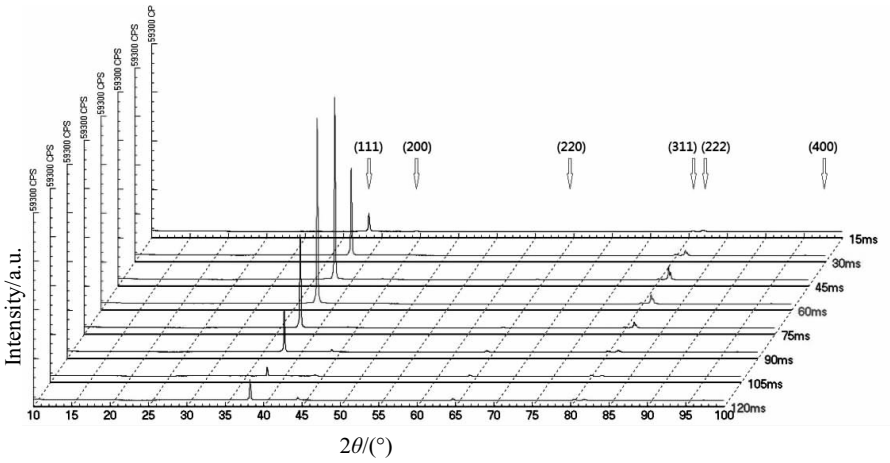

Fig.6 XRD patterns of gold layers prepared at different pulse periods

spectrum peak of each XRD pattern of the electrodeposited gold layers.

Comparing the grain sizes of different gold layers prepared under different experiment conditions (as shown in Table 4), we find gold layers prepared under our experiment condition are composed of nanoscale gold grains. With the change of pulse period, grain sizes of gold plating close to titanium plate (the cathode) vary from 27 nm to 54 nm, and grain sizes of gold plating surface vary from 63 nm to 81 nm.

As shown in Fig.7, we plotted the graph of grain sizes of gold layers close to Ti plate and gold layers surface with the change of pulse period. Grain sizes of layers close to Ti plate originally increases and then decreases with the increase of pulse period. But the grain sizes of gold layers surface have no obvious changing tendency.

In general, pulse period has a remarkable influence on the grain size in the initial stage. But with the increase of thickness of gold layer, grain size will increase. And the change of pulse period has small influence on the grain size of gold layer surface.

Hall-Patch relationship summarizes the correlation between grain size and hardness[7]. According to Hall-Patch relationship, the hardness will increase with the decrease of grain size. Contrast to that, in our experiments, we found gold layers with smaller grain size have no higher microhardness. On the contrary, gold layers with bigger grain size have much higher microhardness. This trend is in violation of Hall-Patch relationship.

Table 4 Comparison of grain sizes from different pulse periods

Pulse period/ ms	Grain size of layer close to Ti plate/nm	Grain size of gold layer surface/nm	$HV_{0.1}$/ ×10 MPa
15	27	63	88.9
30	35	67	91.4
45	47	73	112.5
60	54	73	117.0
75	53	73	114.0
90	46	74	94.7
105	40	81	76.5
120	27	73	75.2

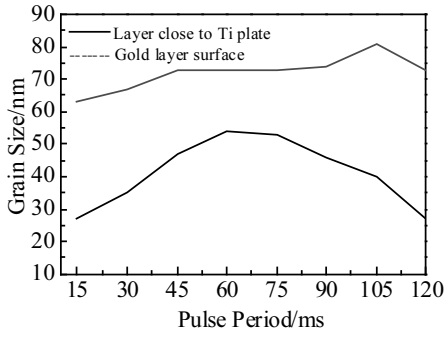

Fig.7 Relationship between pulse period and grain size

Schiotz[8] found when grain size decreased to 10 nm, the relationship between grain size and hardness would have an abnormal law. We made a boldly surmise that decrease of grain size have no direct relationship with microhardness when grain size is nanoscale. So we discussed other possible mechanism between pulse period and microhardness.

2.3 Layer texture

By calculating texture coefficient (TC) of the electrodeposited gold layers under different pulse periods (Table 5), we find these gold layers show strong (111) preferred orientations. Different samples have different texture coefficients (TC). Comparing one sample's Vickers hardness with its texture coefficient, we find electrodeposited gold layers with stronger (111) preferred orientation have higher Vickers hardness.

Gold is face-centered cubic lattice, with (111) crystalline plane possessing the maximum surface atomic density. (111) plane has the biggest hardness in all planes; besides, strong (111) preferred orientation may reduce surface roughness.

Table 5 Comparison of texture coefficient of the main crystal face

Pulse period/ms	Texture coefficient of the main crystal face/%					$HV_{0.1}$/ ×10 MPa
	(111)	(200)	(220)	(311)	(222)	
15	36.71	2.12	36.71	0	24.47	88.9
30	59.31	1.14	0	0	39.54	91.4
45	66.67	0	0	0	33.33	112.5
60	70.59	0	0	0	29.41	117.0
75	63.36	1.22	1.98	1.76	31.68	114.0
90	55.95	7.53	6.99	6.22	23.31	94.7
105	40.00	10.00	10.00	10.00	23.33	76.5
120	25.87	29.85	10.51	10.06	19.40	75.2

Maybe, we could change the preferred orientation of gold layers by adjusting parameters of pulse-reverse power, thus getting gold layers with higher hardness.

2.4 Surface morphology

The surface morphologies of gold layers prepared at different pulse periods are shown in Fig.8. As shown in Fig.8b, 8d, 8f, and 8h, gold layers present different granulated morphologies with grains in different sizes. The surfaces of gold layers are flat, but there are differences between samples prepared at different pulse periods. When pulse period is 60 ms, gold layer surface is the flattest. The surfaces are uneven at the minimum and maximum pulse period.

The nucleation pattern on crystal surface can be formulated by

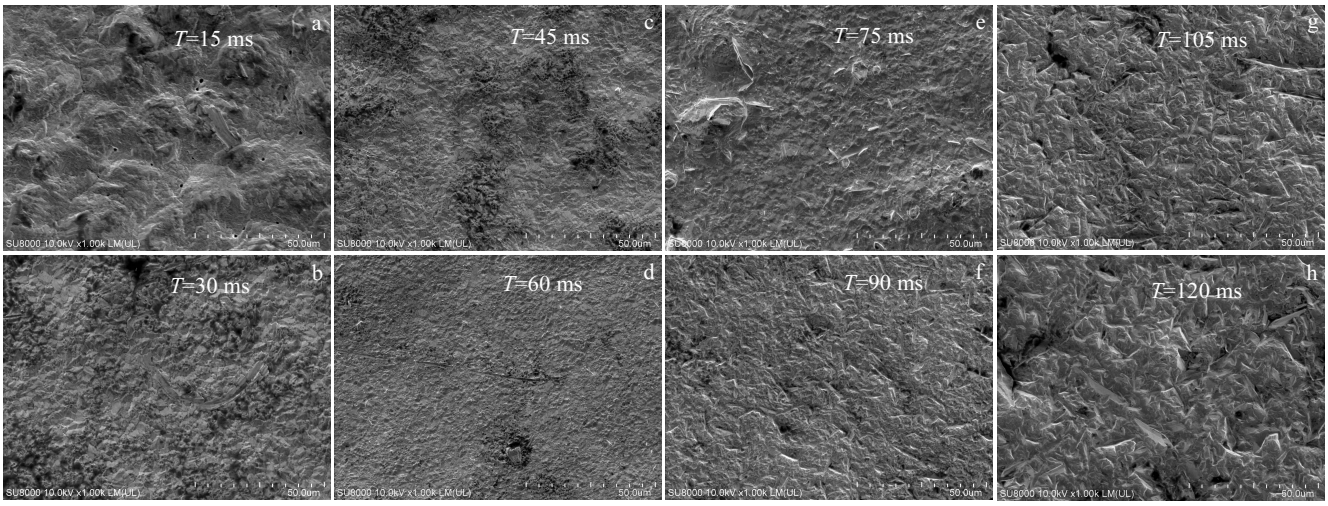

Fig.8 Surface morphologies of electrodeposited gold layer samples prepared at different pulse period

3 dimension progressive nucleation[9]. "Rounded mound" growth structures are found to form hard gold electrodeposits, and the rounded mounds consist of extremely fine gold grains[10].

The influence of pulse period on the morphology of gold layers could be explained as follows. Increase of pulse period would lead to change of microstructure. When pulse period is too long or too short, it could lead to rough microstructure. Pulse period of 45, 60, and 75 ms could result in the formation of flatter micro surface.

Comparing microhardness and microstructure of the same sample, we find that sample with a flatter micro surface has much higher Vickers hardness. In summary, the sample with stronger (111) preferred orientation has flatter micro surface, which results in higher Vickers hardness.

3 Conclusions

1) For the cyanide-free gold electrodeposition system with bidirectional pulse power, pulse period has great influences on properties of electrodeposited gold layer.

2) With the change of pulse period, gold layers obtained under different conditions have different Vickers hardness, the highest of which could reach to 1170 MPa. The gold layer with higher Vickers hardness and smoother surface, has stronger (111) preferred orientation.

3) By changing pulse period, we could get stronger (111) preferred orientation gold layer. Stronger (111) preferred orientation can help us get gold layer with higher hardness and smoother surface.

References

1 Xu Weiyuan. *Plating and Finishing*[J], 1987, 9(2): 7
2 Tang Peter T. *Electrochemica Acta*[J], 2001, 47(1-2): 61
3 Pang Mei, Li Hongyou, Li Zheyi *et al*. *Electroplating & Pollution Control*[J], 2010, 30(1): 11
4 Liu Zhengwei, Zheng Min, Robert D Hilty *et al*. *Electrochimica Acta*[J], 2011, 56(5): 2546
5 Frade T, Bouzon V, Gomes A *et al*. *Surface and Coatings Technology*[J], 2010, 204(21-22): 3592

6 Cheng Minyuan, Chen Keiwei, Liu Tzengfeng *et al*. *Thin Solid Films*[J], 2010, 518(24): 7468
7 Sylwestrowicz W, Hall E O. *Proceeding of the Physical Society. Section B*[J], 1951, 64(6): 495
8 Schiotz Jakob, Jacobsen Karsten W. *Science*[J], 2003, 301(5638): 1357
9 Li Y G, Lasia A. *Journal of the Electrochemical Society*[J], 1997, 144(6): 1979
10 Nakahara S. *Journal of Crystal Growth*[J],1986, 75(2): 212

脉冲周期对黄金电沉积层的影响

郑利珊[1]，袁心强[1]，雷　婷[2]
(1. 中国地质大学（武汉），湖北 武汉 430074)
(2. 武汉工程科技学院，湖北 武汉 430200)

摘　要：在无氰黄金电沉积工艺的基础上，利用双向脉冲电源，经过 20 h 的电沉积可以得到质量较好的厚度达 150 μm 的黄金样品。通过以脉冲周期为单一变量实验，研究了脉冲周期对黄金电沉积层的影响，利用扫描电镜、X 射线衍射仪以及维氏硬度计探讨了黄金电沉积层的微观形貌、平均晶粒尺寸以及维氏硬度。结果显示，当脉冲周期为 45~75 ms 时，电沉积层的维氏硬度 $HV_{0.1}$ 较高，最高可以达到 1170 MPa，且电沉积层具有较强的（111）晶面的择优取向。较强的（111）晶面择优取向伴随着电沉积层更加平整的微观形貌以及更高的维氏硬度。

关键词：双向脉冲；脉冲周期；黄金；维氏硬度；无氰电沉积

作者简介：郑利珊，女，1990 年生，博士生，中国地质大学（武汉）珠宝学院，湖北 武汉 430074，E-mail: zhenglishan901113@163.com