

ZBORNIK RADOVA

Proceedings

pisanih za 5. Međunarodnu konferenciju o
obnovljivim izvorima električne energije

5th International Conference on Renewable
Electrical Power Sources



2017

ZBORNIK RADOVA
pisanih za 5. Međunarodnu konferenciju o
obnovljivim izvorima
električne energije
Sava centar
12. i 13. oktobar 2017.

Izdavač
Savez mašinskih i
elektrotehničkih inženjera
i tehničara Srbije (SMEITS)
Društvo za obnovljive izvore
električne energije
Kneza Miloša 7a/II,
11000 Beograd

**Predsednik Društva za
obnovljive izvore
električne energije
pri SMEITS-u**
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Štampa
BSIDE d.o.o.,
Beograd

Tiraž
450 primeraka

PROCEEDINGS
5th International Conference
on Renewable Electrical
Power Sources
Sava Center
12 and 13 October 2017

Publisher
Union of Mechanical and
Electrotechnical Engineers and Technicians of Serbia
(SMEITS)
Society for Renewable Electrical
Power Sources
Kneza Miloša str. 7a/II,
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Printing
BSIDE d.o.o.,
Beograd

Circulation
450 copies

ISBN 978-86-81505-84-7

CIP - Каталогизација у публикацији - Народна библиотека Србије, Београд

502.171:620.9(082)(0.034.2)

MEĐUNARODNA konferencija o obnovljivim izvorima električne energije (5 ; 2017 ; Beograd) Zbornik radova pisanih za 5. Međunarodnu konferenciju o obnovljivim izvorima električne energije, [Beograd] Sava centar 12. i 13. oktobar 2017. [Elektronski izvor] = Proceedings / 5th International Conference on Renewable Electrical Power Sources ; [organizator Savez mašinskih i elektrotehničkih inženjera i tehničara Srbije (SMEITS), Društvo za obnovljive izvore električne energije]. - Beograd : Savez mašinskih i elektrotehničkih inženjera i tehničara Srbije - SMEITS, 2017 (Beograd : BSIDE). - 1 elektronski optički disk (CD-ROM) ; 12 cm

Sistemski zahtevi: Nisu navedeni. - Nasl. sa naslovne strane dokumenta. - Tiraž 450. - Abstrakti. - Bibliografija uz svaki rad.

ISBN 978-86-81505-84-7

1. Савез машинских и електротехничких инжењера и техничара Србије (Београд).

Друштво за обновљиве изворе електричне енергије

a) Енергетски извори - Одрживи развој - Зборници

COBISS.SR-ID 247351308

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FOREWORD

Intensive technological development, improved standard of living and population growth on Earth demand an increasing consumption of all forms of energy and, on the other hand, cause negative effects on the environment.

Having this in mind, the United Nations have defined the sustainable economic development in the Millennium Development Goals, and the presidents of seven most developed countries, so called G7 Group, signed the declaration in Brussels, in which, inter alia, they emphasised the following goals:

- *reduction of greenhouse gas (GHG) emissions,*
- *improvement of energy efficiency, and*
- *promotion of the use of clean and sustainable energy technologies and continuation of investment in innovations.*

Particularly negative effects on the environment come from the electricity generation plants, taking into account that they are fuelled by fossil fuels. Therefore, the increased use of renewable electrical power sources is expected in the following period, both globally and in this country.

The main goal of the 5th international conference on renewable electrical power sources is to analyse the comparative advantages and disadvantages of modern solutions in the field of renewable electrical power sources used globally and in this country, and to provide a constructive platform for the exchange of competent opinions and ideas related to the development and use of these sources.

This international conference is for the fifth time organised by the Society for Renewable Electrical Power Sources, which has been a part of SMEITS (Serbian Union of Mechanical and Electrical Engineers and Technicians) since 2010.

Belgrade, October 2017

PREDGOVOR

Intenzivan tehnološki razvoj, rast životnog standarda i porast broja ljudi na Zemlji, zahtevaju sve veću potrošnju svih vidova energije, dok se na drugoj strani kao posledica, javljaju negativni efekti po životnu sredinu. Imajući ovo u vidu, UN su definisale održiv ekonomski razvoj u Milenijumskim ciljevima a predsednici sedam najrazvijenih država, takozvane Grupe G7, potpisali su deklaraciju u Briselu u kojoj su, između ostalih, istakli i sledeće ciljeve:

- *smanjenje emisije gasova staklene bašte,*
- *unapređenje energetske efikasnosti, i*
- *promovisanje primene čistih i održivih energetskih tehnologija i nastavak ulaganja u istraživanja i inovacije.*

Posebno negativan uticaj na životnu sredinu imaju postrojenja za proizvodnju električne energije imajući u vidu da kao pogonsko gorivo uglavnom koriste fosilna goriva. Zbog toga se u svetu, kao i kod nas, u narednom periodu očekuje povećanje primene obnovljivih izvora električne energije.

Osnovni cilj 5. Međunarodne konferencije o obnovljivim izvorima električne energije jeste da se analiziraju uporedne prednosti i nedostaci savremenih rešenja u oblasti obnovljivih izvora električne energije koja se primenjuju u svetu i kod nas, i da se obezbedi plodotvorna razmena kompetentnih mišljenja i ideja vezanih za razvoj i primenu ovih izvora.

Ovaj međunarodni skup po peti put organizuje Društvo za obnovljive izvore električne energije koje u okviru Saveza mašinskih i elektrotehničkih inženjera i tehničara Srbije (SMEITS) postoji od 2010. godine.

U Beogradu, oktobra 2017.

ENERGETSKI EFIKASNI PULSNO-REVERZNI REŽIMI GALVANIZACIJE

ENERGY EFFICIENT PULSE-REVERSE REGIMES OF ELECTRODEPOSITION

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Pulsno reverzni režimi se primenjuju u cilju dobijanja metalnih prevlaka sa sličnim ili boljim karakteristikama, u poređenju sa primenjenom konstantnom strujom. Pulsno reverzni režimi povećavaju produktivnost i energetsku efikasnost uz upotrebu većih gustina struje. U ovom radu, istraživana je optimizacija sistema za standardnu elektrodepoziciju pogodnim izborom trajanja i intenziteta impulsa. Pokazano je da se može postići energetska efikasnost procesa uz zadovoljavajući kvalitet prevlaka i bez primene skupih i često opasnih aditiva u elektrolitu.

Ključne reči: Energetska efikasnost, Elektrohemiska depozicija, Pulsno-reverzni režimi, Kvalitet prevlake

Pulse reverse power modes are used in order to obtain metal coatings with similar or better characteristics, compared with the coatings produced by constant current. Pulse reverse modes increase production and energy efficiency of electroplating cells with the use of higher density currents. In this paper, we investigate optimisation of systems for standard electrodeposition by choosing the suitable duration and intensity of the pulses. It was shown that energy efficiency of the process can be achieved with satisfactory quality of coatings and without expensive and often dangerous additives in the electrolyte.

Key words: Energy efficiency Electrochemical deposition, Pulse-reverse regimes, coating quality

1 Introduction

Modern methods of electrochemical deposition of metal coatings need to meet the requirements for: high surface quality (gloss, wear resistance, hardness), good adhesion to the substrate, fast deposition, uniform application even on inaccessible parts, etc [1]. Depending on desired characteristics the appropriate composition of the electrolyte is selected. The complete electrolyte with additives may contain hazardous substances. The tendency is to apply pulse reverse power modes instead of constant current power supply (DC) in order to obtain sufficiently good quality coating using metal salts solutions and thereby avoiding dangerous electrolytes [2,3]. For each specific purpose, it is necessary to determine parameters of power pulse which will provide required quality in such an electrolyte which was the aim of many studies [4-6]. Achieving the energy efficiency of the process by meeting the previous was the main objective of the investigation. Contribution to the mentioned goal for gold, silver and copper will be given in this research.

2 Pulse reverse power modes

Three types of power supply regimes in galvanotechnique that exhibit significant benefits (in economic, energy and environmental terms) compared to the conventional constant current power supply (DC) are: pulse reverse current (PRC), pulsating current (PC) and sinusoidal alternating current superimposed on the constant current (AC) [7,8].

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2.1 Pulsating current

Pulsating current means periodical repeating of rectangular electrical pulses. It is characterized by the intensity and duration of the cathodic current pulse and pause duration (t_0), as shown in Figure 1. Pulsating current is characterized by cathodic current amplitude j_c , time of deposition on the cathode t_c (on period or pulse) and the time period when the system is at standstill (off period or pause).

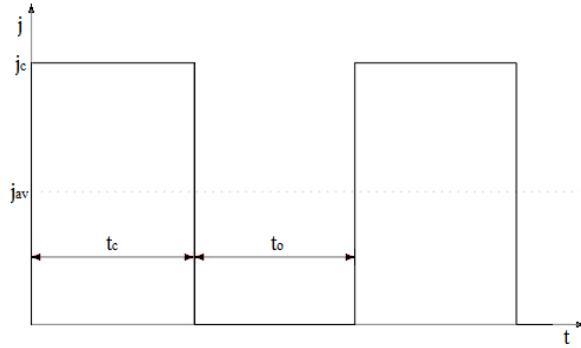


Figure 1. Timing diagram of pulsating current

The mean value of the current density is given by the equation (1):

$$j_{av} = \frac{j_c t_c}{t_c + t_0} \quad (1)$$

By introducing the current pause system relaxes in each period leading to straighter and shinier coat. Besides, high values of overvoltage, which increase energy efficiency, are not reached. The growth of dendrites is greatly reduced even at significantly higher currents (j_{av}) compared with the critical current in DC mode (j_{DC}) [7-11].

2.2 Reverse current

Timing diagram of reverse current is shown in Figure 2. The diagram is characterized by cathodic current density j_c , anodic current density j_a , as well as the duration of impulse in the direction of cathode and anode, t_c and t_a .

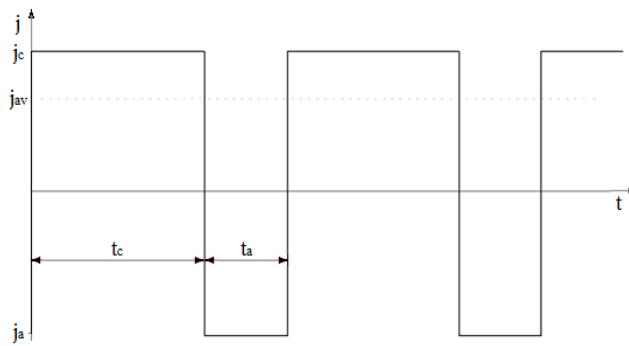


Figure 2. Timing diagram of reverse current

Average value of the current density is calculated by Equation (2):

$$j_{av} = \frac{j_c t_c - j_a t_a}{t_c + t_a} \quad (2)$$

In addition to the uniformity and shininess of coating, the great advantage of this regime is exceptional following of substrate sharp edges and good covering of "concealed" surfaces (narrow and long hole, for example) which is of great importance in the electronics industry [12].

3 Experimental

As a PR power source and process monitoring, system based on the PC and LabVIEW software platform was used, while the hardware interface, power amplifier, and software applications were base on the results of development at the Technical Faculty in Bor [13,14]. Hardware and software that use controlled current regime allow obtaining the galvanic coatings of different metals and alloys (selected by a user; primarily precious metal coatings) with improved quality and energy efficiency. Besides PC, hardware includes commercial ADDA converter and external interface for analog signal processing. Commercially available converter NI 6251 from National Instruments was used for ADDA conversion [15].

The most important characteristics of converter for this application are:

- number of analog input channels 8/16,
- number of analog output channels 2
- IO voltage levels ± 5 or ± 10 V
- Number of AD conversion bits 16
- Number of DA conversion bits 16
- Nonlinearity of amplification 0.024%

Software was the LabVIEW package (National Instruments) [16] that is considered as a system design platform with high standard in measuring techniques and virtual instruments. Voltage measurement is carried out so that the averaging, displaying and memorizing of measured voltage are performed after n sampled values. Also, graphic illustration of voltage changes in time is shown on the control panel. Figure 3 shows the control panel.

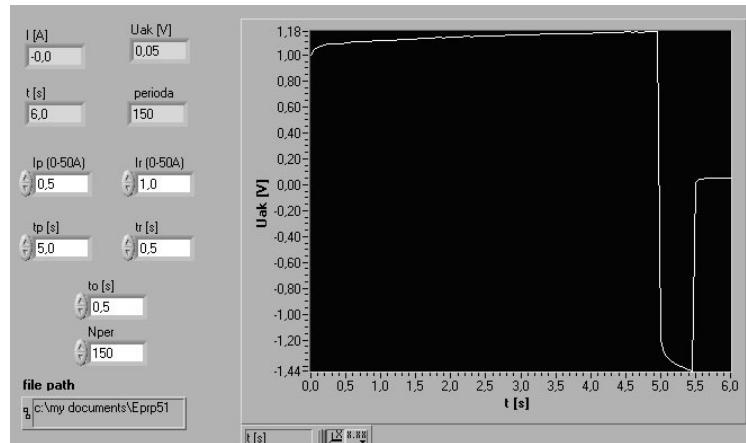


Figure 3. Control panel

3.1 Energy efficiency

The assessment of energy efficiency was carried out based on the measurements of consumed electric energy for obtaining of certain coating thickness on the same substrate using different regimes. Measurements were done by a mono-phase electric energy meter EWG E11. Consumption in DC regime is taken as a reference value, while the savings in PR mode are shown in percentages:

$$W = \frac{W_{DC} - W_{PR}}{W_{DC}} \cdot 100\% \quad (3)$$

4 Results and Discussion

Typical examples for electrochemical deposition of copper, silver and gold in various power regimes were selected from large number of experiments, while all other experiment conditions remain the same.

Microphotographs of copper coating on the copper substrate-wire with diameter of 50 μm in the electrolyte of 1M H_2SO_4 + 0.5M CuSO_4 at room temperature are shown in Figure 4.

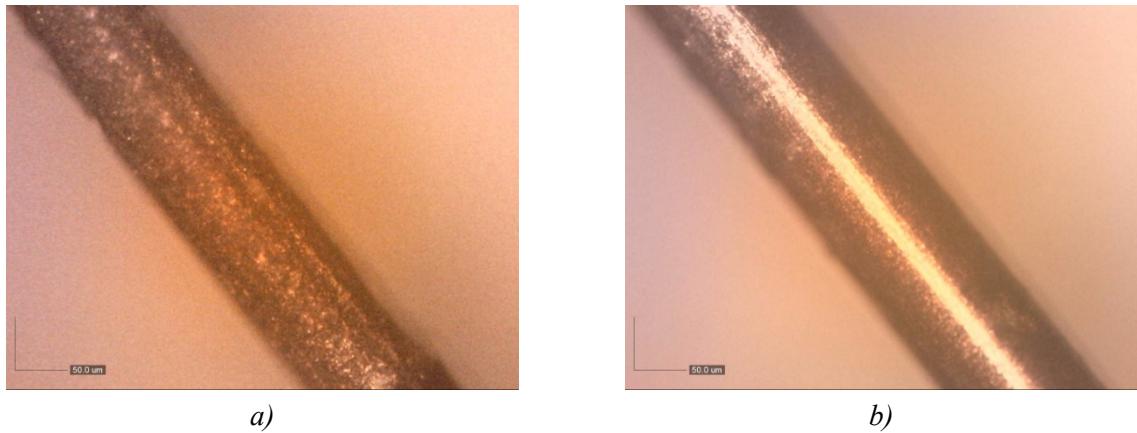


Figure 4. Microphotographs of the copper coating surface under: a) DC regime/mode $j_{dc} = 2.2 \text{ A/dm}^2$ and b) PC regime $j_{av} = 2.2 \text{ A/dm}^2, f = 10 \text{ Hz}$

There are significant differences in the surface quality when PC mode is applied, and the same other conditions of deposition.

Following of sharp edges of substrate is not satisfactory in the DC mode; therefore it is necessary to apply the PRC regime that gives excellent results. Power supply voltage, i.e. voltage between anode and cathode was monitored in each experiment. In case of gilt, diagram shown in Figure 5a was obtained. Result of simulation in software package ORCAD for the same system is shown in Figure 5b. Simple model that satisfy needs in millisecond region of work was applied: serial connection of resistor and capacitor ($R = 11.6 \Omega$ and $C = 15 \text{ mF}$).

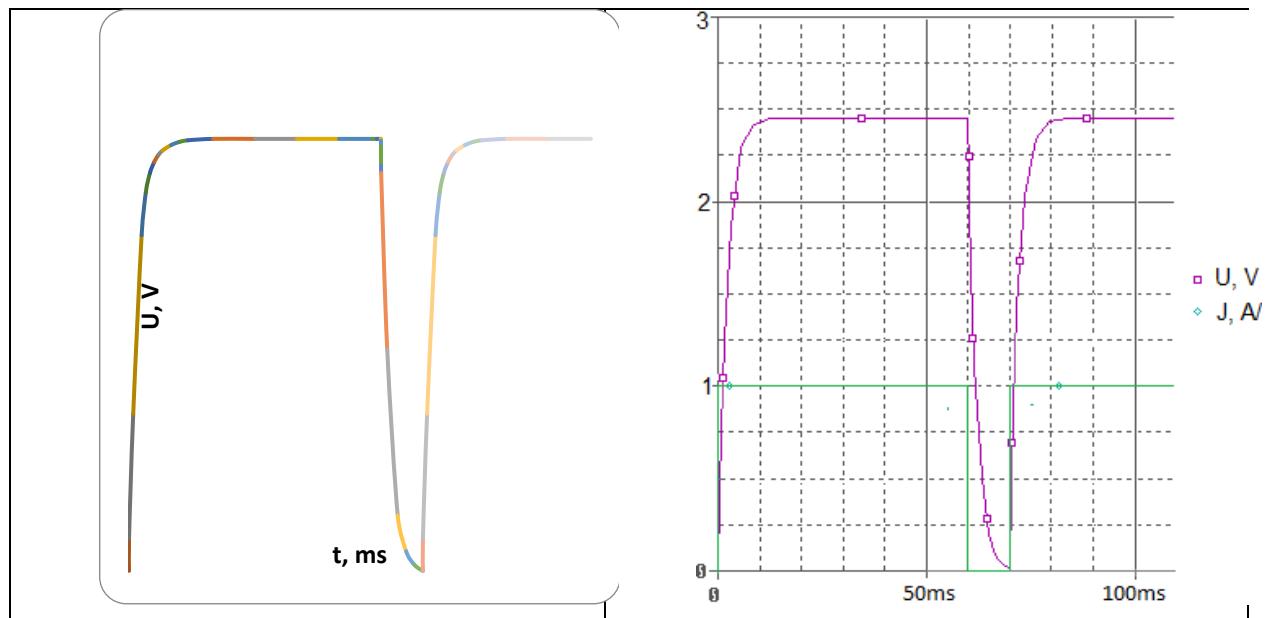


Figure 5. Measured values (a) and result of simulation (b) of voltage supply in PC regime/mode for gilding under $j_{av} = 0.9 \text{ A/dm}^2, f = 14 \text{ Hz}$

Comparative overview of the results and qualitative estimations for three types of examined coatings (copper, silver and gold) using various power supply regimes (DC, PC and PRC) is given in Table 1.

Table 1. Comparative overview of the results

Coating	Regime	Coating quality	Energy savings %	Edges following	Ecological benefit
Copper	DC	Bad	0	bad	0
	PC	Good	5.0	bad	significant
	PRC	Good	4.1	excellent	large
Silver	DC	Bad	0	very bad	0
	PC	good	8.0	bad	significant
	PRC	good	6.4	excellent	large
Gold	DC	bad	0	bad	0
	PC	good	5.5	acceptable	significant
	PRC	good	4.8	excellent	significant

5 Conclusion

The study presented theoretical analysis and experimental results of gold, silver, and copper film plating by applying pulse-reverse regime. Multiply increase of operating current density can be reached by applying of PR regime and thereby to receive equally good and shiny coatings. Also, remarkable following of substrate sharp edges as well as good covering of "concealed" surfaces make this method irreplaceable in some industrial branches. According to the economical aspect, even more important result of application this method of metals deposition is that thinner coatings completely and uniformly covers the surface of the substrate. Significantly higher energy efficiency is confirmed. Series of experiments indicated that expensive and dangerous additives can be eliminated by a suitable selection of the power source parameters.

6 Acknowledgement

The authors gratefully acknowledge financial support from the Ministry of Education and Science, Government of the Republic of Serbia through the Projects No. 172 060.

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