USING PULSE MODES IN NON-CHROMIUM ELECTROLYTES FOR ELECTROPOLISHING

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The effect of different types of electrolysis (direct and pulse mode) on the process of electropolishing of stainless steel AISI-304L in non-chromium electrolytes was studied. Lactic acid, tartaric acid and urotropine were used as inhibitors of etching. Solutions of electropolishing were a mixture of sulfuric and phosphoric acids with a 50:50 mass content. It is established that electrochemical polishing allows improving the appearance of the surface of stainless steel. The brightness of the initial surface had mirror-like appearance starting from 10 minutes of polishing. The use of pulsed electrolysis instead of stationary mode leads to a decrease in metal removal and pitting corrosion of polished surface of stainless steel (AISI-304L) down to 1.5-2 times. Microhardness of stainless steel reduces down to 2 orders of magnitude compared to the initial surface.

Stainless steel is the most frequently used material for construction of vessels, pipelines, valves and various types of equipment used in food processing, chemical, building, medical and marine industries [1, 2, 3].

Well-known methods of surface finishing such as mechanical or chemical polishing allow one to provide the surface roughness over a range of 1.6–0.012 µm. However, such methods have a number of significant disadvantages such as being multistage and having a large labor input, high surface quality requirements, complexity of treating complex-profile details and inability to provide high accuracy requirements to the treated surface, formation of the defective surface layer during treating, negative influence on physical and mechanical properties of the surface, etc [4]. The anodic treatment is a powerful instrument for polishing metal surface [5].

Electropolishing of stainless steel in industry is usually performed in solutions, containing concentrated acids (phosphoric [6], sulfuric, acetic, perchloric [7], or their mixtures [8, 9, 10]) or a mixture of sulfuric acid and chromium (VI) oxide [1] at sufficiently high concentration and relatively high current densities. In some cases, mixtures of mineral and organic acids are used. Etching inhibitors are usually added to the electrolytes of polishing. Leveling and smoothing of the surface microprofile during

electrochemical polishing occurs due to the unequal rate of dissolution of recesses and protruding areas.

There are various explanations of the mechanism of the process. One of the first studies connects smoothing of the surface during electropolishing with the formation of a viscous layer of anodic dissolution products on it. This layer («sticky film») has a high electrical resistance and uneven thickness in different parts of the rough surface of polished metal: the higher in the recesses, the lower over the protruding areas. Since the resistance to the current passage on the recesses is lower than the recesses itself, it dissolves protruding areas, leading to alignment of the surface microroughness. A major role is played by the diffusion rate of products of the anodic dissolution from the electrode surface into the electrolyte, which also varies from the recesses and protruding parts [11]. Due to the fact that the concentration gradient of dissolution products is higher at the anode protruding parts than in the recesses, the former will dissolve protruding parts.

According to another theory, the surface smoothing is explained by the formation of the oxide film on the surface, which is more stable in the recesses and has a higher thickness than the protruding areas. A lower degree of passivation of the protruding sites could be explained by their increased chemical activity and more intensive dissolution of the oxide film over them. The oxide layer on the protruding cites is thinner and has higher concentration gradient than in recesses. The increased solubility of the oxide film on the protruding parts is also associated with higher porosity films on sharp protruding areas [12].

A third theory involves the acceptor mechanism. It is proposed that the acceptors (water or water-related species) are the key factor for starting the effective electropolishing process. Based on this mechanism, the electrolyte usually contains a small quantity of acceptor species, and the adsorbed ions would accumulate on the anode surface to form an adsorbed layer. This layer increases the overpotential of metal dissolution and hinders the solvation of metals ions with acceptors. Theoretically, the mechanism of preferential adsorption of shielding molecules is considered to involve the acceptor mechanism because the quantity of water in the electrolytes is small. Addition of glycerol suppresses the influence of the metal microstructure on the dissolution rate [13, 14].

Pulse current (PC) could be used as a tool of producing surfaces with unique properties not obtainable by direct current (DC). In PC electrolysis three new parameters such as peak current density, current pulse on-time (T_{on}), and current pulse off-time (T_{off}) are introduced. It is known [15] that these parameters could improve the current distribution alter the prevailing mass transport conditions and permit the control surface microstructure [16, 17]. One of the promising methods of

finishing the metal surface is electropulse polishing (EPP). Currently, the EPP is used mainly for finishing the exterior surfaces of products for various applications, providing a reduction in the level of roughness R_a to 0.32–0.06 μm [6].

The use of an appropriate electrolyte and operating conditions in the EPP process will produce smooth and bright surfaces that are free of defects, stress, and contaminations.

Research мethodology

The bath composition and parameters used for electropolishing are listed in Table 1. The anodes were plates of stainless steel AISI-304L with dimensions 30×25×2 mm. Prior to the use, the working electrodes were mechanically grinded with silicon carbide papers (down to R_a 0.25–0.4 μm). Electropolishing was carried out by the steady-state and pulsed galvanostatic techniques. Pulsed galvanostatic mode was conducted by using KRAFT Klex (Sweden). The duty cycle (d.s.) of the pulses [d.s.=$T_{on}/(T_{on}+T_{off})$] was set constant at the value of 67 %. The weight loss of metal (W_i) was determined by weighing the samples before and after polishing and integral quantity of electricity according to Faraday's law. The weight loss of the metal was measured in all the studied solutions at a current density of 0,5 A/cm^2 under stirring at temperature of 50-55 °C. The temperature was controled with a water bath BW-04 (Belarus). Roughness of the surface was measured with a profilograph-profilometer Abris PM7 (Russia). Tendency to pitting corrosion was determined in solution of 3% NH_4Cl and 2% $NH_4Fe(SO_4)_2$ (T=30°C) after an hour of exposure.

Table 1. Bath composition and parameters used for electropolishing of stainless steel

Electrolyte composition			
	№1	№2	№3
H_2SO_4, %	50	50	50
H_3PO_4, %	50	50	50
Tartaric acid, g/l	50	–	–
Urotropine, g/l	–	50	–
Lactic acid, g/l	–	–	40
Electrodeposition conditions			
Temperature	50–55 °C		
Substrate	AISI-304L		
Cathode	AISI-304L		
Current density	0.5 A/cm^2		
Type of current	Direct (DC)or Pulse (PC)		
Duty cycle (d.c.)	67 %		

Results and Discussion

The electropolishing was carried out to a micro-roughness value of 0.015 µm. The results of the dependence of R_a on the polishing time are shown in Fig. 1 (*1*).
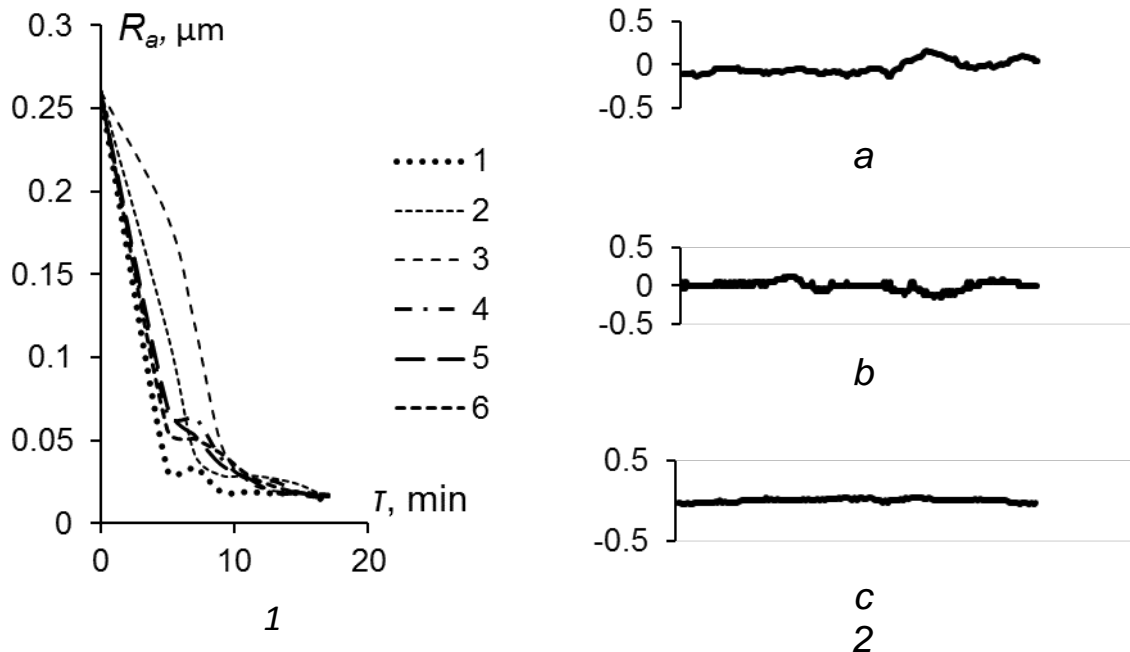

Fig. 1. Dependence of micro-roughness on the time of electrolysis (1); Profilograms of samples in electrolyte with addition of urotropine during electrolysis in stationary mode, min: a – 3; b – 7; c – 17 (2).
Pulsed mode: 1 – tartaric acid; 3 – urotropine; 6 – lactic acid; steady-state mode: 2 – tartaric acid; 5 – lactic acid; 4 – urotropine

Significant changes in the parameter R_a during 9 min of electrolysis were observed. After 9 minutes, the differences in the micro-roughness values are insignificant. The greatest smoothing is observed in the electrolyte with tartaric acid under steady-state electrolysis.

The results of corrosion tests of electropolished stainless steel in the presence of various etching inhibitors are presented in Table 2.

Table 2. Characteristic of pitting corrosion of stainless steel AISI-304L

Type of inhibitor	W_i, g/m²·h	K, g/(m²·year)	Number of pits per cm²
Pulsed current			
Tartaric acid	1.55	92.72	2
Urotropine	0.55	32.72	2
Lactic acid	1.36	81.81	2
Direct current			
Tartaric acid	2.45	180.3	5
Urotropine	2.00	89.36	2
Lactic acid	1.91	95.85	3
Original surface			
–	1.91	96.72	3

It was determined that the surface polished in the stationary electrolysis mode in a solution with addition of tartaric acid has in 2.5 times more pitts than in the pulsed electrolysis. Pulsed electrolysis allows reducing the corrosion rate down to 2-3 times by using tartaric acid and urotropine.
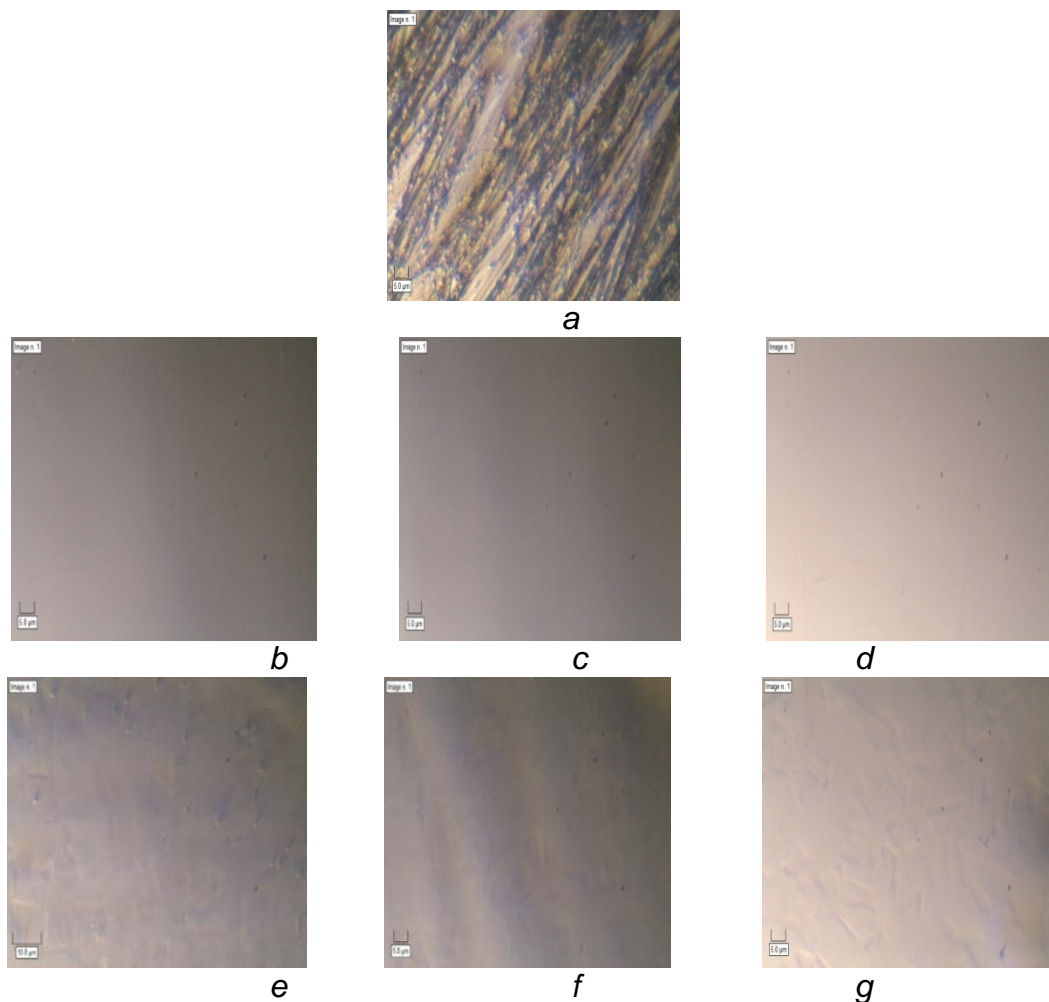
Micrographs of stainless steel are shown in Fig. 2.

Fig. 2. Micrographs of stainless steel surface AISI-304L electropolished for 17 minutes at temperature 50 °C.
a – initial surface; pulsed electrolysis: *b* – urotropine, *c* – tartaric acid, *d* – lactic acid; steady-state electrolysis: *e* – urotropine, *f* – tartaric acid, *g* – lactic acid

Electrochemical polishing allows improving the appearance of the surface of stainless steel. It forms a flat uniform structure. The electrolysis mode does not influence the topography. The brightness of the initial surface was increased due to polishing and had mirror-like appearance starting from 10 minutes of polishing.

Optimal conditions of electrolysis and surface characteristics of stainless steel AISI-304L are presented in Table 3.

As it is shown in Table 3 the use of pulsed electrolysis reduces the value of microhardness from 309 to 172-185 HV. A similar decrease in

microhardness [4] was previously attributed to the removal of the riveted surface layer of the metal during the polishing process. In the case of pulsed electrolysis, the weight loss of metal is 1.5 to 2 times less than that in stationary (steady-state) mode. The lowest loss of metal was observed in the solution with urotropine (0.195 g in pulsed electrolysis, 0.332 g in the stationary mode).

Table 3. Optimal conditions of electrolysis and surface characteristics of stainless steel (AISI-304L) after 17 minutes of polishing ($R_a \approx 0.015$ μm)

Parameter	Urotropine	Tartaric acid	Lactic acid
Initial surface microhardness 309 HV			
Steady-state mode			
Δm, g	0.323	0.290	0.308
Microhardness, HV	176.0	171.6	187.0
v, μm/h	0.014	0.015	0.014
Pulsed mode			
Δm, g	0.195	0.224	0.207
Microhardness, HV	183.0	173.6	185.0
v, μm/h	0.0144	0.0141	0.0140

Conclusions

Thus, the use of pulsed electrolysis instead of stationary mode leads to a decrease in metal removal and pitting corrosion of polished surface of stainless steel (AISI-304L) down to 1.5-2 times. Microhardness of stainless steel reduces down to 2 orders of magnitude compared to the initial surface.

References

[1] A.M. Awad, E.A. Ghazy, S.A. Abo El-Enia, M.G. Mahmoud Electropolishing of AISI-304 stainless steel for protection against SRB biofilm, Surface and Coatings Technology, 206, 3165–3172, 2012.

[2] Hoffman J. Machine Design. 73, 80, 2001.

[3] Chandrasekar M.S., Pushpavanam M. Pulse and pulse reverse plating—Conceptual, advantages and applications, Electrochimica Acta, 53, 3313–3322, 2008.

[4] Sinkevich Yu.V. Electropulsed polishing of iron, chromium and nickel alloys, BNTU, Minsk, 2014.

[5] V. Vignal, J.C. Roux, J.M. Olive, D. Desjardins, V. Genton Morphological analysis of stainless steel scale like surface morphology using STM and AFM, Acta mater., 46, 149–157, 1998.

[6]   S. Feliu, J.A. Gonzalez D.C. and A.C. in the dissolution and electropolishing of steel in organic H_3PO_4 baths, Corrosion Science, 11, 307–318, 1971.

[7]   V. Vignal, J.C. Roux, S. Flandrois, A. Fevrier Nanoscopic studies of stainless steel electropolishing Corrosion Science 42, 1041–1053, 2000.

[8]   S.C. Chen, G.C. Tu, C.A. Huang The electrochemical polishing behavior of porous austenitic stainless steel (AISI 316L) in phosphoric-sulfuric mixed acids, Surface and Coatings Technology, 200, 2065–2071, 2005.

[9]   M. Datta, L.F. Vega, L.T. Romankiw, P. Duby Mass transport effects during electropolishing of iron in phosphoric-sulfuric acid, Electrochimica Acta, 37, 2469–2475, 1992.

[10] L. Ponto, M. Datta, D. Landolt Electropolishing of iron-chromium alloys in phosphoric acid-sulphuric acid electrolytes, Surface and Coatings Technology, 30, 265–276, 1987.

[11] G.H. Sedahmed A mass transfer study of the electropolishing of metals in mechanically agitated vessels, Int. Comm. Mass Transfer, 28, 257–265, 2001.

[12] Kudryavcev N.T., Electrolytic coating by metals, Chemistry, Moscow, 1979.

[13] Chi-Cheng Lin, Chi-Chang Hu, Tai-Chou Lee Surface and Electropolishing of 304 stainless steel: Interactive effects of glycerol content, bath temperature, and current density on surface roughness and morphology, Coatings Technology, 204, 448–454, 2009.

[14] Chi-Cheng Lin, Chi-Chang Hu Electropolishing of 304 stainless steel: Surface roughness control using experimental design strategies and a summarized electropolishing model, Electrochimica Acta, 53, 3356–3363, 2008.

[15] Qu N.S., Zhu D., Chan K.C.,Lei W.N. Pulse electrodeposition of nanocrystalline nickel using ultra narrow pulse width and high peak current density, Surface and Coatings Technology, 168, 123–128, 2003.

[16] Marlot A., Kern P., Landolt D. Pulse plating of Ni–Mo alloys from Ni-rich electrolytes, Electrochimica Acta, 48, 29–36, 2002.

[17] Thiemig D., Lange R., Bund A. Influence of pulse plating parameters on the electrodeposition of matrix metal nanocomposites, Electrochimica Acta, 52, 7362–7371, 2007.