

The Plasma Electrolytic Modification of Metals and Alloys

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By

Pavel Belkin, Sergei Kusmanov,
Sergey Shadrin and Ilya Dyakov

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Fig. 3-34. Dependence of oxide layer thickness of medium carbon steel in 10 % solution of ammonium acetate on heating voltage for 5 min [Grishina, Zhironov, Belkin, and Dikusar 2008, 390-395].

Fig. 3-35. Oxygen concentration profiles in low-carbon steel after its anodic heating in electrolyte containing 10 % ammonium chloride, 5 % nitric acid, 10 % glycerol for 7 min. Saturation temperatures are: 650 °C (1), 750 °C (2), 750 °C (3), 850 °C (4), and 950 °C (5). All samples are cooled in electrolyte, except (3) which is cooled in air [Belkin and Kusmanov 2016, 1046-1063].

Fig. 3-36. Change in concentration of ammonium ions during heating of medium carbon steel at 200 V [D'yakov and Naumov 2006, 4-9].

Fig. 3-37. Change in concentration of chlorine ions during heating of medium carbon steel at 200 V [D'yakov and Naumov 2006, 4-9].

Fig. 3-38. Changing pH of a 10 % solution of ammonium chloride during heating of medium carbon steel at 200 V [D'yakov and Naumov 2006, 4-9].

Fig. 4-1. Dependence of vertical temperature gradient of sample (10 × 10 × 70 mm) on electrolyte flow rate for powder iron-graphite (1) and low-carbon steel with 0.1 % C (2) [Belkin and Kusmanov 2016, 531-546].

Fig. 4-2. Hardness profile along hardened sample-anode ($\varnothing 10 \times 50$ mm, steel with 0.45 % C). 1, 2, 3 – combination of vertical and radial jets; 4, 5, 6 – only vertical jets. Electrolyte flow rate is 2.0 L/min (1, 4), 1.5 L/min (2, 5), and 1.0 L/min (3, 6) [Belkin and Kusmanov 2016, 531-546].

Fig. 4-3. Effect of speed of electrolyte (10 % ammonium nitrate) jet on anode temperature at 250 V. Jet length is 2.5 mm (1), 5.0 mm (2), 10 mm (3), 12.5 mm (4), and 15 mm (5) [Belkin, Belikhov, and Sokolov 2000, 8-11]. Cylindrical samples-anodes ($\varnothing 10 \times 15$ mm, steel with 0.45 % C) are used.

Fig. 4-4. Microhardness profile from surface to interior of cathode hardened steel with 0.3 %C treated during 8 s. DC voltage is 85 V, current density is 2 A/cm². AC voltage is 85 V, current density is 1 A/cm², frequency is 350 kHz [Ioshinory 1977, 116-117]. Cylindrical samples ($\varnothing 10 \times 20$ mm) are used.

Fig. 4-5. Dependence of weight loss of low-carbon steel with 0.3 wt.% C (1) and medium carbon steel with 0.45 wt.% C (2-4) on friction time. 1 – sample with carburized layer (0.75-0.8 mm) and hardness of 40-50 HRC; 2 – hardened sample followed by tempering and hardness of 48-50 HRC; 3 – sample after the surface hardening by heating followed by quenching in oil with layer of 2-2.2 mm and hardness of 48-50 HRC; 4 – sample heated in the solution of potassium carbonate (25 wt.%) during 10 s (current of 150 A) followed by quenching in oil with hardness of 50-53 HRC [Ivanov, Dyachenko, and Alekseeva 1966, 72-73].

Fig. 4-6. Schemes for measurements of structure-sensitive values for non-destructive testing of PEH. 1 – bath; 2 – workpiece; 3 – standard; 4 – AC power supply; 5 – ammeter, 6 – measuring the phase shift; 7 – AC compensator; 8 – AC bridge; 9 – circuit for comparison; 10 – indicator [Mirsalimov 1971].

Fig. 4-7. Dependence of voltage U and workpiece temperature T on processing time for three-stage heating.

Fig. 4-8. Dependence of axial temperature of sample-anode ($\varnothing 10 \times 50$ mm, steel with 0.5 % C) on vertical coordinate. Voltage is 200 V. One jet (1) and four jets (2-5). Distance from jets axes to chamber axis is 10 mm (2), 13 mm (3), 16 mm (4), and 19 mm (5). Solution of 10 % ammonium chloride was used [Suminov, Belkin, Apelfeld, Lyudin et al. 2011, 351].

Fig. 4-9. Hardness distribution on surface of steel sample-anode ($10 \times 10 \times 60$ mm, steel with 0.45 % C) hardened in solution of ammonium chloride (10 %). Voltage is 260 V. 1 – concentrated longitudinal flow with electrolyte flow rate 6.5 L/min; 2 – distributed longitudinal flow (6.1 L/min) where distance of longitudinal jet from chamber axes is 19 mm [Belkin and Kusmanov 2016, 531-546].

Fig. 4-10. Sample-cathode temperature vs processing time at different voltages. Pulse duration is 1 s, duty cycle is 90 %. Cylindrical samples ($\varnothing 8 \times 60$ mm, steel with 0.5 % C) and solution of sodium carbonate (50 g/l) are used [Luk, Leung, Miu, and Pashby 1997, 833-838].

Fig. 4-11. Schematic of plasma electrolytic heater [Tyurin and Pogrebnjak 2001, 293-299].

Fig. 4-12. Dependence of workpiece surface temperature on the heating time (1, 2, 3) and that of cooling one (4, 5, 6, 7) under periodical switching on of electric potential, which has voltage: (1) $U_1 = 320$ V; (2) $U_2 = 200$ V; $U_1 = 320$ V; $U_{cool} = 30$ V; (3) $U = 220$ V as well as in cooling: (4) $U_{cool} = 60$ V; (5) $U_{cool} = 40$ V; (6) $U_{cool} = 20$ V; (7) $U_{cool} = 0$ V [Tyurin and Pogrebnjak 2001, 293-299].

Fig. 4-13. Hardness of quenched layer on alloy surface depending on time of heating and voltage – $U_1 = 320$ V and $U_2 = 200$ V. Processing time (s) is 1 – 5; 2 – 15; 3 – 30 (6 cycles); 4 – 40 (8 cycles); 5 – 50 (10 cycles); 6 – 60 (12 cycles); 7 – 70 (14 cycles) [Tyurin and Pogrebnjak 2001, 293-299].

Fig. 4-14. Distribution of hardness (HRC) on steel plate surface hardened by small portions. Plane samples-cathode (thickness of 50 mm, steel with 0.5 % C) and solution of sodium carbonate (13 %) are used [Kuzenkov 2010, 57-63].

Fig. 4-15. Schematic of devices proposed for PEH of plane surfaces (a, b, c), of edges of (d), periphery of saw disks (e), and inside surfaces (f) [Tyurin and Pogrebnjak 2001, 293-299].

Fig. 4-16. Image of etched layer by scanning electron microscope. a) ball milled for 40 minutes; b) ball milled + 5 min annealing; c) ball milled + 20 min annealing [Liang, Wang, Guo, and Wahab 2011, 510-513].

Fig. 5-1. Chromatogram of VGE at anode PEC of steel in solution of 10 % glycerol and 10 % ammonium chloride at 1000 °C: 1 – formaldehyde, 2 – acetaldehyde, 3 – acetone, 4 – methanol, 5 – ethanol [Kusmanov, Shadrin, and Belkin 2014, 727-733].

Fig. 5-2. Scheme of oxidation (I) and thermal decomposition (II) of glycerol at anodic PEC [Kusmanov, Shadrin, and Belkin 2014, 727-733].

Fig. 5-3. Cross sectional microstructures of 304 steel after its cathodic PEC in 80 % glycerol aqueous solution at different voltages: (a) 280 V; (b) 300 V; (c) 350 V [Xue, Jin, Liu, Jin et al. 2013, 882-887].

Fig. 5-4 Morphology of oxide layer formed in low-carbon steel after its anodic PEC at 900 °C (5 min) in solution containing 10 % glycerol and 10 % ammonium chloride followed by cooling in air [Kusmanov, Shadrin, and Belkin 2014, 727-733].

Fig. 5-5. Microstructure of carburized layer after anodic PEC of low-carbon steel in acetone electrolyte with cooling in air at 900 °C for 10 min [Belkin, Dyakov, Kusmanov, and Naumov 2011, 184-188].

Fig. 5-6. Change in thickness of martensitic layer with increasing concentration of ammonium chloride after PEC in electrolyte containing 10 % glycerol at 900 °C for 10 min [Kusmanov, Dyakov, and Belkin 2009, 7-14].

Fig. 5-7. Effect of concentration of carbon-containing component (1 – acetone, 2 – glycerol, 3 – sucrose, 4 – ethylene glycol) on thickness of martensitic layer after PEC at 900 °C in electrolyte with ammonium chloride concentration of 10 % for 10 min [Kusmanov, Dyakov, and Belkin 2009, 7-14].

Fig. 5-8. Cross-section micrograph of sample: (a) 1000 Hz, dc 60 %; (b) 10 kHz, dc 20 % [Aliofkhaeaei, Rouhaghdam, and Shahrabi 2008, 614-618].

Fig. 5-9. Surface morphology of CP-Ti after anode PEC in solution containing acetone (a), glycerol (b), sucrose (c), and ethylene glycol (d) [Belkin, Kusmanov, Dyakov, Komissarova et al. 2016, 1303-1309].

Fig. 5-10. Cross-section of carburised layer on commercial aluminium [Wu, Liu, Wang, Yang et al. 2015, 119-124].

Fig. 5.11. Dependence of thickness of martensite layer on low-carbon steel on temperature of anodic PEC after 7 min of saturation in electrolytes containing 10 % ammonium chloride and 10 % of one of carbon-containing components: acetone (1), glycerol (2), sucrose (3), or ethylene glycol (4) [Kusmanov, Dyakov, and Belkin 2009, 7-14].

Fig. 5-12. Dependence of square of martensite layer thickness on duration of PEC at 900 °C in acetone 1, glycerol 2, sucrose 3 and ethylene glycol 4 electrolytes [Kusmanov, Dyakov, and Belkin 2009, 7-14].

Fig. 5-13. Surface microhardness of 12Cr18Ni10Ti steel after cathodic PEC in glycerol electrolyte with quenching [Skakov and Kurbanbekov 2012, 155-163].

Fig. 5-14. Distribution of microhardness in layer of steel H13 after cathodic PEC at 150 V (25 min). Sample 1 is treated by DC (899 °C). Sample 3 is carburised by pulsed current at 10 kHz and dc of 90 % (943 °C). Sample 4 is treated by pulsed current at 100 Hz and dc 90 % (917 °C) [Yaghmazadeh and Dehghanian 2009, S168-S172].

Fig. 5-15. Microhardness distribution in layer of steel 1015 after cathodic PEC in carbamide solutions of various concentrations at 240 V [Rezaei, Shokuhtar, Asadi, Hosseinzadeh et al. 2006, 26-31].

Fig. 5-16. Microhardness distribution in low-carbon steel after its anodic PEC under various conditions: a) 10 % glycerol, 10 % ammonium

chloride, 900 °C, 5 min; b) 5 % glycerol, 10 % ammonium chloride, 900 °C, 5 min; c) 10 % glycerol, 15 % ammonium chloride, 900 °C, 5 min; d) 10 % glycerol, 10 % ammonium chloride, 1000 °C, 5 min; e) 10 % glycerol, 10 % ammonium chloride, 900 °C, 10 min; f) 10 % acetone, 10 % ammonium chloride, 900 °C, 5 min [Kusmanov, Shadrin, and Belkin 2014, 727-733].

Fig. 5-17. Microhardness distribution in CP-Ti after anodic PEC (850 °C, 5 min) in electrolytes containing the indicated carbon-containing components [Belkin, Kusmanov, Dyakov, Komissarova et al. 2016, 1303-1309].

Fig. 5-18. Microhardness profile in Ti6Al5Mo5V1.5Cu1Fe alloy after anodic PEC (900 °C, 5 min) in electrolytes containing glycerol (1), acetone (2), sucrose (3), and ethylene glycol (4) [Kusmanov, Dyakov, Belkin, and Parfenyuk 2017, 1-].

Fig. 5-19. Surface profile of untreated low-carbon steel (a) and after anodic PEC (b) in solution containing 10 % glycerol and 10 % ammonium chloride at 900 °C for 5 min [Kusmanov, Shadrin, and Belkin 2014, 727-733].

Fig. 5-20. Surface topology of CP-Ti before treatment (a) and after anodic PEC in ethylene glycol electrolyte (b) at 850 °C for 5 min [Belkin, Kusmanov, Dyakov, Komissarova et al. 2016, 1303-1309].

Fig. 5-21. Morphology of friction tracks on untreated T8 steel (a, b) and carburised steel (c, d) at 380 V for 3 min [Wu, Wang, Zhang, Liu et al. 2016, 50-56].

Fig. 5-22. Wear rate of CP-Ti during friction with lubricant after anodic PEC in solutions containing 10 % ammonium chloride and 10 % of one of indicated components at 850 °C for 5 min [Belkin, Kusmanov, Dyakov, Komissarova et al. 2016, 1303-1309].

Fig. 5-23. Wear rate of Ti6Al5Mo5V1.5Cu1Fe titanium alloy at lubricant friction after anodic PEC in solutions containing 10 % ammonium chloride and 10 % of one of indicated components at 850 °C for 5 min) [Kusmanov, Dyakov, Belkin, and Parfenyuk 2017, 1-6].

Fig. 5-24. Potentiodynamic curves (a) and Nyquist diagram (b) of T8 steel in 3.5 % sodium chloride solution. Equivalent circuits of electrochemical impedance spectroscopy of untreated (c) and carburised (d) steel [Wu, Wang, Zhang, Liu et al. 2016, 50-56].

Fig. 5-25. Polarization curves of CP-Ti in sodium sulphate solution before and after anodic PEC in electrolytes containing various carbon-containing components at 850 °C for 5 min [Belkin, Kusmanov, Dyakov, Komissarova et al. 2016, 1303-1309].

Fig. 6-1. Scheme of interaction of VGE molecules and ions with nitrided steel [Belkin and Kusmanov 2017, 767-789].

Fig. 6-2. Effect of processing time on concentration of ammonium ions in electrolyte solution during PEN in closed (1) and open (2) chambers [Smirnov, Kusmanov, Kusmanova, and Belkin 2017, 413-418].

Fig. 6-3. Effect of processing time on concentrations of ammonium chloride (1) and ammonium nitrate (2) [Belkin, Borisov, Vasin, Krit et al. 2017, 203].

Fig. 6-4. Cross-section of nitrided steel 750 °C: 1 — oxide layer, 2 — nitride-martensite zone, 3 — initial ferrite-pearlite structure [Kusmanov, Kasatkina, Dyakov, Silkin et al. 2017, 99-106].

Fig. 6-5. Dependence of nitrogen concentration in surface layer of low-carbon steel on temperature of PEN in solution containing 10 % ammonium chloride and 15 % carbamide [Kusmanov, Kasatkina, Dyakov, Silkin et al. 2017, 99-106].

Fig. 6-6. Distribution of nitrogen concentration in surface layer of steel after its PEN at 700 °C in solution containing 10 % ammonium chloride and 15 % carbamide [Kusmanov, Kasatkina, Dyakov, Silkin et al. 2017, 99-106].

Fig. 6-7. X-ray diffraction patterns of surface layers after anode PEN in solution of ammonium nitrate (10 %) and ammonium chloride (10 %) during 5 min for different treatment temperatures [Kusmanov, Smirnov, Kusmanova, and Belkin 2015, 308-313].

Fig. 6-8. SEM image of surface profile of medium carbon steel after PEN in solution of ammonium nitrate (10 %) and ammonium chloride (10 %) at 750 °C for 5 min followed by quenching: 1 – surface oxide layer; 2 – nitride-martensite layer; 3 – martensite-ferrite layer; 4 – the original structure [Kusmanov, Smirnov, Kusmanova, and Belkin 2015, 308-313].

Fig. 6-9. EDX nitrogen (a) and oxygen (b) distributions for modified layers after anode PEN in solution of ammonium nitrate (10 %) and ammonium chloride (10 %) during 5 min for different temperatures treatment [Kusmanov, Smirnov, Kusmanova, and Belkin 2015, 308-313].

Fig. 6-10. Distribution of elements in surface layer of steels nitrided at 750 °C for 5 min where nitrogen concentration in 40Cr steel is measured by according to local X-ray spectral analysis (a) [Belkin, Burbelko, Pasinkovsky, Rabinovich et al. 1984, 68-70]. as well as nitrogen and oxygen concentrations in carbon steel (0.45 % C) are determined using Auger spectroscopy data (b) [Belkin and Pasinkovsky 1989, 331-337].

Fig. 6-11. SEM image of cross-section of steel surface after anode PEN at 650 °C (a), 700 °C (b), 750 °C (c), 800 °C (d), and 850 °C (e): 1 —oxide-

nitride zone, 2 — nitride-martensite sublayer, 3 — martensite-pearlite layer [Kusmanov, Smirnov, Silkin, and Belkin 2016 1350-1356].

Fig. 6-12. Distribution of nitrogen concentration over surface profile of 40Kh steel after nitriding in solution of ammonia (5 %) and ammonium chloride (10 %) for 5 min at various temperatures [Kusmanov, Smirnov, Silkin, and Belkin 2016, 1350-1356].

Fig. 6-13. Distribution of nitrogen concentration over surface profile of 40Cr steel after PEN in solution of ammonium nitrate (5 %) and ammonium chloride (15 %) for 5 min at various temperatures (a) and at 750 ° C with different duration of treatment (b) [Kusmanov, Smirnov, Silkin, and Belkin 2016, 2576-2582].

Fig. 6-14. Layer-by-layer X-ray phase analysis of steel 30Cr3MoV nitrided at 690 °C for 7 min with and without deformation. Depth of analysis is surface (a), 10 μm (b), 20 μm (c), and 30 μm (d) [Bernstein, Minkov, Andreeva, Belkin et al. 1983, 65-67].

Fig. 6-15. Change in half-width of line (211) of ferrite along depth of nitrided layer with deformation (1) and without one (2) [Bernstein, Minkov, Andreeva, Belkin et al. 1983, 65-67].

Fig. 6-16. X-ray diffraction patterns of surface layers before and after anode PEN in a solution contained ammonium nitrate (5 %) and ammonium chloride (10 %) at different treatment temperatures [Dyakov, Burov, Belkin, Rozanov et al. 2019, 124-131].

Fig. 6-17. Nitrogen distribution in surface layer of treated steel at different temperatures [Dyakov, Burov, Belkin, Rozanov et al. 2019, 124-131].

Fig. 6-18. Cross-section of 38CrMoAl steel after PEN in solution of ammonia water (60 wt. %) at 220 V for 10 min [Hua, Zhou, Cui, Zou et al. 2013, 304-314].

Fig. 6-19. Surface of steel nitrided at ~ 435 °C for 20 min at low (a) and high resolution (b) and (c) with highlighted pore regions [Roy 2006].

Fig. 6-20. Microstructure of diffusion layer of W6Mo5Cr4V2 steel after PEN at 650 °C for 5 min [Skakov and Rakhadilov 2012].

Fig. 6-21. Surface of W6Mo5Cr4V2 steel after PEN at 550 °C [Rakhadilov, Skakov, Batyrbekov, Erlan et al. 2015, 403-409].

Fig. 6-22. Nuclear backscattering spectra of protons for CP-Ti samples after their anodic PEN at various temperatures [Belkin, Borisov, Vostrikov, Dyakov et al. 2006, 59-61].

Fig. 6-23. SEM image of CP-Ti surface after anode PEN in solution of ammonium chloride (10 %) and ammonia (5 %) at 850 °C for 5 min [Belkin, Zhironov, Belkin, Parfenyuk et al. 2016, 1027-1032].

Fig. 6-24. Effect of saturation temperature on thickness of diffusion layer in CP-Ti after PEN for 5 min [Belkin, Borisov, and Kusmanov 2016, 516-535].

Fig. 6-25. SEM image of Ti6Al5Mo5VCuFe alloy surface after anode PEN in electrolyte containing ammonia (5 wt.%) and ammonium chloride (10 wt. %) at 650 °C (a), 700 °C (b), 750 °C (c), 800 °C (d), 850 °C (e), and 900 °C (f) [Kusmanov, Smirnov, Silkin, Parfenyuk et al. 2016, 1291-1296].

Fig. 6-26. Effect of anodic PEN time on thickness of nitride zone (a) and solid solution of nitrogen in iron (b) at different temperatures [Belkin and Pasinkovsky 1989, 331-337]. Solutions contain 10 % ammonium chloride and 5 % ammonia (I) or 11 % ammonium chloride and 1 % ammonium nitrate (II).

Fig. 6-27. Thicknesses of modified layer (1) and oxide layer (2) vs treatment temperature (a) and time (b), concentration of ammonium chloride (c) and ammonium nitrate (d) at: a) 10 % NH_4NO_3 , 10 % NH_4Cl , 5 min; b) 10 % NH_4NO_3 , 10 % NH_4Cl , 750 °C; c) 10 % NH_4NO_3 , 5 min, 750 °C; and d) 10 % NH_4Cl , 5 min, 750 °C [Kusmanov, Smirnov, Kusmanova, and Belkin 2015, 308-313].

Fig. 6-28. Coordinates of boundaries of oxide layer (1), nitride zone (2) and martensite layer versus treatment temperature (a) and NH_3 concentration (b) at 10 % NH_4Cl for 5 min. Concentration of NH_3 is 5 % (a), PEN temperature is 750 °C (b) [Kusmanov, Smirnov, and Belkin 2016, 133-139].

Fig. 6-29. Growth kinetics of nitrided layers of W6Mo5Cr4V2 steel [Rakhadilov 2014].

Fig. 6-30. Microhardness distribution in modified layer after anode PEN at different treatment temperatures [Kusmanov, Silkin, Smirnov, and Belkin 2017, 239-246].

Fig. 6-31. Microhardness distribution in modified layer after anode PEN of medium carbon steel for different treatment time at 10 % ammonium nitrate, 10 % ammonium chloride, 750 °C [Kusmanov, Smirnov, Kusmanova, and Belkin 2015, 308-313].

Fig. 6-32. Microhardness distribution in diffusion layer after PEN at different saturation temperature [Dyakov, Burov, Belkin, Rozanov et al. 2019, 124-131].

Fig. 6-33. Effect of PEN temperature on hardness of steels 40Cr (1, 2) and medium carbon steel (3, 4) for 5 min. Compositions of solutions are 10 % ammonium chloride and 5 % ammonia (1, 3) or 11 % ammonium chloride and 11 % ammonium nitrate (2, 4) [Belkin and Pasinkovsky 1986, 27-29].

Fig. 6-34. Microhardness of 34CrNi1Mo steel in initial state and after PEN during 5 minutes [Skakov, Yerygina, and Scheffler 2015, 439-443].

Fig. 6-35. Distribution of microhardness in steel 12Cr18Ni10Ti after PEN at 750 °C (1), 700 °C (2), and 800 °C (3) for 7 min [Skakov, Kurbanbekov, Scheffler, and Naltaev 2013, 12-16].

Fig. 6-36. Distribution of microhardness in surface layer of medium carbon steel nitrated in solution of ammonium nitrate (10 %) and ammonium chloride (10 %) at 750 °C for 5 min [Kusmanov, Smirnov, Kusmanova, and Belkin 2015, 308-313].

Fig. 6-37. Microhardness of surface layer of Ti₂Al₃Zr (1, 2) and Ti₅Al₂Mn (3, 4) alloys after PEN in aqueous solution of ammonia (7.5 %) and ammonium chloride (10 %) at 220 V for 5 min with sequence cooling in solution (1, 3) or in air (2, 4) [Blashchuk, Lavrovskaya, Onoprienko, Belkin et al. 1989, 18-20].

Fig. 6-38. Distribution of microhardness in surface layer of Ti₆Al₅Mo₅VCuFe alloy after nitriding in a solution of ammonia (5 %) and ammonium chloride (10 %) for 5 min at various temperatures [Kusmanov, Smirnov, Silkin, Parfenyuk et al. 2016, 1291-1296].

Fig. 6-39. Surface roughness of 40Cr steel after anodic PEN in electrolyte contained ammonium nitrate at different temperatures [Kusmanov, Smirnov, Silkin, and Belkin 2016, 2576-2582].

Fig. 6-40. Surface roughness of 40Cr steel after anodic PEN in ammonia-based electrolyte at different treatment temperatures [Kusmanov, Smirnov, Silkin, and Belkin 2016, 1350-1356].

Fig. 6-41. Surface roughness of high-carbon steel after anodic PEN in solution contained ammonium nitrate at different treatment temperatures [Dyakov, Burov, Belkin, Rozanov et al. 2019, 124-131].

Fig. 6-42. Surface linear profile of layer before treatment (a) and fabricated layer after anode PEN of CP-Ti in 5 % NH₃ and 15 % NH₄Cl solution for 5 min at 800 °C (b) [Belkin, Zhirov, Belkin, Parfenyuk et al. 2016, 1027-1032].

Fig. 6-43. Diagram of intrusion of indenter into nitrated layer [Belkin, Borisov, Vasin, Krit et al. 2017, 234].

Fig. 6-44. Scanning micrograph of fracture of medium carbon steel 45 nitrated in solution of ammonia (5 %) and ammonium chloride (10 %) [Belkin, Borisov, Vasin, Krit et al. 2017, 234].

Fig. 6-45. Effect of sliding distance on dry friction coefficient of samples after PEN in ammonia electrolyte (750 °C, 5 min) as well as untreated samples (1, 5). Normal load is 10 N (1, 2, 4) or 5 N (3, 5, 6). Sliding speed is 0.4 m/s (1-3) or 0.2 m/s (4-6) [Smirnov, Silkin, Belkin, Dyakov et al. 2017, 81-86].

Fig. 6-46. Influence of sliding distance on linear wear of the samples in dry friction include untreated ones (1, 5). Normal load is 10 N (1, 3, 4) or 5 N (2, 5, 6). Sliding speed is 0.4 m/s (1, 2, 4) or 0.2 m/s (3, 5, 6) [Smirnov, Silkin, Belkin, Dyakov et al. 2017, 81-86].

Fig. 6-47. Micrograph and profile of worn surface of untreated sample (a) and treated samples after anode PEN at 650 °C (b), 750 °C (c), 800 °C (d).

Fig. 6-48. Wear tracks of steel S0050A before (left) and after PEN in urea electrolyte (right) [Nie, Wang, Yao, Zhang et al. 2005, 1745-1750].

Fig. 6-49. Influence of normal load on friction coefficient of untreated sample (1) and nitrided at 650 °C (3) and 750 °C (2, 4) for 5 min. Solutions contain 10 % ammonium chloride and 5 % ammonia (2, 3) or 11 % ammonium chloride and 11 % ammonium nitrate (4) [Belkin, Pasinkovsky, Tkachenko, Faktorovich et al. 1981, 43-45].

Fig. 6-50. Linear wear rate versus test duration at a load of 3 MPa. Anodic PEN at 650 °C (1, 2) and 750 °C (3, 4) for 5 min in solutions of 10 % ammonium chloride and 5 % ammonia (2,4) and 11 % chloride and 11 % ammonium nitrate (1, 3) [Belkin, Pasinkovsky, Tkachenko, Faktorovich et al. 1981, 43-45].

Fig. 6-51. Weight loss under lubricated testing condition of untreated and treated samples of 40Cr steel at different PEN temperatures [Kusmanov, Smirnov, Silkin, and Belkin 2016, 1350-1356].

Fig. 6-52. Wear rate under dry testing condition of the untreated and treated samples at different PEN temperatures [Kusmanov, Smirnov, Silkin, and Belkin 2016, 1350-1356].

Fig. 6-53. Micrographs and profiles of wear tracks of treated samples after anode PEN at 650 °C (a), 700 °C (b), 750 °C (c), 800 °C (d), 850 °C (e), and before treatment (f) [Kusmanov, Smirnov, Silkin, and Belkin 2016, 1350-1356].

Fig. 6-54. Steady-state friction coefficient of untreated, tempered, hardened in oil samples, and anodic PEN one treated at different temperatures [Dyakov, Burov, Belkin, Rozanov et al. 2019, 124-131].

Fig. 6-55. Weight loss after wear testing for untreated (1), tempered (2), hardening in oil (4) samples, and anodic PEN ones (3) treated at different temperatures [Dyakov, Burov, Belkin, Rozanov et al. 2019, 124-131].

Fig. 6-56. Micrograph of friction tracks of untreated (a) and nitrided (b) specimens of G3500 cast iron after lubricated friction tests [Nie, Wang, Yao, Zhang et al. 2005, 1745-1750].

Fig. 6-57. The weight wear rate of Ti6Al4V alloy processed at different temperatures after wear testing [Kusmanov, Tambovsky, Korableva, and Belkin 2019, 012036].

Fig. 6-58. Lubricant friction coefficient of Ti6Al5Mo5VCuFe alloy after PEN at different temperatures. Normal load is 209 N (a) and 105 N (b), sliding speed is 0.49 m/s (a) and 0.144 m/s (b) [Kusmanov, Smirnov, Silkin, Parfenyuk et al. 2016, 1291-1296].

Fig. 6-59. Wear rate of titanium alloy after PEN at different temperatures for sliding on steel disk at speed of 0.49 m/s under load of 209 N [Kusmanov, Smirnov, Silkin, Parfenyuk et al. 2016, 1291-1296].

Fig. 6-60. Wear rate of titanium alloy after PEN at different temperatures for sliding bearing steel ball at speed of 0.144 m/s, and load of 105 N [Kusmanov, Smirnov, Silkin, Parfenyuk et al. 2016, 1291-1296].

Fig. 6-61. Wear behaviours of untreated Ti6Al5Mo5VCuFe sample (a) and samples nitrided at 850 °C during 5 min (b) for different sliding speed. Ball-on-disk scheme, 5 N normal load, 240 m sliding distance against Al₂O₃ ball at dry friction.

Fig. 6-62. Micrograph and profile of worn surface of nitrided (a-d) and untreated (e) Ti6Al5Mo5VCuFe samples at sliding speed of 0.05 m/s (a), 0.1 m/s (b), 0.2 m/s (c), and 0.4 m/s (d, e). Ball-on-disk scheme, 5 N normal load, 240 m sliding distance against Al₂O₃ ball at dry friction [Belkin, Kusmanov, Dyakov, Silkin et al. 2017, 2404-2410].

Fig. 6-63. Equivalent electrical circuit of system included steel and 1M NaCl solution, where R_s is electrolyte resistance; CPE is constant phase element [Kusmanov, Grishina, Belkin, Kusmanova et al. 2017, 117-123].

Fig. 6-64. Corrosion potential of steel (0.45 %C) versus duration of corrosion tests in 0.1 M Na₂SO₄ solution for PEN (1) and untreated (2) samples [Revenko, Parshutin, Chernova, Bogdashkina et al. 1985, 56-59].

Fig. 6-65. Corrosion rate of steel (0.45 %C) versus duration of corrosion tests in 0.1 M Na₂SO₄ solution for untreated (1) and PEN (2) samples [Revenko, Parshutin, Chernova, Bogdashkina et al. 1985, 56-59].

Fig. 6-66. Nature of polarization curves of steel (0.45 %C) nitrided in solutions containing 11 % NH₄NO₃ and 11 % NH₄Cl (1, 4); 10 % NH₄Cl and 5 % NH₃ (2, 3) followed by cooling: 1, 2 – in air (1, 2) or electrolyte (3, 4) [Revenko, Chernova, Parshutin, Bogdashkina et al. 1988, 204-210].

Fig. 6-67. Polarization curves of steel (0.45 %C) after PEN in electrolyte containing 15 % ammonium chloride and 5 % ammonium nitrate at processing temperatures (a), that is, 650 °C (1); 700 °C (2); 750 °C (3); 800 °C (4), and 850 °C (5) for 5 minutes, as well as at PEN duration of 2 min(1); 5 min (2), and 10 min (3) at 750 °C include untreated sample (0) [Smirnov, Silkin, Belkin, Dyakov et al. 2017, 81-86].

Fig. 6-68. Anodic polarization curves of 40Cr steel in 0.1 M Na₂SO₄ solution at 20 °C for sample with oxide layer (1), sample without oxide

layer (3), and untreated steel (3) [Chernova, Bogdashkina, Parshutin, Revenko et al. 1984, 408-411].

Fig. 6-69. Potentiodynamic polarization curves of tool steel CrMnW in 3.0 wt.% NaCl solution after its PEN at different temperatures [Dyakov, Burov, Belkin, Rozanov et al. 2019, 124-131].

Fig. 6-70. Effect of PEN temperature on corrosion current density of nitrated samples [Dyakov, Burov, Belkin, Rozanov et al. 2019, 124-131].

Fig. 6-71. Potentiodynamic polarization curves for untreated and treated samples in 60 % ammonia water in 3.5 % NaCl solution [Hua, Zhou, Cui, Zou et al. 2013, 304-314].

Fig. 6-72. Bode diagrams of PEN (a) AISI 304 stainless steel, (b) AISI 316L stainless steel and (c) AISI 430 stainless steel at different voltages for 1 h of treatment [Aliev, Sabour, and Taheri 2008, 402-407].

Fig. 6-73. Polarization curves of Ti6Al5Mo5VCuFe alloy in Ringer's solution before and after PEN in solution of ammonia (5 %) and ammonium chloride (10 %) for 5 min at various temperatures [Kusmanov, Smirnov, Silkin, Parfenyuk et al. 2016, 1291-1296].

Fig. 7-1. Change in concentration of iron ions and electrolyte components (carbamide and ammonium ions) in process of anodic PEN/C of low-carbon steel at 850 °C. Electrolyte is aqueous solution of carbamide (15 %) and ammonium chloride (10 %) [Kusmanov, Parkaeva, Frolov, Naumov et al. 2015, 213-219].

Fig. 7-2. Cross-sectional image of 316L steel after its PEN/C in carbamide-based electrolyte at 700 °C for 2 min [Taheri and Dehghanian 2008, 92-100].

Fig. 7-3. Schematic of structure and phase composition after PEN/C of steel: *a* – layer I, *b* – layer II, *c* – before carbonitriding [Popova, Potekaev, Nikonenko, Klopotov et al. 2020, 1794-1800].

Fig. 7-4. SEM image of cross-section of steel surface after anode PEN/C in solution of ammonia (5 %), acetone (5 %) and ammonium chloride (10 %) for 5 min at 800 °C (1 – oxide layer, 2 – nitrocarburised layer, 3 – martensite layer, 4 – diffusion layer, 5 – initial pearlite-ferrite structure) [Kusmanov, Kusmanova, Smirnov, and Belkin 2016, 164-171].

Fig. 7-5. Cross section of CP-Ti after PEN/C for 3 min at 900 °C [Aliofkhaezrai, Taheri, Rouhaghdam, Sabour et al. 2007, 791-799].

Fig. 7-6. SEM image of cross-section of Ti6Al4V titanium alloy surface after PEN/C at 900 °C, 5 min: 1 – TiO₂ (rutile), 2 – TiO, 3 – diffusion layer [Tambovsky, Kusmanov, Korableva, Tambovskaya et al. 2019, 122-127].

Fig. 7-7. Microstructure of cross section of Ti6Al5Mo5VCuFe titanium alloy after its PEN/C at 950°C in 10 wt % ammonium chloride and 12.5 wt % carbamide electrolyte [Belkin, Tambovsky, Korableva, Silkin et al. 2018, 507-512].

Fig. 7-8 a. Coordinates of boundaries of oxide layer (1), outer nitrocarburised layer (2) and inner diffusion layer (3) vs the duration of treatment (10 % NH₄NO₃, 8 % C₃H₅(OH)₃, 10 % NH₄Cl, 850 °C) [Kusmanova, Kusmanov, Naumov, and Belkin 2016, 637-644].

Fig. 7-8 b. Dependence of thickness of nitrocarburised layer in CP-Ti on square root of PEN/C duration in carbamide electrolyte at 900 °C (1), 800 °C (2), and 700 °C (3) [Aliofkhazraei, Taheri, Rouhaghdam, Sabour et al. 2007, 791-799].

Fig. 7-9. Distribution of carbon over depth of diffusion zone after PEN/C at 850 °C according to method 1 (1), method 2 (2), and method 3 (3). Points are experimental data [Mukhacheva, Dyakov, and Belkin 2009, 38-45].

Fig. 7-10. Microhardness profiles of untreated and PEN/C samples at different frequencies [Noori and Dehghanian 2018, 20-].

Fig. 7-11. Microhardness distribution in low-carbon steel after its anode PEN/C for different temperature. Aqueous solution of 10 % NH₄NO₃, 8 % glycerol, 10 % NH₄Cl, 5 min [Kusmanov, Dyakov, Kusmanova, and Belkin 2016, 1271-1286].

Fig. 7-12. Surface roughness and hardness of Ti6Al4V alloy after cathodic PEN/C vs pulse frequency [Qin, Xiong, Li, and Tyagi 2015, 543-550].

Fig. 7-13. Surface roughness of Ti6Al4V alloy after anodic PEN/C vs processing temperature [Tambovsky, Kusmanov, Korableva, Tambovskaya et al. 2019, 122-127].

Fig. 7-14. Effect of voltage and duration of cathodic PEN/C of medium carbon steel on its surface roughness (a) and wear rate (b) [Rastkar and Shokri 2012, 342-351].

Fig. 7-15. Dependence of weight wear of low-carbon steel along sliding distance of 1000 m on temperature of the anode PEN/C (a), concentration of ammonium nitrate (b) and concentration of ammonium chloride (c). Processing regimens are 10 % ammonium nitrate, 8 % glycerol, 10 % ammonium chloride (a); 8 % glycerol, 10 % ammonium chloride, 850 °C (b); 10 % ammonium nitrate, 8 % glycerol, 850 °C (c) [Kusmanov, Dyakov, Kusmanova, and Belkin 2016, 1271-1286].

Fig. 7-16. Micrograph and profile of worn surface of untreated sample (a) and treated samples after anodic PEN/C at 750 °C (b), 850 °C (c), and 950 °C (d).