Alloying and Modification of Structural Materials under Pulsed Plasma Treatment

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Abstract—In this paper are present investigations of features of surface modification and materials alloying from gas and metallic plasma as a result of the plasma ions mixing with the steel substrate in liquid phase. Modification of constructional steels with powerful pulsed plasma streams results in hardening their surfaces and increasing the wear resistance. The experiments have been carried out with pulsed plasma gun, which generates plasma streams with ion energy up to 2 keV, plasma density 2×10^{14} cm^{-3}, average specific power of 10 MW/cm^2 and plasma energy density in the range of (5-40) J/cm^2. The nitrogen, helium, and other gases and their mixtures can be used as working gases. The regime of plasma treatment was chosen with variation of both the discharge voltage and the distance of the material surface from the gun output. Modification of thin (0.5-2 μm) PVD coatings of MoN, C+W, TiN, TiC, Cr, Cr+CrN and others with the pulsed plasma processing are analyzed also. It is shown that pulsed plasma treatment results in essential improvement of physical and mechanical properties of exposed materials. For example, microhardness of samples with Cr coating, after plasma treatment, increased in 2.5 times. Mechanisms of surface modification of a different alloys and coating irradiated with pulsed plasma streams of different ions are discussed.

Keywords—Plasma treatment, coatings, surface modification, alloying

I. INTRODUCTION

Surface processing with pulsed plasma streams of different gases is found to be effective tool for modification of surface layers of different materials [1-4]. In particular, exposures with pulsed powerful plasma streams result in hardening their surfaces and increasing the wear resistance of industrial steels [5]. Fast heating and melting of treated surface, considerable temperature gradients (~10^6 K/cm) arising in surface layer of material under the pulsed plasma impact contribute to high speed diffusion of plasma stream ions into the depth of the modified layer, during the liquid stage, phase changes in the surface layer, and formation of the fine-grained or quasi-amorphous structures under the following fast resolidification [1, 6, 7]. The cooling speed of ~10^6-10^7 K/s is achieved in this case due to the contact of thin melt layer (h_{melt} ~10-50 μm) with massive bulk of the sample. Plasma can also be considered as a source of alloying elements to be introduced into modified layer structure. That is why nitrogen is preferentially used for pulsed plasma processing of different steels. Another possibility of alloying under the pulsed plasma processing is mixing of previously deposited thin ($h_{coat} < h_{melt}$) coatings of different predetermined composition with the substrate in result of powerful plasma impact.

In this paper, features of materials modification and alloying of surface layer from gas and metallic plasma as well as coating mixing with the steel substrate in liquid phase are investigated in this paper. In particular, modification of thin (0.5-2 μm) PVD coatings of MoN, C+W, TiN, TiC, Cr, Cr+CrN and others in result of pulsed plasma processing are analyzed.

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II. EXPERIMENTAL EQUIPMENT AND DIAGNOSTICS

Surface modification with powerful pulsed plasma streams was carried out with use of pulsed plasma accelerator (PPA) [1, 2]. General view and scheme of the device is presented in Fig. 1. The PPA device consists of coaxial set of electrodes with anode diameter of 14 cm and cathode diameter of 5 cm and vacuum chamber of 120 cm in length and 100 cm in diameter. The power supply system is condenser banks with stored energy of 60 kJ (for 35 kV). The amplitude of a discharge current is ~400 kA, plasma stream duration is 3-6 μs. The pulsed plasma accelerator generates plasma streams with ion energy up to 2 keV, plasma density (2-20)×10^{14} cm^{-3}, average specific power of about 10 MW/cm^2 and plasma energy density varied in the range of (5-40) J/cm^2. Nitrogen, helium, hydrogen and different mixtures can be used as working gases. The regime of plasma treatment could be chosen with variation of both accelerator discharge voltage and the distance of the exposed samples from the PPA output.

High quality coatings of Mo and W were previously deposited using planar rectangular ECR plasma source with a multipolar magnetic field [8]. The working frequency of ECR source and HF power are 2.45 GHz and 300 W, respectively. The ultimate pressure in the vacuum chamber was about 2×10^{-5} torr. The working pressure (2×10^{-3} torr) was defined by variation of the working gas (Ar) flow and the pumping speed. The plasma parameters close to surface of processed target

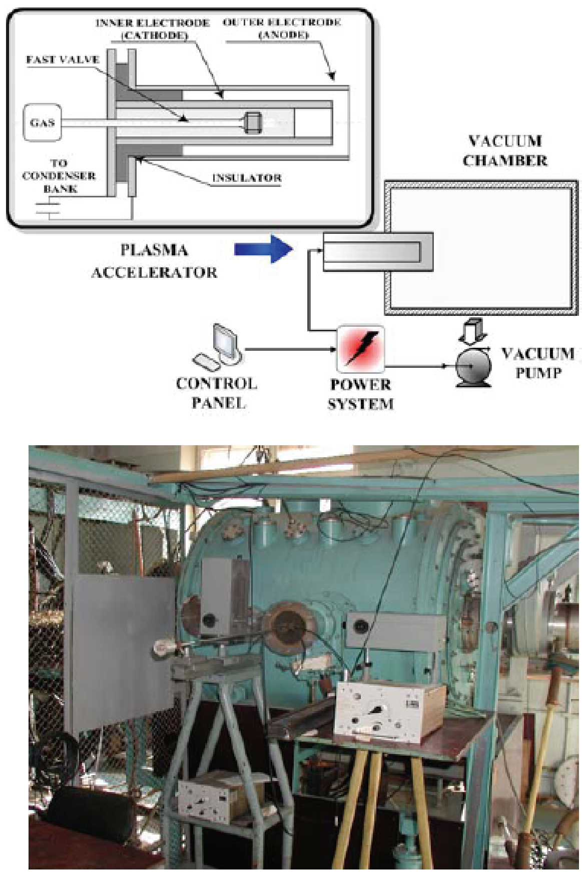

Fig. 1. Scheme and general view of PPA device.

were as follows: electron density up to 10^{11} cm^{-3}, electron temperature ~12 eV, ion current density to the grounded substrate ~3.5 mA/cm^2. TiN, Cr, CrN and other coatings were deposited to the samples surfaces by PVD method in "Bulat" installation [9].

The standard methods were used for measurements of plasma parameters. It description are present in [10]. In particular, radial distributions of the plasma stream energy density were monitored with movable thermocouple calorimeters at the different distances from plasma gun. Measurements of plasma stream pressure were carried out with piezodetector. Plasma stream power and energy densities were also calculated on the basis of measurements of the time dependencies of the plasma pressure, plasma stream density and its velocity. Complex of optical diagnostics included diffractional spectrograph DFS-452, monochromator MDR-23, other compact universal monochromators, photodiodes, and photomultiplier tubes. Microstructure of the treated surfaces and cross-sections of samples were examined with optical microscope MMR-4 and scanning electron microscope JEOL with X-ray analyzer LINK. For surface roughness measurements the Hommelwerke tester T500 was used. Weight loss measurements and XRD analysis were performed also.

III. Experimental Results

The performed experiments have shown that pulsed plasma treatment leads to improvement of physical and mechanical properties of exposed cast iron and steel materials. For example, after plasma treatment the microhardness of samples increases for both cases with and without previously deposited coatings. Table 1 shows that smallest friction coefficient (from 1.5 to 3 times decrease) is measured in wear tests for the samples with previously deposited Cr and CrN coatings, especially for those treated with plasma pulses. Increasing wear resistance is achieved for samples with coatings TiC, C+W, Cr+CrN and Cr with subsequent pulsed plasma treatment. It should be noted that TiN coatings without pulsed plasma processing demonstrate the worst result due to essentially increased indentor wear, which is accompanied by transport and sticking of indentor material to the sample.

Experiments with different steels and cast iron reveal possibility for essential improvement of wear resistance in result of applied combination of coatings deposition with pulsed plasma processing. Alloying of surface layer in result of the coating-substrate mixing in liquid stage allows achievement of desirable chemical composition in surface layers being most loaded in all machine components. In particular, combined plasma processing is found to be prospective for modification of piston rings and other machine parts operating in conditions of bearing or dry friction.

TABLE I
RESULTS OF TRIBOLOGICAL TEST

Type of sample	Indentor wear, 10^{-4} g	Sample wear, 10^{-4} g	Friction Coefficient p = 1 кN	Microhardness kg/mm^2	
				area of contact	outside of contact
Initial	26.5	2.5	0.084	893	785
5 pulses (nitrogen, 28 J/cm^2)	32.0	4.0	0.088	1013	1013
Cr + 5 pulses (nitrogen, 28 J/cm^2)	24.0	3.0	0.074	1100	1630
Cr+CrN	57.0	0	0.076	962 (*)	1420
TiN	655.5	5.5	0.085	695 (*)	2575
MoN	25.5	4.5	0.080	1100	1079
TiC	79.0	2.0	0.084	550 (*)	2232
C+W	23	1.0	0.084	1100 (*)	2232

(*) – transport and sticking of indentor material

TABLE II
ELEMENT COMPOSITION (%MAS.) OF EP-823 STEEL IN RESULT OF PLASMA ALLOYING WITH MO

Element	Reference	Initial	No.1	No.2	No.3	No.4
C	0.17	0.167	1.73	2.51	0.44	0.42
Si	1.69	1.3	1.25	2.5	2.3	1.65
Mn	0.70	0.82	0.064	0.37	1.4	1.48
Cr	12.06	12.1	1.15	6.24	18.15	30.25
Ni	0.84	1.7	0.14	0.6	1.75	1.6
Mo	0.64	0.46	23.76	25.78	0.45	15.87
W	0.71	0.62	0.58	0.66	0.68	0.56
V	0.33	0.34	0.024	0.16	0.6	0.6
Nb	0.2	0.24	0.25	0.22	0.2	0.2
N_2	0.11	0.026	0.14	0.66	0.054	0.075
O	-	0.155	0.93	2.48	0.62	0.53
Ti	-	0.0046	0.4	0.15	0.005	1.38
Co	-	0.055	0.01	0.002	0.023	0.022

TABLE III
MICROHARDNESS OF EP-823 STEEL IN RESULT OF PLASMA ALLOYING WITH MO

	H_v of initial, кg/cm^2	H_v after 5 pulses, кg/cm^2	H_v after 10 pulses, кg/cm^2
EP-823 + Mo coating	400	450	480
EP-823	400	400	385

Plasma exposures of EP-823 steel samples with Mo coatings were performed also. Samples of EP-823 steel which were used in experiments had the size of 10×8×1 mm. Initial microhardness and roughness of the samples were 400 кg/mm^2 and $R_a \approx 0.5$ µm, respectively.

The similar experiments were carried out with the initial (uncoated) and alloyed samples of this material for determination of the influence of molybdenum coating on the surface morphology and physical-mechanical properties of steel EP-823. Element composition of EP-823 steel alloyed by Mo in result of Mo coating mixing with substrate under subsequent pulsed plasma processing is shown in Table 2. These data were obtained in 0.4 µm surface layer using laser mass analyzer EMAL. Sample No.1 with 0.5 µm Mo coating was treated with 10 pulses of He plasma. Sample No.2 with 0.5 µm Mo coating was exposed to 5 pulses, and then coated again and, finally, plasma treatment with 5 pulsed was applied again. Sample No.3 without any coating was treated with 5 plasma pulses. And sample No.4 with initial 1-1.5 µm Mo coating was exposed to 5 plasma pulses.

Thus, it is shown that pulsed plasma treatment provides effective alloying of surface layers with Mo which content achieves 26%. Additional measurements performed in the depth of 10 µm reveal approximately constant concentration in all modified layer, subjected to melting. Performed experiments with EP-823 steel demonstrate the possibility of creation of the modified superficial layer, alloyed a molybdenum and tungsten, which can be used as intermediate layer for subsequent thick coating deposition to EP-823 aimed at the corrosion protection in salts and liquid lead. For sample number 1 strong decreasing of Cr and Ni concentration can be caused by it selective sputtering or evaporation from surface layer with future increasing of pulses number up to 10.

Table 3 presents the results of microhardness measurements for virgin EP-823 samples and those with previously deposited Mo coating after the plasma treatments performed in different regimes. Microhardness of EP-823 with Mo coating increases after 10 plasma pulses, but at the same time microhardness of EP-823 without Mo coating has tendency of slightly decrease after the plasma treatments. Earlier it was shown that modified surface layer represents tense structure characterized by increased strain. Recent comparative results with helium and nitrogen plasmas showed that two mechanisms, both thermal hardening (quenching) and penetration of alloying element, are approximately equally responsible for improvement of wear resistance of processed steels. As to the microhardness, it was increased mainly due to high speed quenching and maximal values were obtained with use of helium plasma. The decreasing of microhardness is caused by an annealing of internal defects with future increasing of plasma pulses. At same time penetration of alloying elements in the crystal lattice led to creation of residual stresses and increasing of microhardness. This demonstrates the important influence of surface layer alloying due to the mixing process on tribological characteristics of modified layer.

The surface morphology has changed significantly due to formation of a wavy structure during of re-solidification of the surface after plasma treatment. Such structure caused an increase of surface roughness (R_a = 2.5 µm). After two consecutive sets of treatment (coating + irradiation plasma + coating + irradiation plasma), the roughness remained stable (R_a = 2.5 µm). Fig. 2 shows the surface morphology of EP-823 with Mo coating before (a) and after (b) two consecutive sets of treatment.

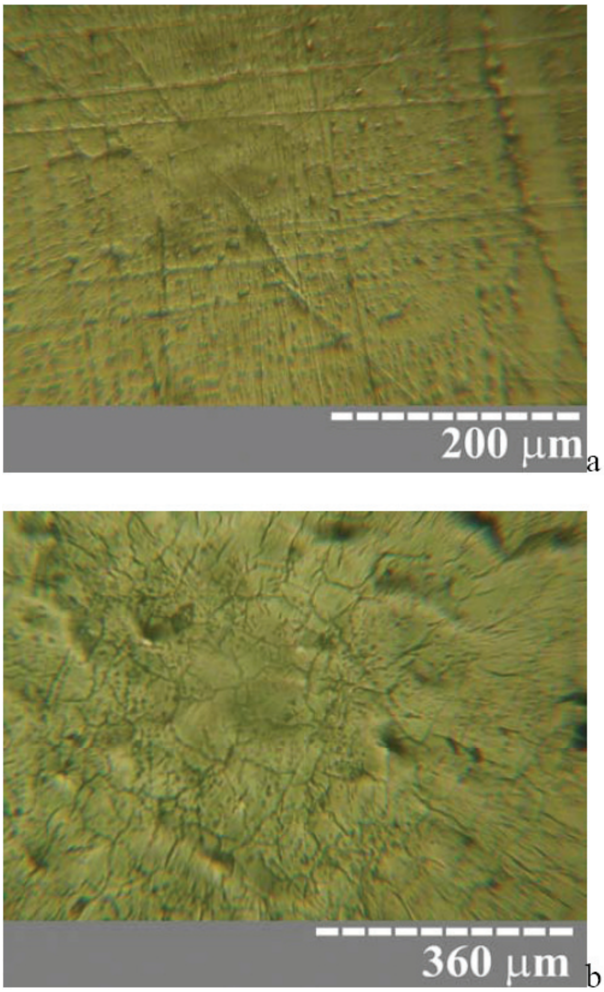

Fig. 2. View of the Mo coating on surface EP 823 (a) and after two consecutive sets of treatment (b).

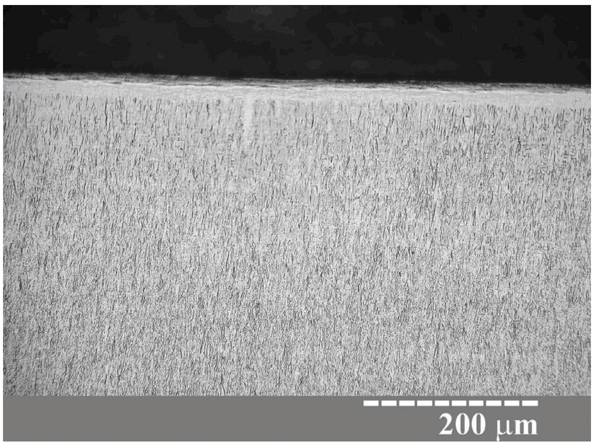

Fig. 3. Cross sections of modified layers on Ti64 coatings processed with nitrogen plasma.

Thus, our researches show possibility of creation of the modified layer alloyed by molybdenum and tungsten. Such layers can be used for future coating of the thick coatings which are necessary for protection of materials against corrosion in salts and liquid lead. For not alloyed coverings, destruction of contact between a coating and a substrate was observed during corrosion tests in experiments by other researchers [11].

The experiments on modifications of thick (h > 200 μm) coatings of Ti64 and Co-32Ni-21Cr-8Al-0.5Y with pulsed plasma streams indicate that pulsed plasma treatment allows considerable decrease both the size of grain and porosity of coating surface layer as well as the roughness which results in the improvement of their operating durability. Thus, in this case it is not necessary to modify all the coating, but only the surface layer, because the coating thickness is determined mainly by heat-resistance reasons with no special requirements to the structure of deep layers.

Result of pulsed plasma treatment of Ti64 alloy coatings of 1 mm thickness is shown by cross section image in Fig. 3. Roughness (R_a) of MCrAl (Co-32Ni-21Cr-8Al-0.5Y) targets exposed by plasma streams is decreases from 5 μm to 1 μm. The modified layer depth achieves 50 μm. It is seen that modified layer has a fine grain structure resistant to etching and also without holes and cavities which are typically observed in original coating structure. Should be mention, that in case of Ti64, the thickness of modified layer is much more than in case of MCrAlY. It is caused by difference of the thermo-mechanical properties (in particular heat conductivity and melting temperature) of these coatings.

IV. Conclusions

Surface modification and material alloying due to the mixing of thin (1-2 μm) coatings with sample substrate under the pulsed plasma processing is investigated. The experiments have shown that pulsed plasma treatment leads to improvement of physical and mechanical properties of exposed cast iron and different steel materials.

Increasing wear resistance is achieved for samples with coatings TIC, C+W, Cr+CrN and Cr with subsequent pulsed plasma treatment.

After alloying of ferritic/martensitic steel EP-823 with Mo the concentration of molybdenum in modified layer achieved 20% for single treatment cycle and 30% after two cycles of processing. Microhardness of EP-823 steel is increased up to 20% after two cycles of alloying with Mo whereas pulsed plasma treatment of uncoated steel leads to decreasing microhardness, probably due to annealing of defect structure on exposed surface.

The experiments on modifications of thick coatings (0.3-1 mm) of Ti64 and Co-32Ni-21Cr-8Al-0.5Y with pulsed plasma streams show that pulsed plasma treatment allows considerable decrease both the size of grain and porosity of coating surface layer as well as the roughness which results in the improvement of their operating durability.

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