Multielemental alloying of steel surface layer under the action of compression plasma flows

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Abstract. The microstructure, phase and element composition, microhardness of the carbon steel surface layer simultaneously alloyed with molybdenum and chromium atoms under the impact of compression plasma flows were investigated in this work. X-ray diffraction analysis, scanning electron microscopy, energy dispersion microanalysis and microhardness measurements were used for the investigation of the alloyed layer structure and properties. The findings showed that an increase of the plasma pulses number led to a decrease of the molybdenum and chromium atoms concentration in the alloyed layer as well as to the growth of alloying elements distribution homogeneity. The alloyed layer contained solid solutions on the basis of α-Fe and γ-Fe according to the data of the phase composition analysis. Plasma impact resulted in 3.5 times microhardness increase due to structure refinement.

1. Introduction

High energy particles can be effectively used for materials surface layer alloying by elements resulting in the material exploitation characteristics increase. Alloying is carried out by preliminary deposition of an alloying element film or a coating and subsequent treatment by ion, electron, laser and plasma beams [1-9]. Convective mass transfer in the melt is the main mechanism of coating and main material mixing when treatment results in melting of the surface layer. Mixing homogeneity will be increased with the growth of melt life time. Compression plasma flows (CPF) generated by quasi-stationary plasma accelerators are of special interest in this field due to relatively high pulse duration ~ 100 μs [8, 9]. A large number of experimental data have been accumulated on the elemental and phase composition, structure, properties of the metals and alloys surface layer formed by CPF treatment of the coating/material system. But most of the data were received when the coating consisted of one element only. At the same time simultaneous alloying by a few elements is of special interest for the application in industry, too. That is why it is necessary to investigate the main regularities of the elements concentration change in this case.

The investigation of element and phase composition, structure and strength properties of the plain carbon steel surface layer simultaneously alloyed by Mo and Cr atoms under the action of compression plasma flows was the main aim of this work. The choice of alloying elements was made due to the fact that these elements dissolve in each other without limits [10]. Thus, Mo-Cr coating...
should consist of one phase and possess equal thermal characteristics in each local area, providing greater homogeneity of Mo and Cr distribution inside the alloyed layer. Besides being the main alloying elements in steel these elements are widely used in surface alloying realized by impact of high energy particles on coating/substrate system [6-9].

2. Experimental

The samples of plain carbon steel (concentration of the alloying elements in wt.%: 0.2 C, 0.2 Si, 0.5 Mn) were investigated objects. Mo-Cr coating with the thickness of 2 μm was deposited on samples before CPF treatment. The coatings were deposited using the vacuum arc vapor deposition technique with two cathodes. The operating parameters were as follows: the arc current was 100 A, the negative bias voltage on the samples was ~ 120 V, the deposition time was 5 minutes. Chromium concentration in the coating was 15 at. %. The samples with the coating were treated by compression plasma flows generated in the magneto-plasma compressor of compact geometry. Treatment was carried out by 1, 3 and 5 pulses at the interval of ~ 5 s. The energy density of heat flux absorbed by the sample was 13 J/cm² per pulse (registered by calorimetric measurements). The experiments were performed in the “residual gas” mode, i.e. the vacuum chamber was filled with the nitrogen gas at the pressure of 400 Pa.

The structure and phase composition of the surface layer were investigated by means of the X-ray diffraction (XRD) method using the Ultima IV RIGAKU diffractometer in Bragg-Brentano geometry with parallel beams in Cu Kα radiation. The analysis of cross-section morphology was carried out by means of scanning-electron microscopy (SEM) using the LEO 1455 VP microscope. The element composition of the modified surface layers of the samples was determined by the energy dispersion X-ray microanalysis using the Oxford X-ray detector. The microhardness was measured by the Vickers diamond indenter under the load of 0.98 N using the PMT-3 device.

3. Results and discussion

The analysis of the samples cross-section structure carried out by SEM showed that CPF impact on the (Mo,Cr)/steel system resulted in the formation of the steel surface layer alloyed by Mo and Cr atoms (Figure 1). The thickness of the melted layer after one pulse of treatment was 5.3-7.5 μm (Figure 1c). It increased up to 10.0-13.3 μm with the growth of the pulses number (Fig. 1e). The action of convection processes provided alloying elements distribution in the whole volume of the melt. The thickness of the alloyed layer after one pulse of CPF treatment was equal to 8 μm and after five pulses of treatment increased up to 10 μm according to the data presented in Figures 1d and 1f. These values correspond to the thicknesses of the melted layer in the areas chosen for the element analysis. Thus, an increase of the pulses number at the used value of energy absorbed by the surface layer led to the growth of the melted and, hence, alloyed layer in the investigated system. Besides, the pulses number growth led to an increase of elements distribution homogeneity in the alloyed layer (Figures 1d and 1f). This effect occurred due to the growth of the melt life time and thus due to an increase of convective processes duration that led to elements distribution homogenization.

The pulses number growth also resulted in diminishing the molybdenum and chromium concentration in the alloyed layer (Figure 2) that can be caused by two main reasons: redistribution of alloying elements in the melt with greater thickness, surface erosion during plasma impact. Hydrodynamic flow of the melt under pressure of plasma flow spreading along the surface is the main mechanism of erosion [11]. It should be noted that the ratio of chromium and molybdenum concentrations in the alloyed layer corresponded (within the measurement error) to that in the coating (Figure 2).

The results of the phase composition analysis before and after CPF treatment are presented in Figure 3. One can see that a solid solution Mo(Cr) was the main phase in the coating deposited on the steel surface. Besides, the diffraction line is observed in the area of 39.5 degree that can be attributed to molybdenum oxide. This oxide can be formed due to interaction with molecules of residual atmosphere in the vacuum chamber during deposition.
Figure 1. Cross-section morphology (a, c, e) and distribution of elements along the line (b, d, f) in the sample with the coating (a, b) and the samples treated by CPF by one pulse (c, d) and five pulses (e, f).
Figure 2. Dependence of the alloying elements concentration and their ratio in the steel surface layer on the number of pulses.

Figure 3. Diffraction patterns of the steel sample with the coating and the samples treated by CPF with different number of pulses.

The diffraction lines of Mo(Cr) at the diffraction patterns of the samples treated by CPF are not observed. α-Fe and γ-Fe solid solutions containing alloying elements were the main phases found in the alloyed layer. α-Fe diffraction lines are shifted to the area of smaller angles due to the lattice parameter increase, thus indicating formation of substitution solid solution α-Fe(Mo,Cr). α-Fe lattice parameter derived using (211) diffraction line was equal to $0.2865\pm0.003$ nm before CPF treatment. After one pulse of treatment it increased up to $0.2886\pm0.003$ nm and after five pulses - $0.2883\pm0.003$ nm. According to the equilibrium phase diagrams of Fe-Cr and Fe-Mo and the
elements composition analysis data (Figure 2) one can expect that all chromium atoms will take part in the formation of the solid solution on the base of α-Fe while molybdenum atoms can take part both in the formation of a solid solution and Fe₂Mo intermetallide though Fe₂Mo diffraction lines are not found in the diffraction patterns. One can see that α-Fe lattice parameter does not depend on the number of pulses. It means that molybdenum solid solubility limit in α-Fe can be reached after five pulses of treatment. Thus dispersed Fe₂Mo precipitates irresolvable by XRD analysis can exist in the alloyed layer. Earlier it was found [12] that diffusion of nitrogen atoms from residual atmosphere of vacuum chamber into the surface layer was the main reason of γ-Fe existence.

The surface layer structure change led to the the modification of its strength characteristics (Figure 4). Microhardness of the initial steel sample (without the coating) was 210±50 HV. The increase of the pulses number led to the microhardness increase. After five pulses of CPF treatment the microhardness of the surface layer was 3.5 times higher than that of steel before treatment.

![Figure 4](image_url)

**Figure 4.** Dependence of samples microhardness on the number of pulses.

The increase of the pulses number resulted in the alloying elements concentration decrease which in turn, can lead to diminishing solid solution hardening and disperse hardening (due to possible formation of dispersed intermetallide precipitates) contributions to the microhardness increase. Therefore, structure refinement that occurred due to repeated plasma treatment can be the main hardening mechanism. This supposition is confirmed by SEM data. The mean size of α-Fe grains in the alloyed layer after one pulse of treatment was 0.75 μm, while after five pulses of treatment it became 0.25 μm (insert in Figure 1e).

### 4. Conclusions

The findings showed that compression plasma flows impact on the (Mo, Cr)/steel system led to the formation of the steel surface layer alloyed by Mo and Cr atoms with the thickness up to 13 μm. The growth of pulses number resulted in an increase of the alloyed layer thickness, an increase of elements distribution homogeneity and a decrease of Mo and Cr concentration inside the alloyed layer. The ratio of Cr and Mo concentration in the alloyed layer remained constant within the measurements error. α-Fe and γ-Fe solid solutions containing alloying elements were the main phases found in the alloyed layer. The microhardness of the alloyed layer after five CPF pulses treatment became 3.5 times higher in comparison with the initial steel because of structure refinement.
References

[1] Kalin B A, Yakushin V L, Vasiliev V I, Tserevitinov S S 1997 Surf. Coat. Tech. 96 110
[2] Zhang C, Lv P, Cai J, Peng C-T, Jin Y, Guan Q 2017 Applied Surface Science 422 582
[3] Zhang C, Lv P, Cai J, Zhang Y, Xia H, Guan Q 2017 J. Alloy Compd. 723 258
[4] Rotshtein V P, Ivanov Yu F, Markov A B, Proskurovsky V I, Karlik K V, Oskomov K V, Uglov V V, Kuleshov A K, Novitskaya M V, Dub S N, Pauleaue Y, Shulepov I A 2006 Surf. Coat. Tech. 200 6378
[5] Leivi A Ya, Yalovets A P, Krasnikov V S 2013 High Temp. Mater. 17(1) 15
[6] Makhlay V A, Garkusha I E, Bandura A N, Byrka O V, Chebotarev V V, Fedorchenko V D, Medvedev A V, Tereshin V I 2009 Eur. Phys. J. D 54 185
[7] Pogrebnyak A D, Bakharev O G, Sushko V V, Bratushka S, Mikhailov A D, Ivanov Yu F, Markov A B, Proskurovskiy D I, Rotstein V P, Valyaev A N 1998 Surf. Coat. Tech. 99 98
[8] Uglov V V, Anishchik V M, Cherenda N N, Stalmashonak A K, Astashinski V M, Kuzmickii A M, Kostyukevich E A, Kovyazo A V 2005 Vacuum 78 489
[9] Uglov V V, Cherenda N N, Anishchik V M, Stalmashonak A K, Astashinski V M, Mishchuk A A 2007 Vacuum 81 1341
[10] Lyakishev N P 1996 Equilibrium diagrams of binary metal systems (Moscow: Mashinostroenie) vol. 2 p 1024
[11] Tereshin V I, Garkusha I E, Bandura A N, 2003 J. Nucl. Mater. 313–316 685
[12] Cherenda N N, Shimanskii V I, Uglov V V, Astashinskii V M, Ukhov V A 2012 J. Surf. Invest.-X-ray+ 6(2) 319