

## MIXING OF “TANTALUM-CARBON STEEL” SYSTEM BY COMPRESSION PLASMA FLOW

A.H. Sari<sup>1)</sup>, V.M. Astashynski<sup>2)</sup>, Yu.A. Petukhou<sup>3)</sup>

<sup>1)</sup>*B.I. Stepanov Institute of Physics, National Academy of Sciences of Belarus,  
70 Nezavisimosti Ave., Minsk 220072, Belarus*

<sup>2)</sup>*A.V. Luikov Heat and Mass Transfer Institute, National Academy of Sciences of Belarus,  
15, P. Brovki Str., Minsk 220072, Belarus*

<sup>3)</sup>*Belarusian State University of Informatics and Radioelectronics, 6 Brouki Str., Minsk 220013, Belarus  
Tel. +375 29 2510726, e-mail: a.sari@dragon.bas-net.by*

A microstructure and phase and element compositions of a plasma-mixed “tantalum/U8A carbon steel” system have been investigated. Surface alloying of carbon steel with tantalum has been performed using a compression plasma flow (CPF). In this technique, the action of relatively short ( $\sim 100 \mu\text{s}$ ) and high-energy (up to  $20 \text{ J/cm}^2$ ) plasma pulses leads to the melting of the near-surface layer of the steel substrate together with the pre-deposited Ta film ( $\sim 1 \mu\text{m}$  thick). A rapid liquid-phase mixing in the molten state occurs, resulting in the formation of new phases during fast re-solidification. It is observed that plasma treatment of the system causes both tantalum nitride and the tantalum-iron intermetallic compounds to form.

### Introduction

In last two decades, the surface modification of materials by high power treatment using laser [1, 2], ion [3], and electron [4-6] beams and plasma flows [7] has been intensively investigated. A pulsed plasma source is one of the most suitable sources for material processing due to high temperatures and energy densities transmitted to a target, ease of control, etc. In contrast to the laser and electron beams, the ion and plasma pulses also transport to the target some material species. Whether or not these species play any role in the modification of a given target material depends both on the processed material and on the type, dose, and energy of these species. A magneto-plasma compressor (MPC) is a quasi-stationary plasma accelerator capable of producing supersonic compression plasma flows (CPF) [8]. The weakly diverging, high energy density (up to  $30 \text{ J/cm}^2$ ) CPF has been used to modify a surface layer (up to tens of micrometers) in an extremely short time ( $\sim 100 \mu\text{s}$ ). The surface treatment of ferrous materials and various type of steels by CPFs was found to result in a significant improvement of their tribological properties [9-14]. In this connection, the modification of low-alloyed steels with different elements is of special interest [11, 14].

In our previous works, Ti, Zr, Mo, and Cr had been chosen as alloying elements for carbon steel. In this study, carbon steel (U8A) with a pre-deposited tantalum coating was subjected to the CPF action. Tantalum coatings can effectively protect steel against corrosive and erosive wear. Its high melting point, toughness, and exceptional resistance to chemical attack make it an attractive coating material for components exposed to high temperatures, wear, and harsh chemical environments. The presence of a refractory metal (e.g. Ta or Mo) film on an iron substrate has been reported to result in the increased thickness and lifetime of the molten iron layer and the decreased cooling rate and solid/liquid interface velocity during high current electron beam mixing [6]. The melting point of Ta ( $2997^\circ\text{C}$ ) is comparable with the boiling temperature of iron ( $2872^\circ\text{C}$ ). In this case, equilibrium phase diagrams of a Fe/Ta system reflect a full inter-solubility of the components in the liquid phase and a limited solubility in the solid state, which

makes mixing difficult. Taking into account a wide spectrum of compounds, phases, and solid solutions produced in the Fe-Ta system, as well as the extremely non-equilibrium conditions of phase formation in the case of CPF treatment, an analysis of Ta film/carbon steel after the CPF action is considered to be a complicated problem. The analysis of the changes in the phase and element composition and in the microstructure properties of the carbon steel alloyed by tantalum is the aim of the present study.

### Experiments

The tantalum layer (about  $1 \mu\text{m}$  thick) was deposited on a U8A carbon steel (C $\sim 0.7$  wt.%, Fe  $\sim 98$  wt.% and Si, Mn, Ni, S, P, Cu and Cr up to 0.2 wt.%) sample using ion beam sputtering and deposition technique. The method yields new-generation protective coatings by using dual ion beams. In this system, one of the ion beams is used to sputter and the other to pre-treat (ion cleaning and activation) the substrate surface before coating deposition [15]. The prepared samples were treated by CPFs in the magneto-plasma compressor of compact geometry (fig. 1). The MPC was operated in “residual gas” mode: the pre-vacuumed compressor chamber was filled with a plasma forming gas (nitrogen) up to 400 Pa pressure. Samples were fixed at a distance of 12 cm from the cathode tip and exposed to single CPF or a series of three pulses.

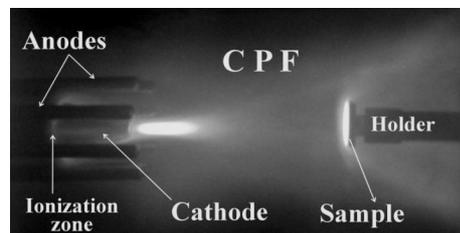


Fig. 1. The photo of CPF treatment of a typical sample

The plasma flow parameters were as follows: pulse duration  $\sim 100 \mu\text{s}$ , energy density absorbed by the target varied from  $2 \text{ J/cm}^2$  to  $20 \text{ J/cm}^2$ . There are two ways to increase total energy absorbed by the target, first by rising the plasma power density (either by increasing the initial capacitor voltage or by decreasing the distance between the MPC's cathode

and target sample), and the second by using a higher number of pulses. In this study, we have used different pulse numbers ( $n=1$  and  $3$ ). The surface morphology of samples was analyzed by scanning electron microscopy (SEM), using a LEO1455VP device equipped with an energy dispersive X-ray analyzer (EDX). The studies were performed in elemental contrast mode. The phase compositions of the untreated and CPF treated samples were investigated by means of X-ray diffraction (XRD) analysis using a DRON-4-13 diffractometer with a Bragg-Brentano focusing geometry and Cu emission.

## Results and Discussions

The SEM images of the CPF treated sample surfaces are demonstrated in figures 2 and 3. Figure 2 shows the morphology of the Ta/U8A sample after single pulse CPF treatment (absorbed energy density  $E=5 \text{ J/cm}^2$ ) and the corresponding EDX elemental profiles of Ta and Fe measured along the AB line.

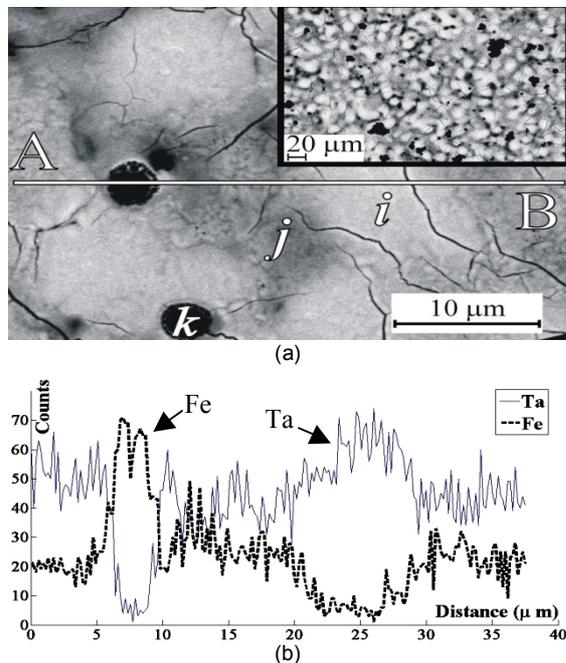


Fig. 2. (a) SEM image of Ta/U8A-steel sample after treatment by single CPF pulse at  $E=13 \text{ J/cm}^2$ , (b) corresponding EDX elemental profiles measured along the AB line

The structure of the surface in figure 2 (a), shows three regions, *i*, *j* and *k*, which differ in the elemental composition. These regions were also observed at other energy densities (e.g.  $3$  and  $5 \text{ J/cm}^2$ ). EDX analysis demonstrated that the light and dark regions (*i* and *k*) mainly consisted of Ta and Fe, respectively. On the other hand, the grey areas (*j*) contain a mixture of Fe and Ta. The regions *i* and *j* in fig. 2 (a) occupy about  $46\%$  and  $44\%$  of the total surface area, respectively. Therefore, a process of mixing by the CPF action on the sample is effective in the *j* region, i.e. only at  $44\%$  of the subjected surface. Such a non-uniformity of mixing seems to be related to local inhomogeneities in the thermal energy, hydrodynamic instabilities arising at the interface between

the plasma of the chock-compressed layer and the surface of the melt, non-uniformity of coating and partial ablation of its surface (due to explosion boiling). CPF treatment by the series of pulses changes the surface structure and makes the alloying metal distribution more homogeneous (see figure 3 a, b). In this regard, the EDX analysis showed that the tantalum concentration decreases with the growth of  $n$ . This effect may be due to the increase in the modified layer depth and the diffusion of tantalum to the pre-surface layer [13].

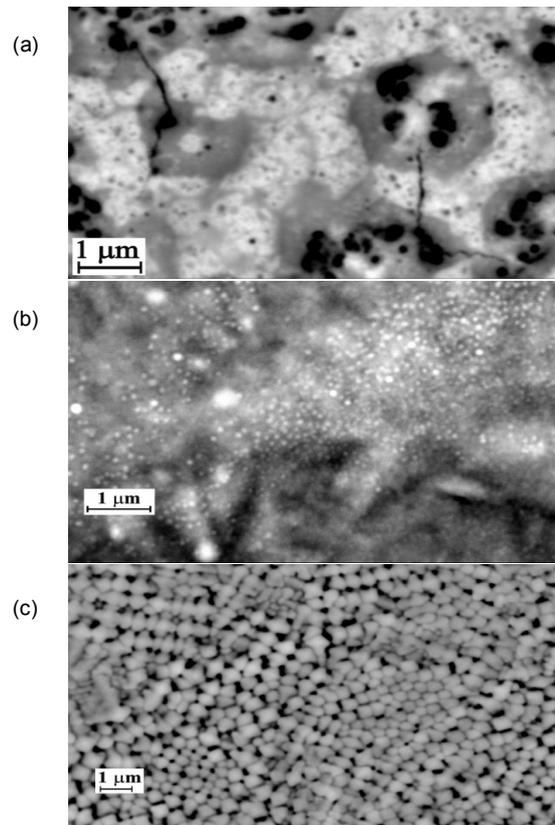


Fig. 3. The SEM images of samples after CPF treatment, (a)  $E=5 \text{ J/cm}^2$ ,  $n=1$  pulse, (b)  $E=5 \text{ J/cm}^2$ ,  $n=3$  pulses and (c)  $E=20 \text{ J/cm}^2$ ,  $n=3$  pulses

The increase in both the energy density and number of pulses results in the formation of a distinguishable cellular structure consisting of hexagonal cells (fig. 3.c). The size of the cells varies within  $0.2$ - $0.6 \mu\text{m}$ . This structure is caused by the existence of concentrated and undercooled melt in which the crystallization proceeds at temperatures below the solidification point (because of the presence of interstitial nitrogen). Non-uniform mixing leads to the formation of local areas with different concentrations of components. These areas can belong to different parts of the equilibrium phase diagram. Thus a variety of phases can be expected according to the phase diagram [16]. The XRD analysis data for the samples before and after CPF treatment at different energy densities absorbed by the target are presented in figure 4. They show that the CPF action results in the formation of crystalline phases of oxide and nitride ( $\text{Ta}_2\text{O}_5$ , TaN), intermetallic compounds

(corresponding to FeTa as equilibrium phase and Fe<sub>5</sub>Ta<sub>3</sub> as non-equilibrium phase), and  $\gamma$ -Fe. The formation of tantalum nitride is due to the interaction of Ta with the plasma-forming substance (nitrogen). It is known that, in terms of the affinity for nitrogen, tantalum has a high probability to form nitrides (standard enthalpy of TaN is 251.5 kJ/mol [17]).

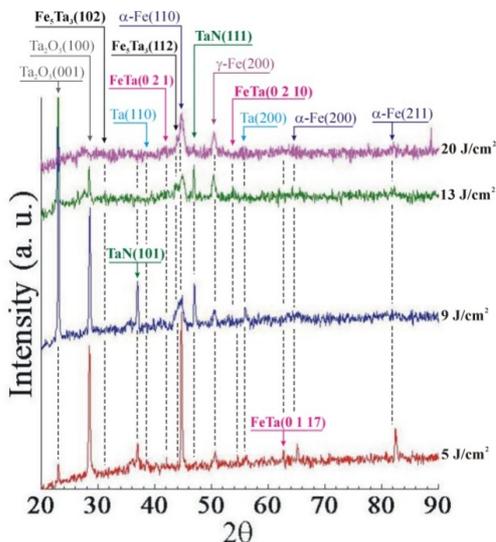


Fig. 4. The XRD patterns of samples before and after CPF treatment at different energy densities absorbed by target and  $n=1$  pulse

The XRD patterns also show that CPF treatment leads to the formation of tantalum oxide (even at the lowest CPF energy density) while there is no line in the untreated Ta film/steel substrate spectrum to correspond to the oxide phase. It has been reported that the presence of Fe can catalyze the oxidation of Ta [18]. In other words, Ta is more susceptible toward oxidation in the presence of Fe. Oxygen for the unintentional oxidation originates from residual gas contamination. The observations confirm that even small oxygen contaminations are sufficient to oxidize Ta. Formation of the surface nitride phase will prevent diffusion of impurities from the residual gas in the vacuum chamber into the sample bulk. Increase in the CPF energy density to 20 J/cm<sup>2</sup> results in vaporization and partial splitting (due to explosion boiling) of the Ta film. As a consequence, at high energy densities, the decrease of the nitride and intermetallic compounds as well as tantalum oxide phase is found.

## Conclusions

Efficient Ta/steel mixing by the CPF action was achieved at 44% of the subjected surface. Such a non-uniformity of mixing is suggested to be related to local inhomogeneities of the thermal energy, hydrodynamic instabilities arising at the interface between the plasma of the shock-compressed layer and the surface of the melt, irregularities of the coating, and its partial ablation. The CPF treatment of the "Ta/carbon steel (U8A)" system, in the nitrogen atmosphere at the pressure of 400 Pa, successfully results in the formation of tantalum nitride (TaN) in the surface layer. The formation of the iron-tantalum

(FeTa and Fe<sub>5</sub>Ta<sub>3</sub>) intermetallic compounds was identified by the XRD analysis. The presence of Fe can catalyze the oxidation of Ta and formation of Ta<sub>2</sub>O<sub>5</sub>. The unintentional oxidation originates from residual gas contamination. CPF treatment by series of pulses increases the homogeneity of the alloying metal distribution. The increase in CPF energy density intensifies the evaporation process of the Ta film. As a consequence, the contents of both the nitride / intermetallic compounds and the tantalum oxide phase start diminishing.

## References

1. C.W. Drapper, J.M. Poate, Int. Met. Rev. 30 (1985) 85; J.M. Poate, G. Foti, D.C. Jacobson // Surface Modification and Alloying by Laser, Ion and Electron Beams, Plenum Press, New York, 1983.
2. N.N. Rykalin, A.A. Uglov, I.V. Zuev, A.N. Kokora (Eds.), Lasernaya i Electronoluchevaya Obrabotka Materialov, Publ. House Mashinostroenie, Moscow, 1985.
3. A.D. Pogrebnyak // Phys. Stat. Sol. A. -1990. - 117. - P. 17.
4. J. Gyulai, I. Krafscic // Nucl. Instr. and Meth. B. - 1989. - 37/38. - P. 275.
5. Y. Nakagawa, T. Arioshi, M. Itamy, Y. Fujii // Jpn. J. Phys. - 1988. - 27. - P. L719.
6. A.D. Pogrebnyak, S. Bratushka, V. I. Boyko, I. V. Shamanin, Yu. V. Tsvintarnaya // Nucl. Inst. and Meth. B. - 1998. - 145. - P. 373-390.
7. B.A. Kalin, V.L. Yakushin, V.I. Vasiliev, S.S. Tserevitinov // Surf Coat Technol. - 1997. - 96. - P. 110.
8. V. M. Astashinskii, G. I. Bakanovich, E. A. Kostyukevich, A. M. Kuz'mitskii, A. A. Man'kovskii and L. Ya. Min'ko. // J. Applied Spectroscopy. - 1989. - 50. - P. 549.
9. V.V. Uglov, V.M. Anishchik, V.V. Astashynski, E.K. Stalmoshonok, D.P. Rusalsky, N.N. Cherenda, I.N. Rumyancheva, V.V. Askerko, A.M. Kuz'mitski, Surf Coat Technol. - 2004. - 108. - P. 180-181.
10. N.N. Cherenda, V.V. Uglov, V.M. Anishchik, A.K. Stalmashonak, V.M. Astashinski, A.M. Kuzmickii, A.V. Punko, G. Thorwarth, B. Stritzker // Surface & Coatings Technology. -2006. - 200. - P. 5334 - 5342.
11. V.V. Uglov, V.M. Anishchik, N.N. Cherenda, A. K. Stalmashonak, A.M. Kuz'mitski, E. A. Kostyukevich, Kovyazo // Vacuum. - 2005. - 78. - P. 489-493.
12. N. N. Cherenda, V. I. Shimanskii, V. V. Uglov, V. M. Astashinskii, and V. A. Ukhov // Journal of Surface Investigation. - 2012. - Vol. 6, No. 2. - P. 319-325.
13. N.N. Cherendaa, V.V. Uglov, V.M. Anishchik, A.K. Stalmashonak, V.M. Astashinski, A.M. Kuzmitski, G. Thorwarth, B. Stritzker // Vacuum. - 2007. - 81. - P. 1337-1340.
14. V.V. Uglov, N.N. Cherenda, V.M. Anishchik, A.K. Stalmashonak, V.M. Astashinski, A.A. Mishchuk // Vacuum. - 2007. - 81. - P. 1341-1344.
15. M.A. Andreev, E.D. Manojlo, A.I. Shevtsov, N.M. Chigri-nova // Inzhener-mekhanik (in Russian). - 2009. №. 1. - P. 25-28.
16. O.A. Bannykh, P.B. Budberg, S.P. Amkova, Diagrammy Sostoyanii Dvoynykh i Mnogo-Komponentnykh Sistem na Osnove Zheleza, Spravochnik, Publ. House Metallurgiya, Moscow, 1986. - P. 440.
17. E. A. Brandes, G. B. Brook, Smithells Metals Reference Book, Seventh Edition, The Bath Press, G.B. Brook, 1999.
18. B. C. Bayer, S. Hofmann, C. Castellarin-Cudia, R. Blume, C. Baetz, S. Esconjauregui, C. T. Wirth, R. A. Oliver, C. Ducati, A. Knop-Gericke, R. Schlogl, A. Goldoni, C. Cepek, J. Robertson. // J. Phys. Chem. - 2011. - 115. - P. 4359-4369.