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Zoya Duriagina, Tetiana Tepla
Lviv Polytechnic National University, Lviv, Ukraine

MODIFICATION OF SURFACES OF SPECIAL ALLOYS BY NITROGEN FOR POWER ENGINEERING

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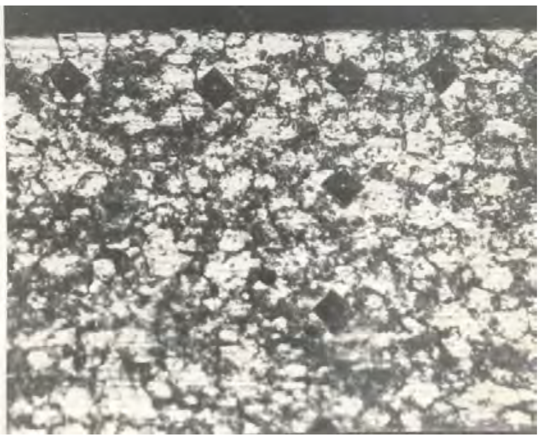
Abstract. The use of nitrogen as an alloying element presents a great interest for the improvement of properties of alloyed steels and special alloys. Superficial layers were formed by ionic implantation and by melting the surface by nitrogen plasma. After this kind of treatment, there form a continuous defect-free layers with a good adhesion to the surface. Surface treatment of steels and vanadium alloys increases their corrosion resistance and microhardness of surface layers. A combined supply of alloying elements into the melting area allows us to control the type and the density of secondary phases which are formed as the result of the reaction diffusion. In this way, depending on external needs, it is possible to increase either corrosive-electrochemical properties of the surface (when alloyed layers consist mainly of nitride or oxinitride phases) or wear resistance (when carbide or carbonitride phases will constitute a greater specific volume in the formed layers).

Introduction

As is known, nitrogen has a negative influence on the property of stainless steels and nonferrous metals [1; 2]. To remove it you have to apply a refining process which is complex, power consuming and, consequently, uneconomical [2; 3].

At the same time, the use of nitrogen as an alloying element presents great interest for the improvement of properties of alloyed steels and special alloys [3]. Measuring out the amount of nitrogen and regulating the alloying modes we can achieve formation of a superficial layer with such a content of nitrogen that will have the protective properties specified beforehand (Fig. 1) [4]. It is confirmed by calculations of the thermodynamics stability of phases in and by a high cognation of vanadium and titanium to nitrogen [3; 4].



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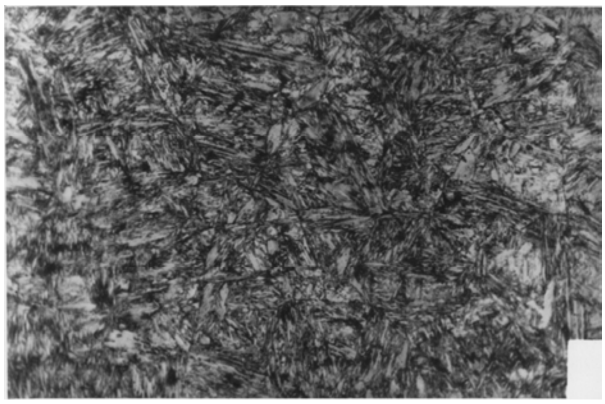


b)

Fig. 1. Micrographs of ferrite–martensitic stainless steals without surface treatment:
a - steel ЭП 823, x 500, b –steel 20X13, x 500

Stating of the main material

Our research was conducted on special alloys already used in the power industry, and on candidate materials for thermal nuclear energy. Among the known materials of energy vanadium alloys are the least studied group of alloys. Scientific schools in the USA, Japan and Russia are engaged in the development and research of these alloys. According to the research conducted in the USA within a wide spectrum of alloys of the system V – Cr – Ti, it is proposed to use V – (4 – 5) Cr – (4 – 5) - Ti alloys taking into account the optimum ratio of mechanical and technological properties and small sensitiveness to helium penetration into them. Russian schools are considering the limits of alloying vanadium alloys in the wider interval V – (10 – 15) Cr – (5 – 10) Ti. These alloys are characterized by diminishing plasticity at high temperatures and have a low swelling resistance. As the result of the research we determined the optimum chemical composition of vanadium alloys, which is V- (5 – 12) Cr – (5 – 20) Ti.

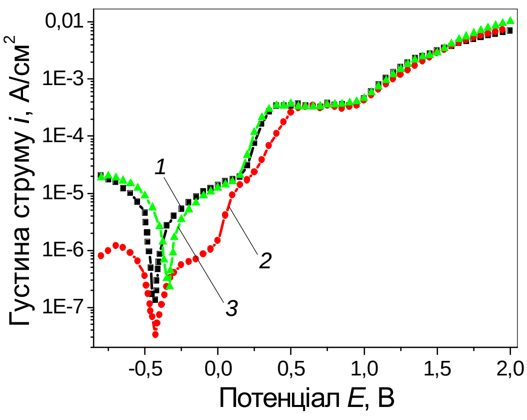
Superficial layers were formed:

- by ionic implantation of nitrogen by using ionic implanter MPB – 202 by «Balzers», that develops the maximum power of 180 keV. Power can be changed to this limit to produce layers of the required thickness;

- by melting the surface by nitrogen plasma on plasmotron HO – 01 as an electromagnetic shock pipe, with the impulse of the duration 1 - 5 mks at different pressures of plasma. Energy of the plasma radiation impuls is inversely proportional to the pressure of plasma, thus accelerating the tension to 34 kV allowed us to change the energy of the impulse within the limits 50 - 150 J/cm^2.

Taking into account the previous research results, the parameters of ionic implantation providing maximum nitrides formation on the external and internal interphases were selected: ionic implantation by mode 1 – with the energy of radiation E=40 keV, the dose of nitrogen implanted into the surface D = 2 * 10^{16} ion/cm^2, ionic implantation by mode 2 – at the energy of radiation E = 45 keV, the dose of the nitrogen implanted into the surface D = 1 * 10^{17} ion/cm^2.

After ionic on-the-spot implantation of vanadium alloys there form a continuous defectless layer with a good adhesion to the surface. By the x-ray structural phase analysis and raster electronic microscopy, secondary phases were identified which were formed after the ionic implantation of nitrogen. Namely, the density of nitrides of Cr_2N, VN, TIN increases with the increase of the content of alloying elements and the dose of irradiation. It is in complete accordance with the thermodynamic prognosis of the probability of the secondary phase formation. In such modes, on the surface of the corrosionresistant steel ЭП 823 there forms phase γ' – (Fe_4N) which is characterized by a well-ordered position location of nitrogen atoms and vacancies, nitrides Cr_2N, VN, CrN and carbides (Fig. 2). The formed phases increase the level of the compression tension on the surface, thus increasing the corrosion and mechanical firmness of the investigated materials.



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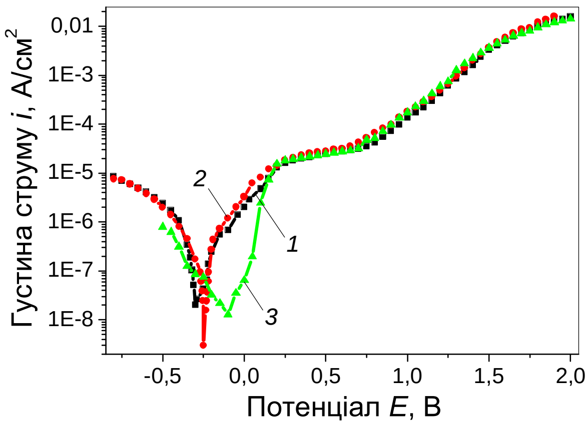
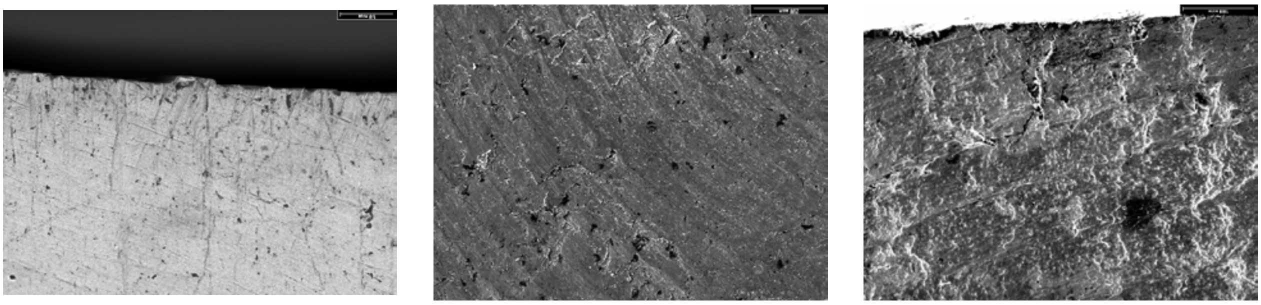


b)

Fig. 2. The effect of ionic implantation on the corrosion-electrochemical behaviour of steels 20X13 in 3% solution NaCl pH 2 (a) and pH 6.2 (b): 1 – initial surface, 2 – after ionic implantation by mode – 1, 3 - after ion implantation by mode – 2

The processes of ionic implantation in the investigated materials proceed by different mechanisms. Thus, for double vanadium alloys of the system V – Cr, due to isomorphicity of their grates, there is a correlation interaction of a bunch of ions with grate atoms, which stipulates the effect of tunneling with the formation of nitrides of VN, Cr_2N. In V – Cr – Ti vanadium alloys and steels, the formation of nitride phases (VN, Cr_2N, TIN, Fe_4N) is carried out through the mechanism of radiation stimulated diffusions (Fig. 3).



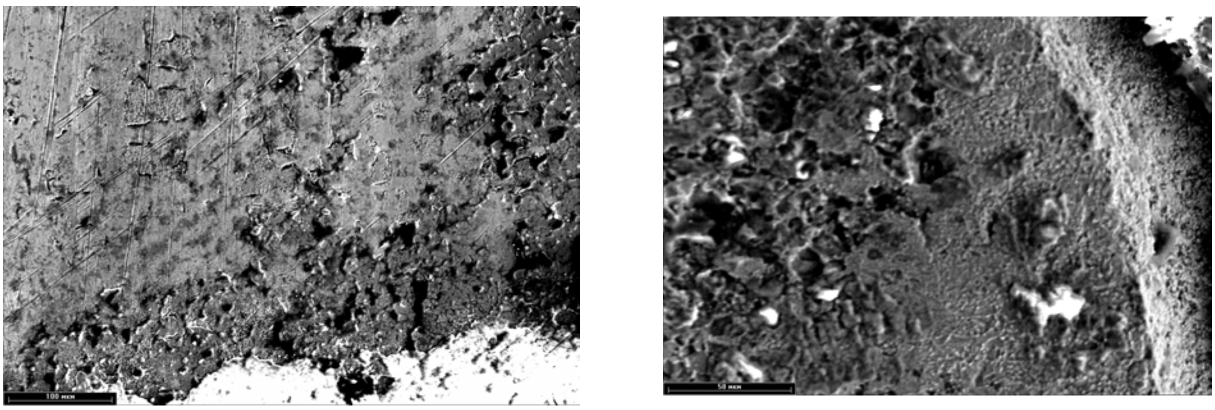
a) *b)* *c)*

Fig. 3. The micrographs of vanadium alloys after ionic implantation from by nitrogen: a – the surface, × 50, b – ionic implantation surface, × 100, c – ion implantation surface, × 200

Corrosive-electrochemical research showed that superficial layers of the alloys of the system V – Cr – Ti, formed by the ionic implantation by nitrogen, regardless of the pH of the environment, have higher corrosive-electrochemical properties in comparison than the alloys of the system V – Cr. Ionic implantation causes an increase of corrosive-mechanical properties in the environment with pH 11 and pH 6.2 for vanadium alloys in a greater degree than for corrosion resistant steels.

At the melting of V – Cr – Ti vanadium alloys by nitrogen plasma, on its surface there forms a protective barrier layer with a different structural-phase state, 35 – 50 mkm thick. This layer possesses increased corrosive-mechanical properties. By the x-ray spectral and x-ray-structural phase analyses, after plasma treatment, on the surface of vanadium alloys of the system V – Cr – Ti there occurs a redistribution of the alloying elements, namely, segregation of vanadium and titanium to the surface and diminishing the amount of chrome in the superficial zone area. This leads to the formation of secondary phases identified as nitrides and oxinitrides of vanadium and titanium, carbides of chrome and intermetalides. By the x-ray-structural phase analysis which was conducted on x-ray diffractometer DRON – 3 in Cu-Kα – radiation it was determined that the density of distributions increases, which testifies to the appearance of internal microtensions. This leads to dispersing the structure, which strengthens the barrier effect.

Modification of the surface of corrosion-resistant steels by nitrogen plasma intensifies diffusive processes in superficial layers. By the non- dispersive x-ray photograph and local micro x-ray analyses, the formed secondary phases are identified as nitrides of titanium, which is confirmed by the distribution of the power dispersion on the cube inclusion of steel 12X18H10T (Fig. 4). By the results of measuring microhardness, steels show lower values than vanadium alloys.

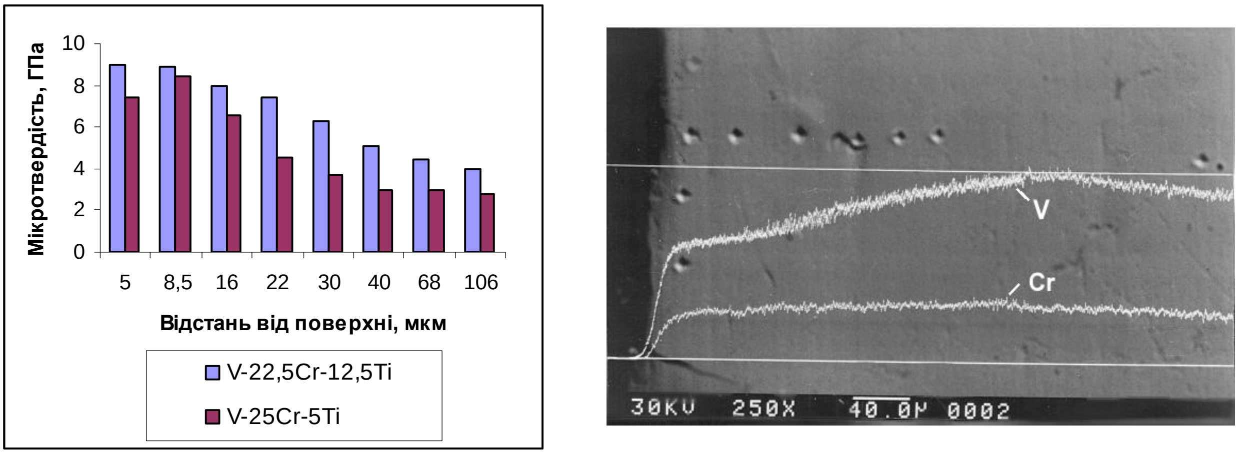


a) *b)*

Fig. 4. Micrographs of ferrite–martensitic steel 20X13 after ionic implantation by nitrogen: a – ionic implantation by mode – 1, × 200, b – ionic implantation by mode – 2, × 500

By the corrosive-electrochemical research it was determined that plasma treatment of the investigated materials and complex modification of steels 20X13 and ЭП 823 by nitrogen and niobium increase their corrosive-electrochemical properties.

By the conducted research into wear firmness it was established that complex modification of the surface of corrosion resistant steels 12X18H10T and ЭП 823 by niobium and nitrogen increases their wear firmness 2 - 3 and 10 times accordingly, in comparison with their untreated state (Fig. 5).



a) *b)*

Fig. 5. The character of distribution of microhardness of vanadium alloys after plasma treatment by nitrogen (a) and distributing of vanadium and chrome of V-25Cr-5 Ti alloy (б), ×250

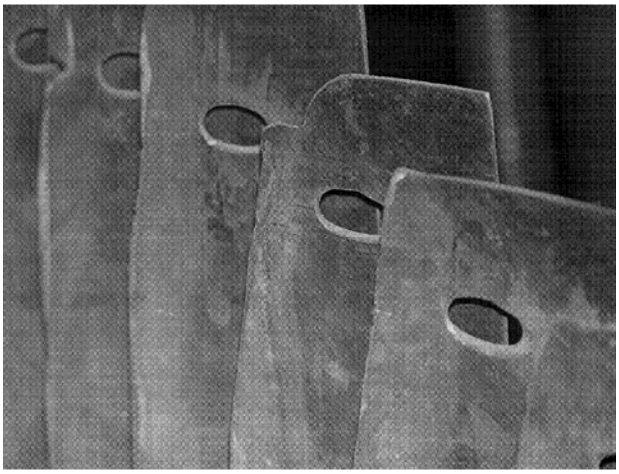
A combined supply of alloying elements into the melting area allows us to manage the type and specific density of secondary phases which are formed as the result of the reaction diffusion. In this way, depending on external environments, it is possible to increase either corrosive-electrochemical properties of the surface (when alloyed layers consist mainly of nitride or oxinitride phases) or wear firmness (when carbides or carbonitride phases will constitute a greater specific volume in the formed layers).

Approbation of the conducted research was carried out under the patronage of Galremenergo on the Dobrotvir, Burshtyn TES and «LVIVORGRES». Thus, on the Dobrotvir TES the workings surfaces of the turbine shoulder-blades were renewed. They work as parts of the LP rotor. Each rotor has 98 shoulder-blades of the height 1100 mm. Taking into account the geometric size of a separate shoulder-blade and the speed of the rotor rotation (3000 turn/min), a disbalance of the rotor in 1 kg of weight causes a formation of a centrifugal force with the amplitude 30 microns. At greater amplitudes an abrupt stop is used for the prevention of destructions. Traditional protection of shoulder-blades of the turbines by stellite plates is ineffective. For 5 years of exploitation it has been subjected to destruction in the form of cracks, pittings and ulcers (Fig. 6).

At the same time, the shoulder-blade of the turbine, modified according to our elaboration by the plasma treatment by the powder of niobium which was blown into the active zone in the atmosphere of argon at the impulse $1*10^{-5} – 2*10^{-6}$ seconds for obtaining a critical thermal flow of the order $(2 – 6)*10^{-9}$ Vat/m^2, has not shown any damages for 5 years of its exploitation and eliminated the possibility of the rotor disbalance (Fig. 7).

Conclusions

The use of nitrogen as an alloying element presents great interest for the improvement of properties of alloyed steels and special alloys. Superficial layers were formed by ionic implantation and by melting the surface by nitrogen plasma. After this kind of treatment, there form a continuous defectless layer with a good adhesion to the surface. Surface treatment of steels and vanadium alloys increases their corrosion resistance, microhardness of surface layers. A combined supply of alloying elements into the melting area allows us to manage the type and specific density of secondary phases which are formed as the result of the reaction diffusion. In this way, depending on external environments, it is possible to increase either corrosive-electrochemical properties of the surface (when alloyed layers consist mainly of nitride or oxinitride phases) or wear firmness (when carbides or carbonitride phases will constitute a greater specific volume in the formed layers). The advantage is the ecological cleanness of the process, and also the fact that overcoating does not need special equipment and can be easily automated at scheduled repair.



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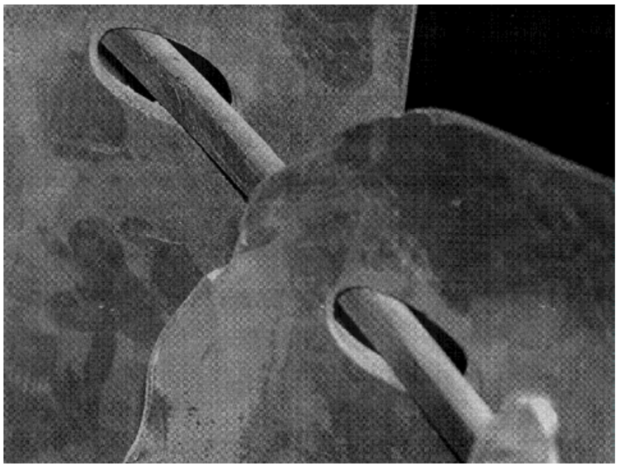

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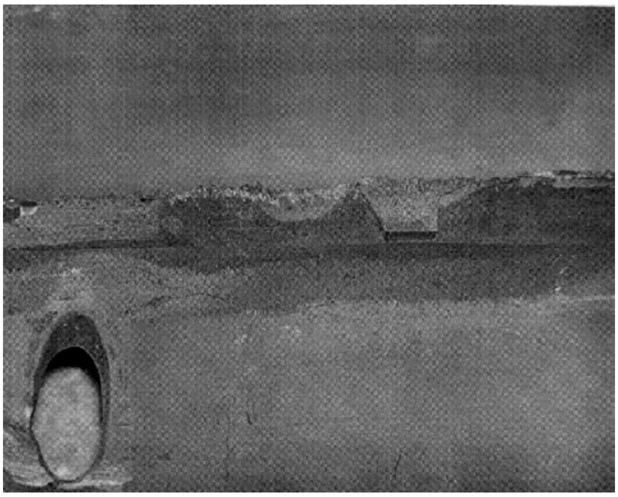

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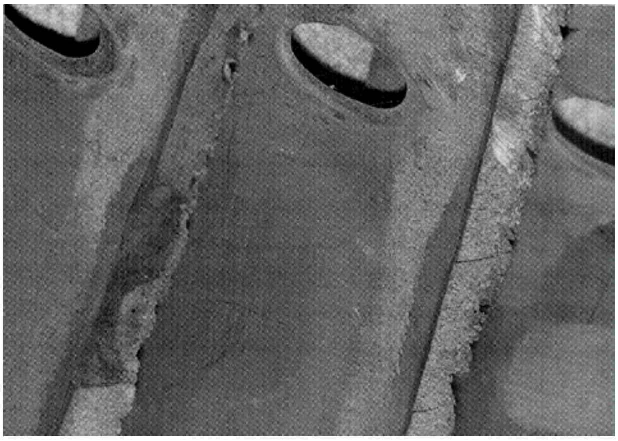

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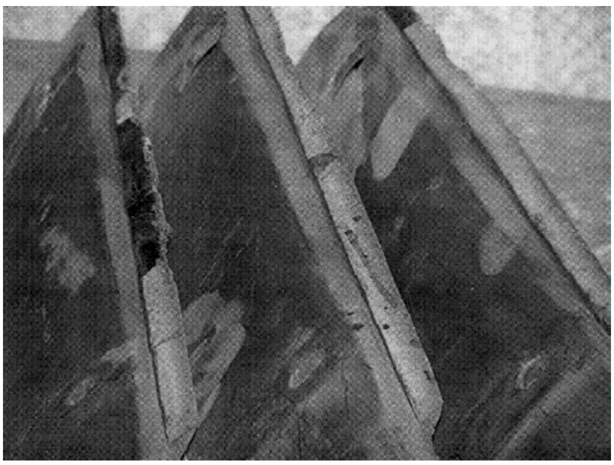
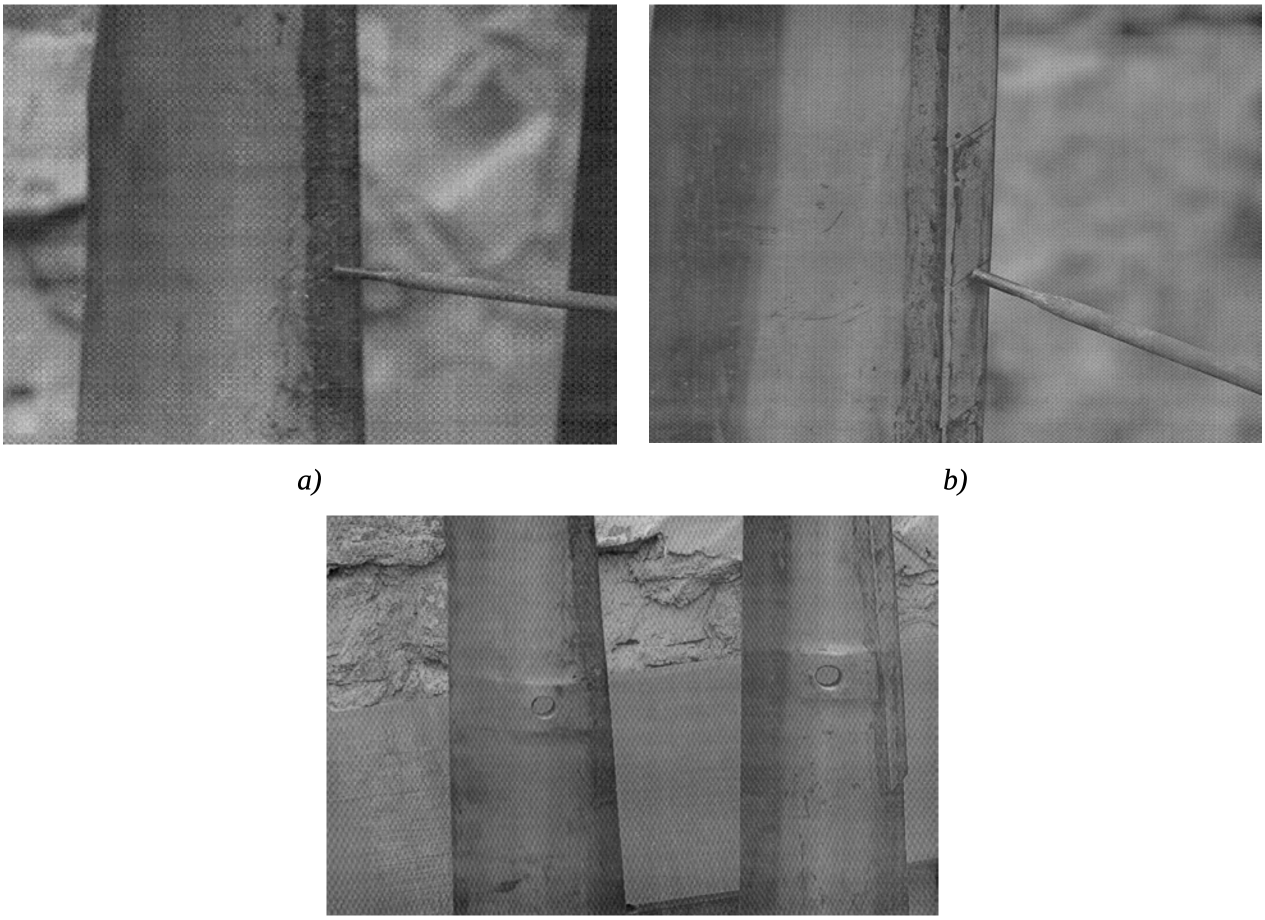


e)

f)

Fig. 6. Main damages of the shoulder blades of the LP turbine of steel 20X13: a, b – abrasive wearing, c – MKC; d – pitting with ulcer corrosion; e, f – cracks



a) *b)*

c)

Fig. 7. Protection of the working surface of the shoulderblade of the LP turbine: a – by means of the plasma melting of the surface; b – traditional, with a stellite plate; c – comparison of the two methods

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