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Forecast the formation of nitrides on the surface of titanium alloys during nitriding in a glow discharge

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ABSTRACT

Purpose: This article is devoted to methods for predicting the results of surface modification of titanium alloys in glow discharge nitriding. With this advantage, it is given to the analytical criteria as the most appropriate for design automation of processes processing.

Design/methodology/approach: The methodology is the position that the nitriding process is a combination of several competing processes leading to the formation of both nitrides, nitrogen diffusion into the depth of the surface and to spray it. The main principle of assessing the intensity of each of them is that each elementary process is the most successful in the case when it created for optimal energy conditions.

Findings: Developed a system of analytical criteria - relative energy factors, which qualitatively and adequately reflect the real processes of nitriding of titanium alloys in a glow discharge. Compliance with these indicators were tested in experimental treatment of samples resulting in an energy generating process model.

Practical implications: The results were primarily used for computer-aided design modification processes, the optimal choice of the technological nitriding mode, the basis for the software control systems equipment for the processing of titanium alloys.

Originality/value: The proposed energy model for the nitriding process in a glow discharge has no current analogues in the world.

Keywords: Titanic alloy; Nitriding in glow discharge; Layer formation; Analytical criteria

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MATERIALS

1. Introduction

Operational characteristics of titanium alloys defined physical-mechanical characteristics of the surface and their phase composition, which depend on the process parameters of nitriding. In papers by Arzamasova BM, Lakhtina Yu.N., Panagiotou TA, and Kaplun VG, it is shown that the process of nitriding in a glow discharge is characterized by the presence of two competing components: diffusion and reverse sputtering. In sources

[1-3], the theoretical foundations of a physical nitriding process in hydrogen-free environments is developed, taking into account the effect of energy flux of particles bombarding the surface (beyond the stream), and introduced the concept of relative energy factors (REF) depending on process parameters of nitriding. Certain provisions of the energy model used for low-temperature nitriding of titanium alloys in the glow discharge [4]. Approbation admissibility application of analytical indicators was carried out by comparing the results of calculations with real structures of the nitrided titanium alloys, which confirmed the quality of their adequacy and ability in design and process optimization, depending on the requirements of operation 199.

In sources [1,5] an assumption was formulated that the probable cause of having an extremum effect of pressure in the discharge chamber should be considered as a non-linear nature of the effect the number of particles in a gaseous medium on the intensity of the ionization and recombination processes. At first, with increasing amounts of particles in a gaseous medium comes increases in the total cross section of the collision, but later mutual overlapping sections become more significant, which reduces the relative intensity of the collision. It was theoretically and experimentally demonstrated [6,7], that the formation of a nitrogen diffusion layer is subject to the rule: the nitrogen layers are formed in the same sequence in which the line crosses the monophasic domain isotherm diagram Fe-N. Based on a critical analysis of the Kolbelya Lakhtina model, there is a proposed [8] model, where the leading role is played by the atomic ions of nitrogen.

Design process is conducted mainly using a technology model, which is actually the basis of data obtained by the nitriding processes experienced. The main drawback of this method is a significant deviation from the actual experimental conditions. In addition, this method does not allow for automating the development of technology, and, accordingly, development of algorithms for automated process control surface modification of alloys.

2. Analytical criteria for the formation of nitrides in titanium alloys during nitriding in a glow discharge

The energy flow model of the interaction of the metal surface is formed on the basis of examining the process of transferring energy at the nano-particle level [1,3]. Assumptions for the model of energy transfer are as follows. Part of the flow, which has the energy ε_β and hence speed V_β, comes into collision with the metal atom in a random impact with parameter ρ. This parameter defines the angle between the direction of motion of the particle and the normal to the surfaces of the colliding particles at the contact point. It is this angle together with the mass ratio of the collision of the particles that affects the amount of energy that can be transmitted from a particle stream, which impinges the particle surface. This basic condition that enables chemical reactions on the surface is that the energy transfer should be in the range of energies of formation of titanium nitride ε_D to the sublimation energy ε_{sb}. The latter is accepted as an energy threshold, beyond which it begins spraying the surface. Moreover, for the molecular ions in the stream, the lower energy limit value is incremented by the molecular dissociation energy ε_d. The energy level is determined by its flow energy spectrum, the shape of which depends on the process parameters: composition of the gaseous medium between the electrodes, the voltage U, the density a current j, the surface temperature T, pressure p in the discharge chamber. Thus, the energy spectrum of the flow depends on the fluid characteristics and parameters of the process which form the energy of this flow does not depend on the type and composition of the metallic surface. Formation of the energy spectrum of the flow, its appearance and characteristics, exactly how and methodology and software were taken from sources [2,9].

Thus, when creating a model forming the separation layer, it undergoes extension of the nitrides energy spectrum using only the energy levels that are necessary and sufficient for reaction to form nitrides. The amount of energy transmitted by the surface of the particles on impact depends largely on the energy of the particle flow and the angle of transmission. The entire process flow interaction with the surface can be displayed via a system of key performance indicators that are divided into two groups: factors of formation of nitrides in the surface layer (they depend on the parameters listed above by technological regime and the chemical composition of the surface) and the factors that are determined by the characteristics of the gas medium. For the latter, the composition of the metal surface doesn't matter since they change depending on the conditions in a glow discharge nitriding reviewed in [4]. Within this work, dedicated to technological peculiarities of formation of a nitride layer on the surface of titanium alloys, it is advisable to only note that the second group of indicators of impact of the incident flux on the surface include: the relative energy factors (REF), which reflect the ability of the flow of ionized and neutral parts to contribute to its spraying or diffusion of the nitrogen in the depth of the surface layer, and the energy levels of the sum of products of all kinds of particles on their relative volume (the relativity concept arises from the fact that the energy spectrum is compared with the energy level of the first cathode layer free path portions).

For the variety of titanium alloys within the first group, these factors are calculated:

F_N – total REF formation of nitrides,

F_{NA} – atomic component of total REF formation of nitrides,

F_{NM} – the same molecular structure.

These factors and components are calculated energy levels for all possible combinations for all parts of the flow surface and which is generally composed of k elements grades (the energy spectrum is formed as a discrete distribution of the dispersion at a certain rate). Therefore, the formation of nitrides components REF component surface grades k, which correspond to a certain energy level:

$$F_{Nik} = 2 j_{\varepsilon vMk}(\varepsilon_i) \int_{\theta_{\min Mki}}^{\theta_{\max ki}} w_\theta(\theta)\, d\theta + j_{\varepsilon vAk}(\varepsilon_i) \int_{\theta_{\min Aki}}^{\theta_{\max ki}} w_\theta(\theta)\, d\theta = \tag{1}$$

$$= 2 j_{\varepsilon vMk}(\varepsilon_i) \int_{\theta_{\min Mki}}^{\theta_{\max ki}} \cos\theta\, d\theta + j_{\varepsilon vAk}(\varepsilon_i) \int_{\theta_{\min Aki}}^{\theta_{\max ki}} \cos\theta\, d\theta$$

where:

$j_{\varepsilon vMk}(\varepsilon_i)$, $j_{\varepsilon vAk}(\varepsilon_i)$ – relative energy flux spectra of molecular and atomic ions [9],

$w(\theta)$ – the probability distribution of the angle θ of the transmission pulse energy in collisions of particles and surface flow.

Limits of variation of the angle as the boundaries of integration of the probability distribution are determined from the minimum and maximum pulse energy, as noted above, namely, the limit value of the angle calculated in general form:

$$\theta_{\lim} = arc \cos\left(\frac{\varepsilon_{\lim}}{K_{enk}\ \varepsilon_i}\right)^{0.5} \tag{2}$$

where:

ε_{lim} – energy level of the minimum or maximum limit,

K_{enk} – power transmission coefficient, which takes into account the ratio of the masses of the incident and part of the surface of the *k-th* class,

ε_i – the current value of the discrete energy spectrum of the flow.

3. Experiments

Surface modification of titanium alloys were carried out by low-temperature nitriding in a glow discharge in hydrogen-free environment. The main advantage of this method lies in the absence of hydrogen embrittlement and complete environmental safety process. Experimental set nitriding in a glow discharge in hydrogen-free environments was developed in Khmelnytsky National University. The installation includes the discharge chamber vacuum system, the preparation of the gaseous medium, and power supply and management. The latter was primarily designed to maintain the glow of electric discharge in the gas and at least short-term exclusion of its transition to the arc.

Technical characteristics of the installation:

- Power 40 kW;
- Three-phase alternating current, 50 Hz 380 V;
- The maximum voltage in the cell 1500 V;
- The diameter of the vacuum chamber 600 mm;
- The height of the vacuum chamber 1000 mm;
- Minimum vacuum of 1 Pa;
- Operating temperature range 400-1100°C;
- Maximum weight of 500 kg cages.

There was control over the composition of the gaseous medium, the temperature, the pressure in the discharge chamber, the voltage on the electrodes and the current camera therein (respectively – the current density) during the process. As noted above, a feature of the installation is to use a hydrogen-free gas mixture. However, the absence of hydrogen, which is a reducing metal and neutralizes oxygen requires especially pure gas (99.9%) and a completely sealed gas supply system and vacuum chamber. Even a small amount of oxygen (0.1%) causes the formation of oxides on a metal surface and greatly reduces the efficiency of the process up to its total cessation. Therefore, in contrast to systems that operate with hydrogen – saturating fluids (ammonia, a mixture of nitrogen and hydrogen), this unit has separators for oxygen and moisture. Application of the glow discharge can not only speed up the process by the order of the diffusion surface saturation with nitrogen, but also significantly alters the kinetics of the process and quality of the nitrided layer, in particular its physio-mechanical properties and phase composition. This allows for the optimization of the mechanical properties of the surface layer depending on the operating conditions of structural elements and also improves their wear resistance.

For research purposes, the standards from an α+β alloy Ti-Al6-Cr2-Mo2.5 were used. Nitriding in glow discharge was conducted after different regimes, the technological parameters of the process were varied in such scopes: temperature (T°C) within the limits of 540-700°C, pressure (P, Pa) – 80-400 Pa, time (min) – 20-240 min, maintenance of argon (Ar%) – 0-96%. Research of fretting-resistant titanic alloy Ti-Al6-Cr2-Mo2.5 were conducted on the special options which are described in work [1]. Chemical composition of titanium alloys in Table 1.

4. Results and discussion

For reliable analysis of the OEF formation of nitrides, calculations were done for several types of titanium alloys with 162 combinations of the technological regime. The obtained values of parameters that were compared with similar data for VT1-0, which is chosen as the base for comparison. It was found that the OEF formation of nitrides ratio (but not the values themselves!) varied very little depending on the parameters of the technological regime, and only vary significantly for different grades of titanium alloys. The variation of the relationship compared with the average value for the alloy VT8 are within 0.961-1.022, for VT3-1 – 0.959-1.023, for VT14 – 0.97-1.018, etc. For this reason, a further comparison of the characteristics in Table 2 were performed using mean values range fluctuations.

Comparison of the data in Table 1 (based on the initial hardness) indicates the presence of an adequate relationship between the results of nitriding and REF formation of nitrides of different alloys. Thus, the comparison of the calculated values of the formation of nitrides factors reliably predict change in the surface of microhardness after nitriding in a glow discharge of various titanium alloys.

Let's analyze the relationship of analytical criteria with real structures of titanium alloys nitrided in a glow discharge. Modification of the surface nitriding in a glow discharge in the most general form is a set of processes of formation of nitrides, nitrogen diffusion into the depth of the surface layer and the last spray. Regarding the first part, there are several theoretical models, which are based, as a rule, in the question of the primacy of the accumulation of nitrogen in the surface layer with the gradual formation of nitride or nitride formation of a continuous transformation, the release of nitrogen and its diffusion into its depth (the formation of a layer of solid solution) [10-12]. Energetic model [1,3] is reduced, primarily to ensure that the problem is solved according to the primacy of the specific process conditions: the material and surface conditions of the above process parameters regime. The set of conditions marked justifies the primacy of one of the above components of the process. Typically, a significant role is played by the intensities of the formation of nitrides and diffusion and the spraying of the air flow. The last two factors are mainly determined by the characteristics of the gaseous medium, the properties of the surface material of the most important is the sublimation energy surface components. As a result of the cumulative effects of these factors are primarily the processes that under specific conditions, the most energetically favorable. The probability of any one of them is determined by comparing and matching the energy spectrum of the incident flux values in the energy range within which it is possible. The essential role played by adsorption phenomena, as falling through the adsorption bed to the flow substantially affects both the surface which is modified, and the components of the gaseous medium accumulated on the surface.

Table 1.
Chemical composition of titanium alloys

Allow grade	Structure after annealing	Content items, wt.%						
		Al	Cr	Mo	Zr	Si	Fe	V
VT1-0	α							-
VT8	α+β	5.8-7.0	-	3.5	0.5	0.3	0.3	-
VT3-1	α+β	5.5-7.0	0.8-2.3	2.0-3.0	0.5	0.1-0.4	0.5	-
VT14	α+β	3.5-6.3	-	2.5-3.8	0.3	0.15	0.25	1.4
VT19-1	β	2.5-3.5	4.0-5.0	5.0-6.0	0.5-1.5	0.15	0.25	3.5
VT20	α	5.5-7.5	-	0.5-2.5	1.5-2.5	0.15	0.3	0.8-1.8

Table 2.
Comparison of relationship: nitriding in a glow discharge with REF formation of nitrides

Allow grade	Microhardness $HV_{0.1}$ before treatment	Microhardness $HV_{0.1}$ after treatment	Average relations of REF for the formation of nitrides
VT1-0	180	276	1
VT8	360	495	1.134
VT3-1	360	612	1.183
VT14	400	483	1.11
VT19-1	360	590	1.174
VT20	380	583	1.153

Unfortunately, the lack of well-known models of the process means, first and foremost, that they practically do not include the impact and importance of the factors determining the particle energy flux, because almost all known technological modes are absent on the electrical characteristics of the discharge. At the same time in the school of Arzamasov B.N. there is a marked effect in the relationship of minimum discharge power with optimum results nitriding. Since the power of discharge voltage is formed (component determines energy particle flux) as is current density (quantitative characteristic flux intensity), it is clear that the optimum ratio between these parameters and determines the minimum capacity. At the same time, the optimum logic should show, firstly, that part of the energy spectrum, where the conditions of energy transfer occur during collisions of the particles, is during the formation of nitrides, and secondly – when a sufficient number of particles are included in a collision.

Furthermore, for some materials, especially – for some of those that are active to nitrogen, it is also important to ensure optimum conditions for the sputtering nitride as a thin dense layer of nitride that is formed instantly in this case on the surface, inhibits all diffusion processes. Development of analytical criteria by which it becomes possible to design processes to predetermined outcomes, is based on the energy approach due to nitride formation and surface components, and spraying the surface structures require some energy transferred in the collision parts flow to the surface. It is also important that this energy lies within the optimum range. To create nitrides energy should not be below the rate of their growth, but not higher than the sublimation energy, on the contrary, to spray – not below the last threshold. It is on this principle a system of analytical criteria is established – REF. These factors are divided into two groups: analytical indicators of the formation of nitrides and the factors that characterize the spray and diffusion properties of gaseous media. The complete complex of these indicators generally characterizes qualitative indicators about the formation of the modified surface layer. This work is devoted to the question of applicability of the use of analytical criteria for practical forecasting results of nitriding of titanium alloys in the glow discharge.

To confirm the adequacy of the quality of calculated values with practical results, a metallographic examination was conducted of samples made of different alloys and titanium nitrided at different combinations of values of the process parameters (specific combination of these parameters indicated by an arrow at a certain place in graphics of molecular component REF formation of nitrides). The results of the analysis of qualitative relations are shown in Fig. 1 alloy VT1-0 and in Fig. 2 alloy VT8.

Relative energy factor formation of nitrides formed from atomic and molecular components. The best indicators of growth rate observed in the thickness of the nitride is their approximate equality [1,4]. Note that considering the marked work that harmonious relationship of both components is provided at a certain optimal value of the pressure. Interestingly, this is the same order which was established by analyzing the electrical characteristics of the discharge. This explains the effect mentioned above minimum capacity. From Fig. 1 it is implied that at a pressure that is less than optimal, the energy flow equation is quite high, which contributes to spray a layer of nitrides, its transformation and nitrogen diffusion in depth. The optimum pressure provides a significant band width nitrides. At high pressure a barely noticeable area of ε-phase is observed. Quality indicator ratios formed in nitride layers correspond to the formation of nitride OEF ratio in the central plot. Fig. 2 shows a much better ability of the alloy VT8 nitrided, because in all cases the thickness of the nitride layer is larger, as compared with Fig. 1. And for this alloy, the range of possible combinations of parameters of technological regime is even greater. This confirms the formation of nitrides WEF range in which the zone corresponding to the optimal ratio is a greater range of pressures. The nature of the change is similar to the thickness of the nitride zone remark to Fig. 1 and fully adequate change REF formation of nitrides. For this reason, at a pressure that is less than optimal, there is a thin nitride layer, as close to the optimal ratio between the atomic and molecular components as is observed within a significant range of pressures.

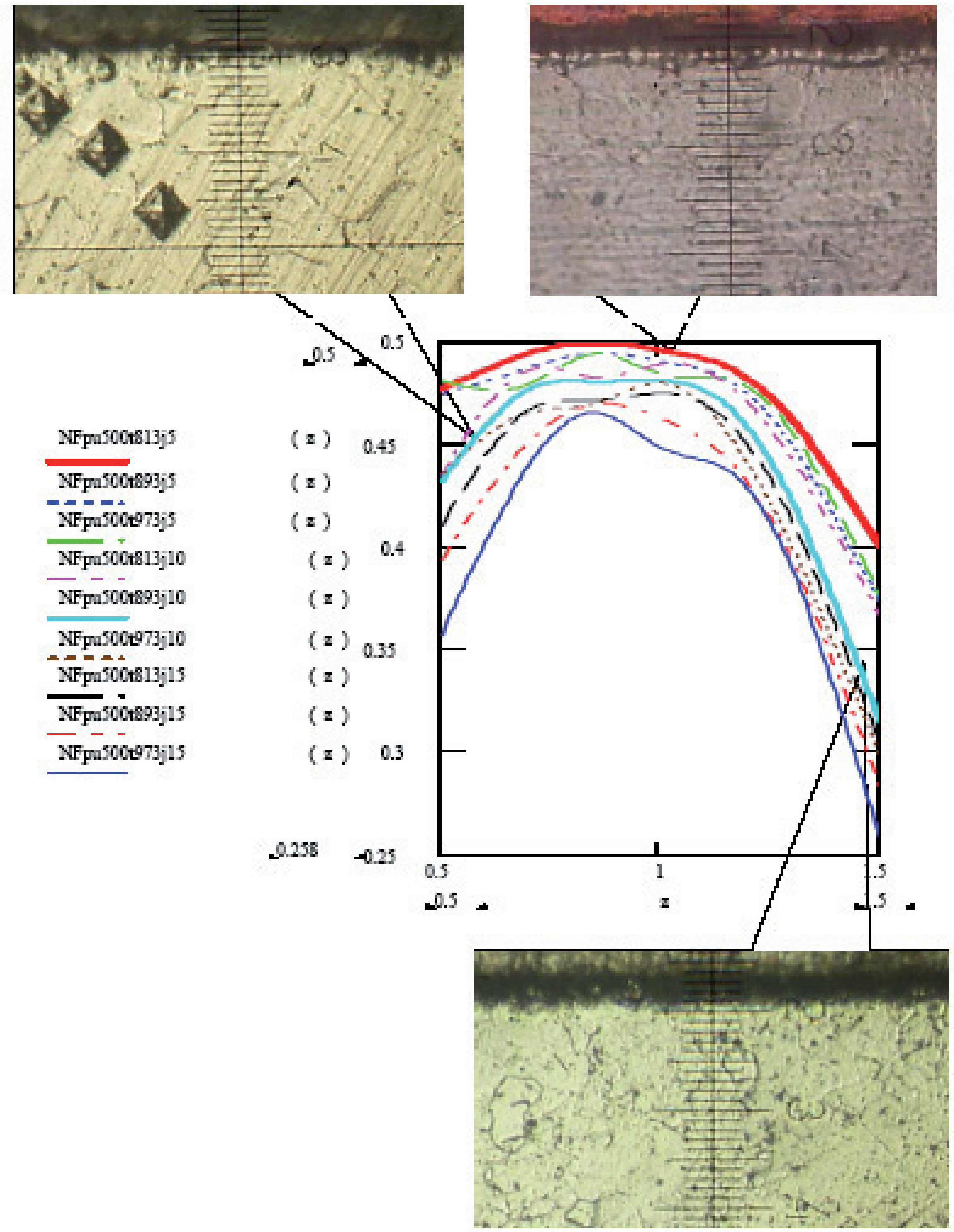

Fig. 1. Microstructure of titanium alloy samples VT1-0, nitrided at different combinations of process parameters

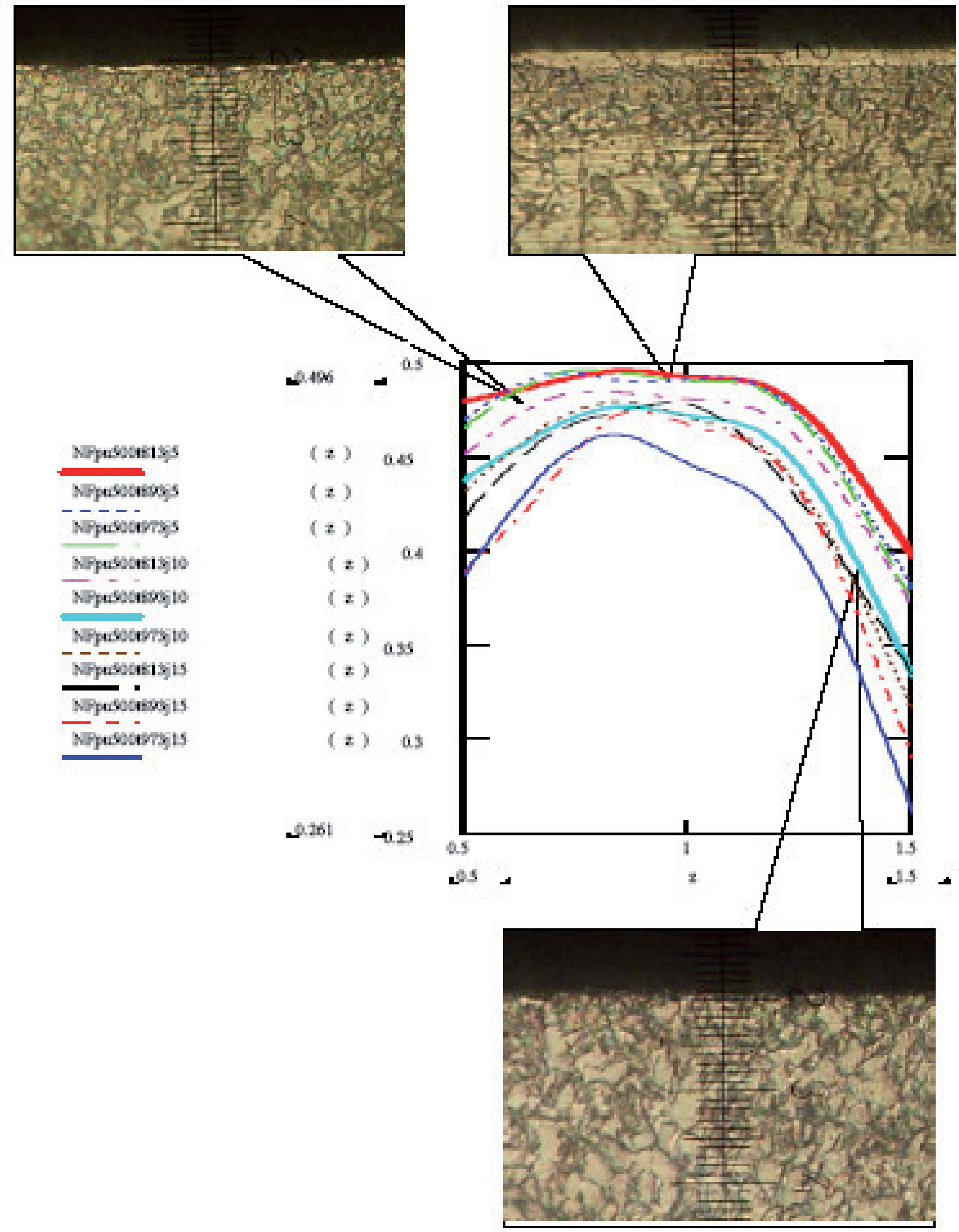

Fig. 2. Microstructure of titanium alloy samples VT8, nitrided at different combinations of process parameters

Comparison of indicators listed in Table 2, with a range of change of the absolute values of the formation of nitrides REF confirms the correlation between them. Figs. 3 and 4 compares the microstructure of samples nitrided at the optimum mode for different grades of titanium alloys (Fig. 3 – N75Ar25 gas environment with a predominance of nitrogen – 75% nitrogen 25% argon, Fig. 4 – N10Ar90 with a predominance of argon – 10% nitrogen, 90 % argon).

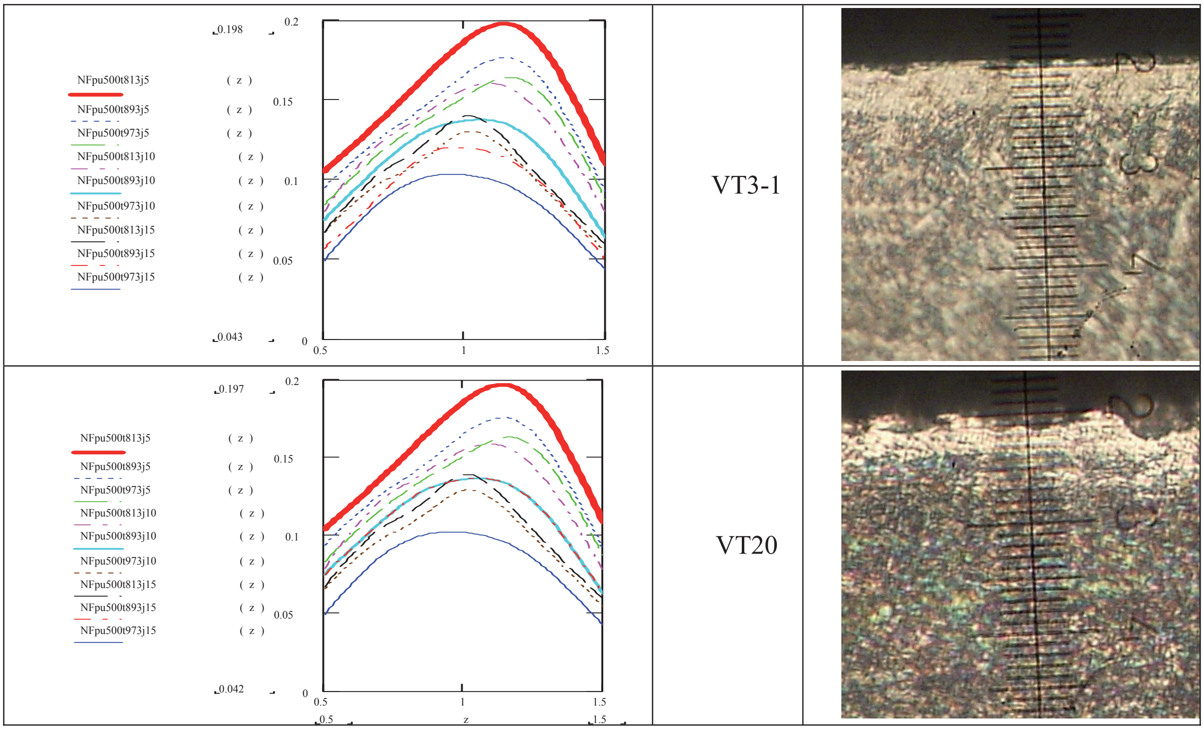

Fig. 3 Influence of absolute values of OEF formation of nitrides on the formation of nitrides (gas N75Ar25, 1.2 torus pressure, temperature 620˚ C, the current density $5 A/m^2$)

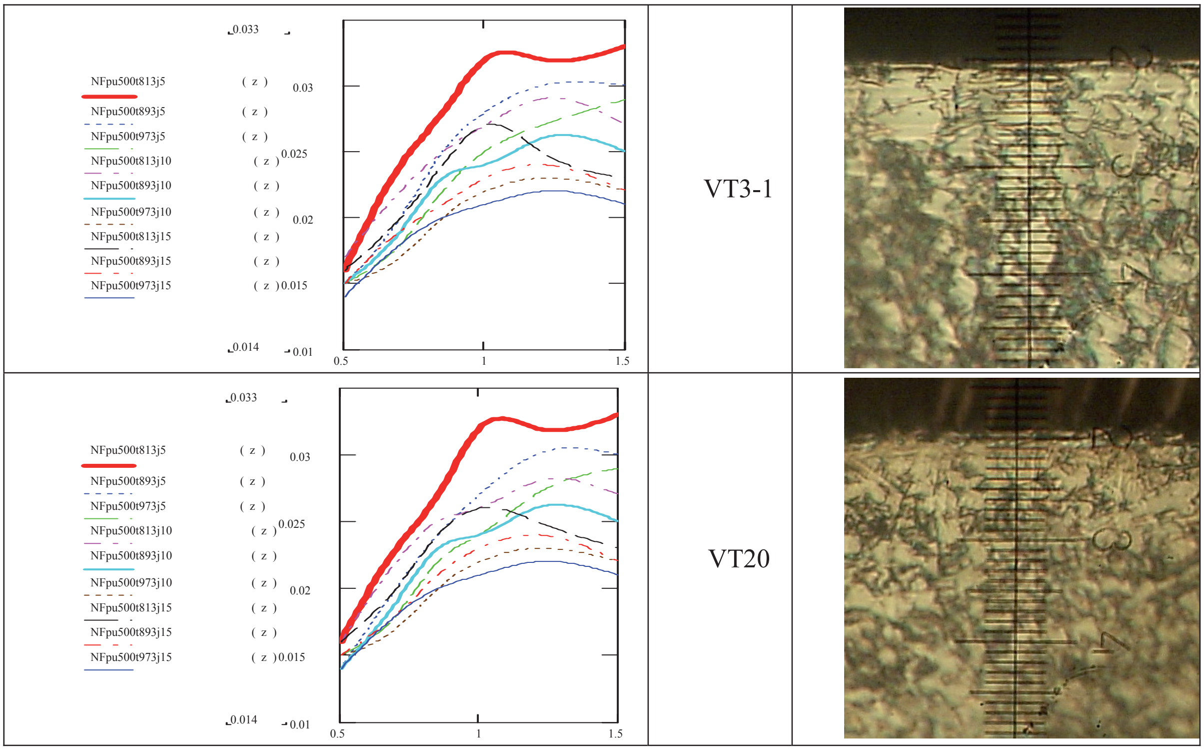

Fig. 4. Influence of absolute values of OEF formation of nitrides on the formation of nitrides (gas N75Ar25, 1.05 torus pressure, temperature 620˚ C, the current density $5 A/m^2$)

As noted above, the comparison shown in Figs. 3 and 4 microsections certifies compliance with those previously noted in the Table. 2 trends on the impact of brand alloy REF formation of nitrides and, accordingly, the thickness of the nitride structure : the maximum values of this index are growing in the sequence Table. 1 from VT1-0 to VT3-1. In most cases, the formation of nitrides REF depends on the pressure in the changes in discharge chamber of an extreme type: for each variant of the initial conditions there exists an optimal value of the pressure at which the formation of nitrides REF reaches its maximum value, as noted above. All photos of microsections were performed at the same magnification (X400, graduation – 4 microns) because the available range allows you to actually compare the sizes of the nitride layer thickness. Naturally, the gas atmosphere of argon with a predominant content (Fig. 4) has a lower ability to form nitrides on the surface layer, because the thickness of the nitride layer is substantially lower in comparison with the nitriding in an environment where nitrogen dominates (Fig. 3). This adds more value to the energy transfer coefficient at the time of collision of the particles in the surface of the argon, as the weight ratio in this case is larger than for nitrogen. This fact leads to more intensive spraying of the surface, i.e. newly formed structures of nitrides. Therefore, the type of structure shown in Fig. 4 compares to the others in Fig. 3. Here there prevails a diffusion zone that clearly confirms the theoretical conclusions about the combined effect on the surface as modifiable factors that display the intensity of the reaction in the formation of nitrides and diffusion- flow spray action. If the formation of the metal nitride on the surface of the structures is determined by factors of the formation of nitrides, it is competing with the sputtering surface that depends on factors which are based on the properties of the gaseous medium, and the ratio of these properties with some surface characteristics of particles, in particular – with an energy of sublimation. Thus, the design of the surface modification process should be guided by an integrated approach taking into account the combined effect of all kinds of factors.

5. Conclusions

1. Applying a system of analytical criteria imposed on the basis of the energy model is fully adequate to meet the real processes of nitriding of titanium and its alloys in a glow discharge, and these indicators can be used for the analysis, design and optimization of technology.
2. Based on a comparison of these criteria, one can compare the parameters of the technological regime, in terms of grades of materials, obtaining projected results of nitriding processes to stimulate the formation of nitrides or diffusion layers.
3. Relative energy factors, as indicators of energy system analysis model of the nitriding process in a glow discharge properly display the real processes, primarily qualitatively explaining the interaction of process parameters during the formation of the modified layers. This allows the use of marked characteristics as a basis for optimization of technological regimes and forecasting results modification. Another aspect of the use of the proposed system of key performance indicators, which is of practical importance, is the design modification processes, given the predetermined final characteristics were formulated taking into account the operating conditions of the work pieces.

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