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Chemico-Thermal Treatment of Titanium Alloys – Nitriding

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1. Introduction

Titanium and its alloys are widely used in aircraft, rocket production, shipbuilding, machine industry, chemical and food industry, medicine due to their high specific strength, good corrosion resistance and biological passivity. However, titanium has properties which limit its application as construction material. Particularly, tendency to surface adhesion and galling at friction results in its lowest wear resistance among construction materials. The application of titanium alloys in friction units and in the places of direct contact is impossible without additional surface treatment for higher strength. The corrosion resistance of titanium alloys is not often satisfactory. Therefore titanium alloys also need the additional protection in the aggressive media.

The chemical heat treatment, particularly nitriding, allows to extend the functionality of titanium alloys, enhancing the wear resistance and providing the high anticorrosion characteristics in aggressive media. However, the molecular nitrogen is a reactionless gas as a result of significant bond strength in molecule ($\Delta H_0=940$ kJ/mole). Therefore it is very important to intensify the interaction between titanium and nitrogen and to elaborate the relevant nitriding methods.

2. Basic regularities of high-temperature interaction of titanium alloys with nitrogen

One of the ways to solve the problem of intensification of nitriding of titanium alloys is the high-temperature saturation based on temperature dependence of diffusion coefficient of nitrogen in titanium. Therefore we will consider the basic regularities of nitriding of titanium alloys at high temperatures.

2.1 Kinetic regularities of high-temperature interaction of titanium alloys with nitrogen

Kinetics of nitrogen absorption by titanium alloys was widely studied by both the thermogravimetric analysis, when the mass change after different exposures in nitrogen at constant temperature is fixed and the manometric method, when the change of nitrogen pressure in the closed system is determined. The results of these studies in a wide temperature range (550...1600 °C) showed that the process of nitrogen absorption by

titanium is described by the parabolic dependence. That is the dependence of relative mass increase of the nitrided samples on time can be presented by a function:

$$(\Delta m/S)^2 = K \tau,$$

(1)

where $\Delta m = (m_2 - m_1)$ – difference between sample’s mass after and before nitriding; S – nitriding surface square; τ – nitriding duration; K – parabolic constant of nitriding rate.

The appreciable deviations from the parabolic law caused by the presence of negligible quantity of oxygen impurities in nitrogen are observed at the initial stage of reaction.

With the rise of temperature during isothermal exposure the intensity of interaction of titanium with nitrogen increases substantially. The parabolic constant of nitriding rate (K) is determined by the tangent of angle of inclination of straight lines of time dependence of square of mass increase. It characterizes quantitatively the relative intensity of saturation process (table 1). Values K increase practically on order with the rise of temperature on one hundred degrees (for example, at 900 °C $K = 8,6 \times 10^{-12} \text{ g}^2/\text{cm}^4 \times \text{s}$ and at 1000 °C $K = 3,5 \times 10^{-11} \text{ g}^2/\text{cm}^4 \times \text{s}$).

Alloy	$K_p = K_o \exp (E/RT)$	
	$K_o, \text{g}^2/(\text{cm}^4 \times \text{s})$	-E, kJ/mole
VT1-0	0,11	214
OT4-1	0,42	229
VT5-1	0,6	248
VT20	0,16	241
PT-7M	0,8	250
OT4	0,02	223
VT6s	1,9	258
VT6	0,9	267
VT23	0,4	252
VT32	0,4	240
VT35	0,1	238

Table 1. Parameters of temperature dependence of parabolic constant of nitriding rate K_p

The temperature dependence of parabolic constant of nitriding rate is described by Arrhenius equation:

$$K = K_o \exp (-E/RT),$$

(2)

where E – activation energy of nitriding process, J/mole; K_o – preexponential multiplier, $\text{g}^2/\text{cm}^4 \times \text{s}$; R – gas constant; T – temperature. Activation energy of nitriding determined by many researchers has different values for the certain temperature ranges and it increases with the rise of temperature of isothermal exposure as a rule. It allows to assert that process which determines the nitrogen absorption rate is changed with temperature.

The value n in law:

$$(\Delta m/S)^n = K \tau$$

(3)

change of mass increase of the nitrided samples of titanium alloys in time determined by treatment of nitriding isotherms of each investigated alloy in the double logarithmical coordinates $\ln(\Delta m/S) - \ln \tau$ (cotangent of angle of inclination of the received straight lines) are near to 2 that corresponds to the parabolic law of interaction (1) as well as for the unalloyed titanium.

The calculated constants (K , K_0 , E) of the dependences (1, 2) at the use of corresponding mathematical models (Matychak et al., 2007, 2008, 2009, 2011) at the predetermined temperature and duration of saturation process allow to forecast the thickness of the phases formed during the nitriding process or determine time and temperature parameters of nitriding at which the thicknesses of the formed layers would be predetermined.

The results of investigation of kinetics of saturation process of titanium alloys by nitrogen testify that alloying influences on nitriding rate (fig. 1).

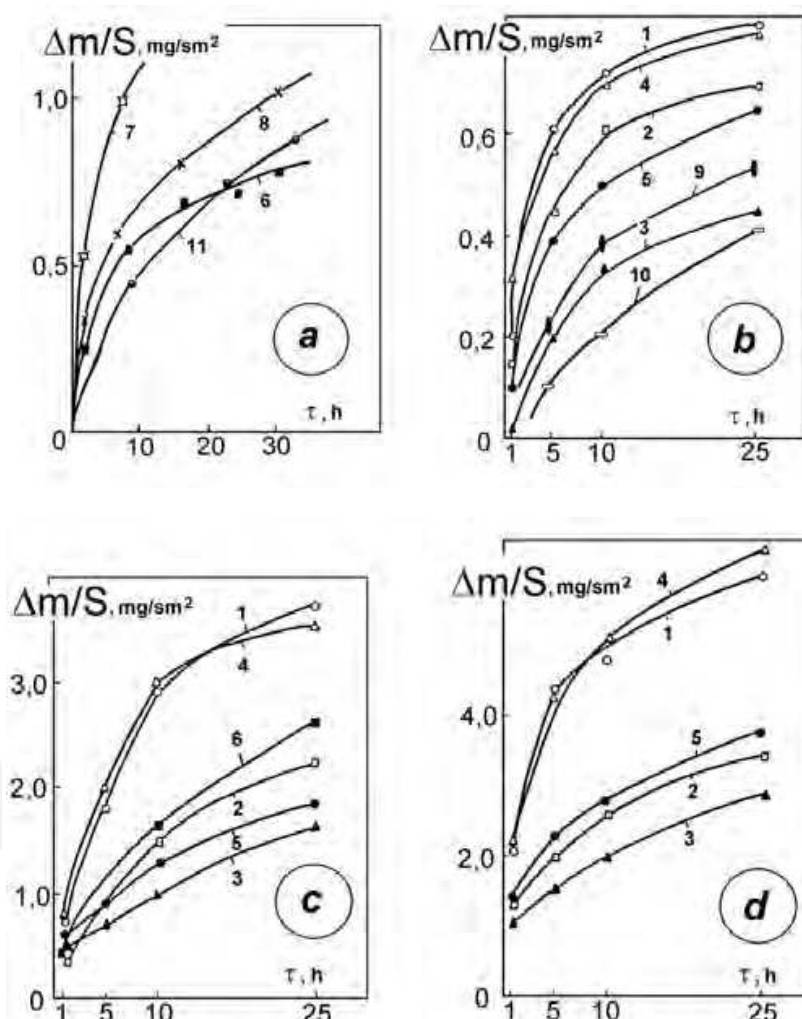


Fig. 1. Kinetics of nitriding of titanium alloys : a - 950 °C; b - 900 °C; c - 1000 °C; d - 1100 °C; 1 - VT1- 0; 2 - PT-7M; 3 - VT5- 1; 4 - OT4- 1; 5 - VT6s; 6 - VT5; 7 - VT1-D; 8 - VT3- 1; 9 - VT6; 10 - VT20; 11 - VT23.

With the rise of temperature of isothermal exposure the influence of alloying elements on the nitriding process increases that confirmed by the increase of distance between the

isotherms of nitriding (fig. 1): difference in the mass increase of titanium alloys with different chemical composition at saturation by nitrogen increases.

As opposed to the unalloyed c.p.titanium the nitriding rate of titanium alloys, as a rule, is less. The mechanism allowed the alloying elements to decrease the nitrogen diffusion rate in titanium does not discussed in literature. However, as diffusion in titanium nitrides is interstitial, the influence of alloying elements effects either on the decrease of sizes of interstitial intervals in the titanium lattice or on their filling.

Thus, the process of high-temperature interaction of titanium with nitrogen is described by parabolic dependence which is the result of forming of chemical reaction products – nitrides on the metal surface that slows down the behavior in time. The presence of alloying elements in titanium does not change the process substantially and only slows its. Besides, as a result of heterogeneous reaction titanium–nitrogen the considerable dissolution of gas into the metal with formation of solid solution of nitrogen in α and β titanium (gasing) is observed. Therefore the study of nitriding process by only determination of general mass of absorbed nitrogen which includes both the nitride formation and gasing is incomplete and not quite correct. The differential estimation of contribution of both nitride formation and gasing during nitriding is necessary.

2.2 Features of nitride formation at nitriding of titanium alloys

The well coherent with matrix nitride film of the golden color is formed on the surface of titanium alloys during the isothermal exposure in the nitrogen at temperatures above 800 °C. The film can have different tints of base golden color (from bright to mat) which depends on temperature and duration of nitriding, chemical composition of the nitrides. The film loses the brightness at the temperature behind 900 °C. The thickness of the nitride film and the degree of saturation by nitrogen are stipulated by the time and temperature parameters of nitriding and chemical composition of the saturated material. It allows to assert that the change of colour gamut and reflection power of film depends on its thickness and degree of saturation by nitrogen because titanium nitrides, in particular TiN, is characterized by the wide homogeneity region (27...52 at.%).

Nitride film formed at temperatures below 1000 °C repeats the contours of metallic matrix. In the case of the long exposures and temperatures below 1000 °C and above there are growths of film. On fig. 2a the characteristic topography of surface of the nitrided samples is presented: wavy inequalities forming net on surface, which, most probably, repeats the net of grains boundaries of the material matrix. These formations are most noticeable and reach the large sizes at the nitriding temperatures which are higher than temperature of $\alpha \leftrightarrow \beta$ polymorphic transformation (fig. 2b). $\alpha \leftrightarrow \beta$ phase transformation during the processes of heating and cooling causes the strain hardening, volume changes and formation of surface relief. The origin of considerable compression stresses at forming of nitride film causes the plastic deformation. It promotes the formation of quantities of inequalities. The surface topography, more or less expressed, is observed after nitriding at temperatures even lower than polymorphic transformation, and not arises after nitriding at the certain temperature. With the rise of nitriding temperature there is the growth of fragments of surface net like the growth of grain of titanium matrix. More active nitride formation on the grains boundaries promotes the forming of surface net, and processes, accompanying $\alpha \leftrightarrow \beta$ transformation,

assist to enhance the surface relief. Alloying weakens the formation of surface relief owing to the rise of temperature of polymorphic transformation of alloys.

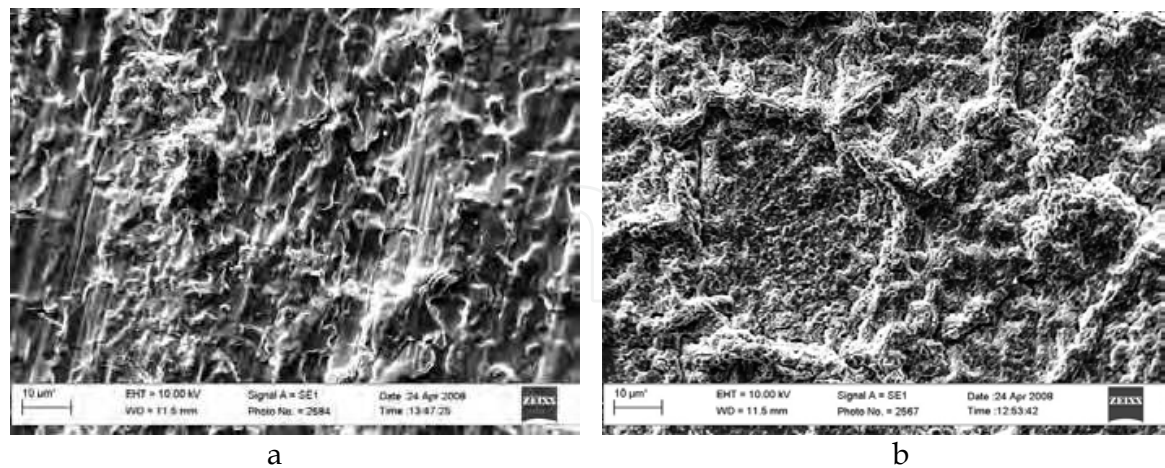


Fig. 2. Surface of nitrided VT1-0 alloy: a – 850 °C, 12h; b – 950 °C, 8h.

The formation of surface relief worsens the quality of nitrided surface with the nitriding temperature rising (fig. 3). For example, nitriding of VT23 alloy at 900°C results in change of surface roughness parameter (R_a) from 0,08 to 0,2 µm. After isothermal exposure in nitrogen at 950°C R_a is 0,4 µm, that is the surface roughness became worse on two classes. The substantial worsening of surface quality during nitriding at high temperatures complicates the obtaining of smooth surface. Therefore the use of nitriding with the purpose to increase the wear resistance of titanium foresees either limitation of process temperature (≤ 900 °C) or additional surface treatment of the nitrided details.

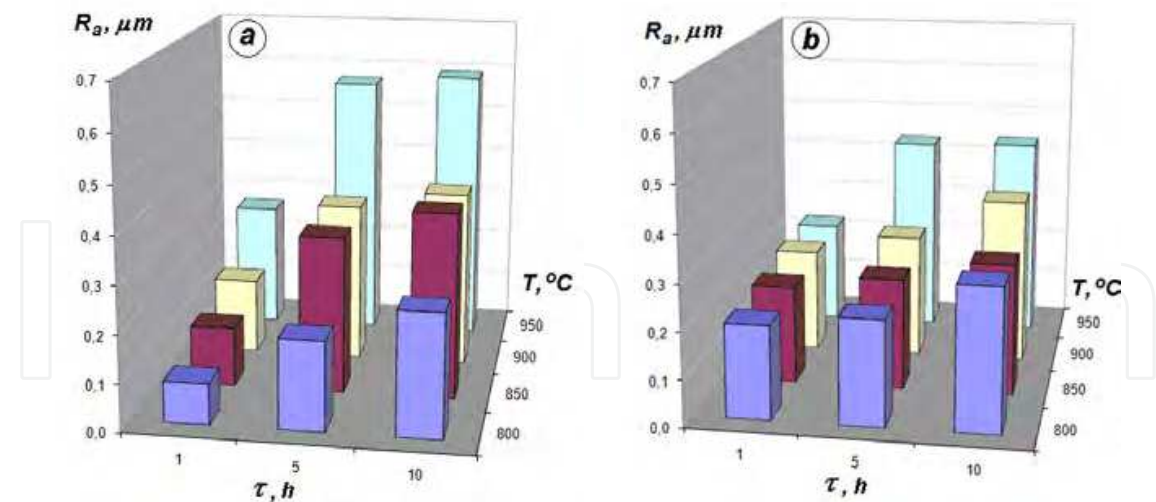


Fig. 3. Surface roughness of VT6 (a) and VT22 (b) titanium alloys after nitriding.

The nitride film consists of only nitrides of base metal – δ -(TiN) and ϵ -(Ti₂N). The grains of nitride phases have predominating orientations (table 2, 3). It is better expressed for ϵ -Ti₂N grains, which are mainly oriented on planes [002]. It should be noted that the texture of ϵ -phase is formed only during the process of nitride film growth (the redistribution of reflexes' intensity is not observed after short-term exposures when nitride film is thin).

Parameters of nitriding	Alloys			
	VT6		VT22	
	$I_{(111)}/I_{(200)}$	$T_{(200)}$	$I_{(111)}/I_{(200)}$	$T_{(200)}$
800 °C, 1 h	-	-	-	-
800 °C, 5 h	1,3113	0,4327	1,0510	0,4876
800 °C, 10 h	1,1015	0,4758	1,0690	0,4893
850 °C, 1 h	1,2053	0,4535	-	-
850 °C, 5 h	1,2047	0,4537	0,9726	0,5069
850 °C, 10 h	0,9864	0,5034	1,0642	0,4845
900 °C, 1 h	-	-	1,105	0,4751
900 °C, 5 h	1,1129	0,4733	1,0209	0,4948
900 °C, 10 h	1,0759	0,4817	0,8165	0,5505
950 °C, 1 h	1,2308	0,4483	1,1349	0,4684
950 °C, 5 h	1,0634	0,4846	0,9272	0,5189
950 °C, 10 h	1,2248	0,4495	0,9865	0,5034

Table 2. The ratio $I_{(111)}/I_{(200)}$ and coefficient of texture plane (200) $T_{(200)}$ * of TiN_x (* $T_{(200)}= I_{(200)}/(I_{(200)}+I_{(111)})$ (Hultman et al., 1995)).

Parameters of nitriding	Reflexes Ti_2N (hkl)	Alloys			
		VT6		VT22	
		I, arb. units	$I_{(111)}/I_{(200)}$	I, arb. units	$I_{(111)}/I_{(200)}$
800 °C, 1 h	(111)	254	2,7609	430	2,9861
	(002)	92		144	
800 °C, 5 h	(111)	152	0,4199	268	0,4401
	(002)	362		609	
800 °C, 10 h	(111)	236	0,3758	249	0,3522
	(002)	628		707	
850 °C, 1 h	(111)	265	1,3731	345	1,1616
	(002)	193		297	
850 °C, 5 h	(111)	251	0,5529	139	0,1154
	(002)	454		1205	
850 °C, 10 h	(111)	121	0,1157	-	-
	(002)	1046		2006	
900 °C, 1 h	(111)	316	1,5960	493	4,0410
	(002)	198		122	
900 °C, 5 h	(111)	275	0,6643	406	0,7719
	(002)	414		526	
900 °C, 10 h	(111)	268	0,8845	440	0,7666
	(002)	303		574	
950 °C, 1 h	(111)	259	-	-	-
	(002)	-		91	
950 °C, 5 h	(111)	235	1,5359	216	1,1676
	(002)	153		185	
950 °C, 10 h	(111)	387	3,5833	-	-
	(002)	108		212	

Table 3. Relative intensity of diffraction reflexes (111) and (002) of Ti_2N on the diffraction patterns from VT6, VT22 and T110 alloys after nitriding.

The thin outer layer of golden color consists of TiN and the thick inner layer of white color – Ti₂N. The perceptible growth of TiN is observed only at the long exposures.

Due to the large brittleness of nitride layer the measuring of its quantitative characteristics is complicated. Therefore there are few articles on the kinetics of nitride formation. This explains the substantial spread and certain discordance of the results received by different researchers.

The alloying elements of titanium alloys does not participate in the process of nitride formation. According to the thermodynamic activity of elements in relation to nitrogen (fig. 4), except of formation of titanium nitrides, zirconium nitrides are formed probably at nitriding of titanium alloys. The information about their formation is not found in literature, although at nitriding of alloys with 3...4 % Al, 8...12 % Zr, 1,2...2,6 %V the formation of phase (Ti, Zr)N with the lattice parameter of 0,4283 nm was fixed (Kiparisov & Levinskiy, 1972).

Alloying of titanium influences on the depth of nitride layer. In according with the recent results the nitrided area in (α+β)-alloys is less than in α- and pseudo-α-alloys (fig. 5).

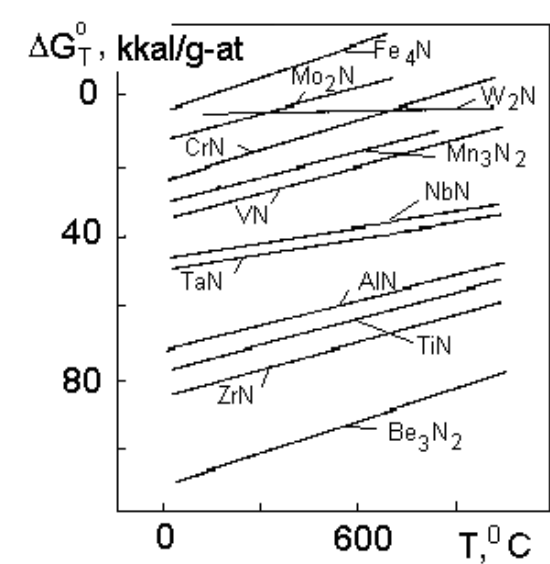


Fig. 4. Change of Gibbs thermodynamic potential ΔG_T^0 on 1 g-at of titanium depending on temperature for the reactions of formation of some nitrides (Kiparisov & Levinskiy, 1972).

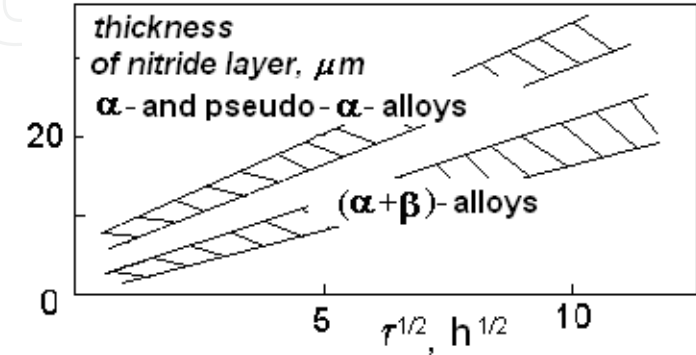


Fig. 5. Thickness of nitride layer on titanium alloys depending on duration of nitriding at 1000 °C.

The beginning of active nitride formation influences on the surface microhardness which depends on the nitrided material and ranges in 4,5...7,0 GPa. The rise of temperature leads to the increase of surface microhardness due to the activating of nitride formation (fig. 6).

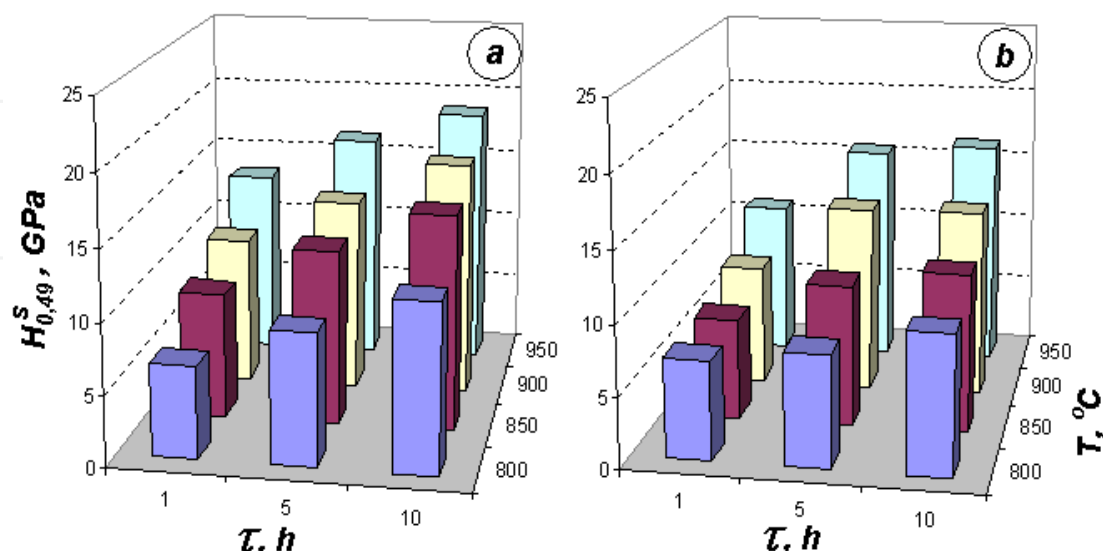


Fig. 6. Dependence of surface microhardness of VT6 (a) and VT22 (b) alloys on duration and temperature of nitriding.

Thus, during the nitriding the growth of nitride film has columnar character (mainly on the grain boundaries). It assists in the rising of surface relief that worsens the surface quality at higher nitriding temperature. During the growth of nitrides the texture Ti_2N is formed mainly on plane [002]. The change of thickness of nitride film with duration is described by parabolic dependence, thus the thickness of nitride film on β - and $(\alpha+\beta)$ -titanium alloys is less than on α -alloys. The texture growth increases with the rise of nitriding temperature resulting to the increase of imperfectness and heterogeneity of nitride film.

2.3 Regularities of formation of gas saturated layer – Morphology of the nitrided layers

At the high-temperature interaction of titanium alloys with nitrogen, except for formation of nitride area on the metal surface, nitrogen diffuses into the alloy, dissolves and forms the area with increased microhardness, so-called gas-saturated area. This area is identified as α -titanium with the increased lattice parameters (solid solution of nitrogen in α -titanium). The grains of α -solid solution are oriented mainly on plane [211]. The layers with the higher nitrogen concentration are characterized by the texture of α -solid solution.

The process of gasing of titanium alloys is connected with the process of nitride formation. Surface microhardness (H_{μ}^s), strengthening level of gas-saturated layer ($H_{\mu} = f(\ell)$) and its depth (ℓ) are determined by time and temperature parameters of nitriding and depend both on chemical and phase composition of alloys. The surface layer of α - and pseudo- α -titanium alloys is the most strengthened (fig. 7). This effect weakens considerably at transition to $(\alpha+\beta)$ - and, especially, β -alloys. Considerably bigger depth of gas-saturated layer of β -alloys as compared to α -alloys is determined by the values of nitrogen diffusion coefficients in α -

and β -phases of titanium. For pseudo- α - and $(\alpha+\beta)$ -alloys when the saturation process occurs at low ($\leq 850\text{ }^{\circ}\text{C}$) temperatures and undurable exposures ($\leq 5\text{ h}$) the depth of gas-saturated layer is decreased with the increase of coefficient of β - stabilization of alloy. High temperatures and long exposures assist in the increase of depth of gas-saturated layer with the increase of coefficient of β -stabilization.

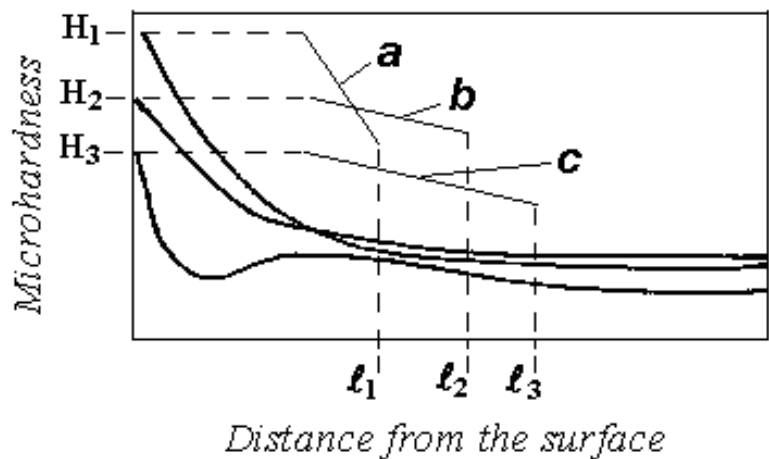


Fig. 7. Distribution of microhardness through cross section of surface layers after nitriding of α - and pseudo- α - (a), $(\alpha+\beta)$ - (b) and β - (c) titanium alloys at temperatures of $T > T_{\alpha\leftrightarrow\beta}$.

The morphology of gas-saturated layers after nitriding depends on temperature and metal’s phase composition. Let’s consider the influence of these factors on the morphology of the gas-saturated layer.

At the temperatures of nitriding below the polymorphic transformation the morphology of gas-saturated layer does not depend on phase composition of alloys (fig. 8a). The layer consists of two parts. The first part contains α -grains with high microhardness due to their strengthening by nitrogen (*α -solid solution stabilized by nitrogen*). The solubility of nitrogen in

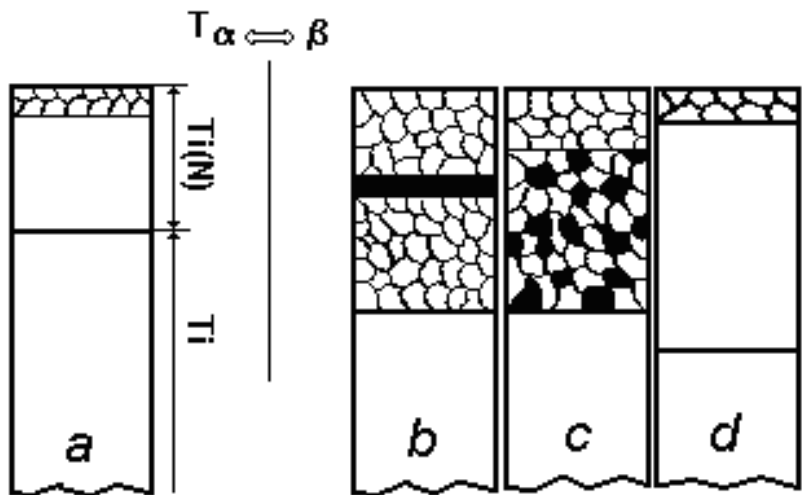


Fig. 8. Structure of gas-saturated layer of α - and pseudo- α - (a, b), $(\alpha+\beta)$ - (a, c) and β - (d) titanium alloys nitrided at the temperatures of $T < T_{\alpha\leftrightarrow\beta}$ (a) and $T > T_{\alpha\leftrightarrow\beta}$ (b-d).

α -titanium is high. Based on the titanium - nitrogen phase diagram, the deformation of lattice at the dissolution of nitrogen is considerable, which results to the significant increase of microhardness of this part of gas-saturated layer. The thickness of this part of gas-saturated layer increases with nitriding time and temperature parameters and connects with the redistribution of alloying elements. The second part of gas-saturated layer is not nearly differ from the alloy matrix. The level of saturation by nitrogen of this part is less substantially than the first part. The microhardness gradient and the redistribution of alloying elements are insignificant. The thickness of gas-saturated area fixed by metallographic method does not give the real depth of nitrogen penetration into the alloy's matrix and as a usual is less than that determined by measuring the microhardness.

At the nitriding temperatures higher than temperature of polymorphic transformation the gas-saturated layer also consists of two parts. However the structure of every part is determined by phase composition of nitrated alloy (fig. 8, b-d). The gas-saturated layers of α -, pseudo- α - and ($\alpha+\beta$)-titanium alloys are separated by the phase boundary from the matrix which at the nitriding temperature was β -titanium. During the cooling β -phase is decomposed but the boundary fixed at the high temperature maintains at the room temperature as well as the structure of α -phase formed in result of $\alpha\leftrightarrow\beta$ transformation. α -phase which stabilized by nitrogen and $\alpha\leftrightarrow\beta$ transformed phase but saturated by nitrogen have significant differences. The morphology of gas-saturated layer of β -titanium alloys does not almost depend on the nitriding temperature. That is caused by the absence of both polymorphic transformations of matrix and part of gas-saturated layer below the level of α -phase stabilizing.

The first part of gas-saturated layer formed at the temperatures of ($\alpha + \beta$) - β - area is α -phase (grains of α -solid solution of nitrogen in titanium). The high microhardness of this part is caused by large solubility of nitrogen in α -titanium (21,5 at.% in α -titanium against 0,95 at.% in β -titanium at 1000 °C). It should be noted that microhardness of this part of gas-saturated layer for α - and pseudo- α -titanium alloys exceeds insignificantly the same layer for ($\alpha + \beta$)- and β -alloys (18...7 GPa against 10...5 GPa). It is determined by the different nitrogen solubility in α - and β -phases of titanium. The second part of gas-saturated layer consists of metal $\beta \rightarrow \alpha$ transformed and enriched by nitrogen. It is separated from the first part by the phase boundary. For α - and pseudo- α -titanium alloys this boundary is detected metallography as a dark band of high etching. For α - and pseudo- α -titanium alloys this part is α -grain of smaller size but with the increased degree of etching compared with α -structure of the first part. For ($\alpha + \beta$)-alloys it is mainly α -phase (α -plates) in β -transformed structure (mixture of α - and β -phases). The second part of gas-saturated layer of ($\alpha + \beta$)-titanium alloys is often called "the transition area" between the gas-saturated layer and alloy's matrix because of the sharp structural difference as compared to the first part.

With the rise of nitriding temperature and duration the size of the second part of gas-saturated layer decreases, and the size of the first part increases. In addition, there is a coarsening of the structural components of both parts, and also a change of phase correlation in the direction of increasing the quantity of α -phase. The typical microhardness redistribution through the gas-saturated layer of α - and pseudo- α -titanium alloys is shown in fig. 7. It represents the gradient of nitrogen concentration from the surface into the matrix. Some tendency to stabilization of microhardness in the second part of gas-saturated layer for ($\alpha+\beta$)-alloy can be explained by different nitrogen solubility in α - and β -phases of titanium.

The structure of gas-saturated layer of β -titanium alloys does not depend on the nitriding temperature and is analogical to the structure of alloys nitrided below temperature of $\alpha \leftrightarrow \beta$ transformation when the structural difference between the alloy's matrix and second part of gas-saturated layer is absent (fig. 8). The first part is α -phase stabilized by nitrogen with the boundaries decorated by initial β -grains.

For β -alloys the microhardness distribution of gas-saturated layer has the original regularity (fig. 8): the curve passes through a minimum on the boundary of the part of gas-saturated layer stabilized by nitrogen.

For β -titanium alloys the strengthening of surface layers is significantly lower than for alloys of other structural classes (microhardness distribution curves are in the region of lower hardness values) (fig. 7).

Thus, the basic characteristics of gas-saturated layer i.e depth and degree of strengthening of surface layers (surface microhardness, hardness redistribution), depend on the phase composition of nitrided material. The most strengthening of surface layers is proper for α - and pseudo- α -titanium alloys and substantially decreases at the transition to $(\alpha + \beta)$ - and, especially, to β -alloys. The depth of gas-saturated layer of β -alloys is considerably larger than depth of gas-saturated layer of α -alloys. The morphology of gas-saturated layer of titanium alloys depends on nitriding temperature and phase composition of the nitrided alloy. For β -alloys the morphology of gas-saturated layer does not depend on the nitriding temperature and thus is identical to alloys with other structures nitrided in α -area.

2.4 Redistribution of alloying elements

The strengthened surface layer consists of nitride and gas-saturated area. As it was shown above, it is the result of the high-temperature interaction of titanium with nitrogen. This interaction is accompanied with the redistribution of alloying elements in alloy's surface layers. Let's consider the general regularities of alloying elements redistribution at nitriding of titanium alloys.

The alloying elements of titanium alloys are categorized as α - (Al), β - (Mn, V, Mo, Cr, Fe, Nb, Si, W) - stabilizers and neutral reinforcers (Zr, Sn). During the saturation of Ti-alloys by nitrogen there is the redistribution of alloying elements between the nitrided layer and matrix as well as in the gas-saturated layer.

The increase of electron concentration during the nitrogen dissolution leads to the decrease of solubility of alloying elements in titanium due to the limited solubility and also because the formation of continuous series of solid solutions. It assists in redistribution of alloying elements in the surface layers of titanium alloys: their separation from solid solution and diffusion into titanium matrix.

Thus, at thermodiffusion saturation by nitrogen there is diffusion of elements separated from solid solution into the alloy (fig. 9). The intensity of this diffusion is determined by the solubility and diffusion mobility of alloying elements.

The alloying elements have different solubility and diffusion coefficients in α - and β -modifications of titanium. According to the calculations, taking into account the diffusion

constants, the diffusion mobility of alloying elements is decreased in a sequence $\text{Fe} \rightarrow \text{Mn} \rightarrow \text{Zr} \rightarrow \text{Cr} \rightarrow \text{Al} \rightarrow \text{Sn} \rightarrow \text{Nb} \rightarrow \text{V} \rightarrow \text{Mo}$. With regard to solubility, then the solubility of zirconium is unlimited, and tin and aluminum are characterized by high solubility in α -titanium. Vanadium, molybdenum and niobium are less soluble in α -titanium but dissolve indefinitely in β -titanium. Iron, chromium and manganese are limitedly solubles in β -titanium and solubility in α -titanium is small. Iron, manganese and chromium are redistributed the most actively in surface layers because their solubility is minimal and diffusion mobility is the highest. The solubility of zirconium, aluminum and tin in α -titanium is high and diffusion mobility is low. Therefore, the substantial redistribution of these elements does not occur. Molybdenum, vanadium and niobium redistribute more active than zirconium, aluminum and tin but more weaker than iron, manganese and chromium.

Except for diffusion, there is the concentration of β -stabilizing elements separated from solid solution of nitrogen in α -titanium on the boundary of nitride - gas-saturated areas, even with high diffusion constants. These effects are caused by no occupied bonds between atoms located on the phases' interface and possible anomalous value of electron concentration in these areas.

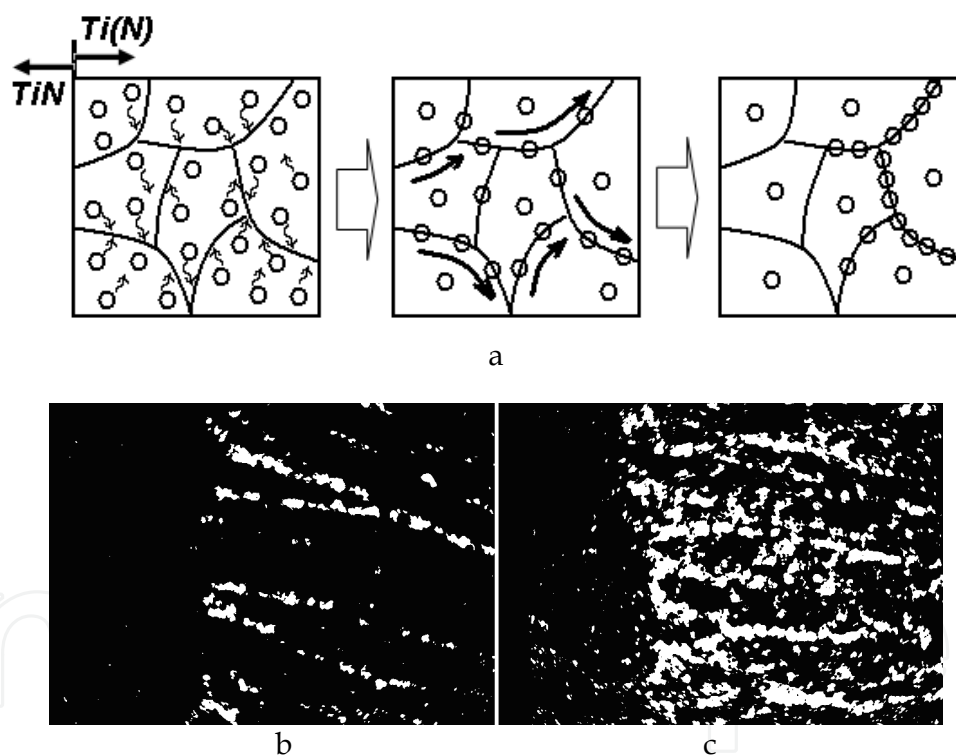


Fig. 9. Scheme of redistribution of alloying elements in the gas-saturated layer of titanium alloys at nitriding (a) and images of surface layers of OT4-1 (b) and VT6s (c) alloys in the characteristic rays $K_{\alpha}\text{Mn}$ and $K_{\alpha}\text{V}$ (1100 °C, 1 h).

Among these elements the special attention deserves aluminum. Since aluminum is α -stabilizer with high affinity to nitrogen (ΔH_{298}° is -318,0 and -335,0 kJ/mole for AlN and TiN respectively), the increase of electron concentration of alloy during stabilization of hexagonal close-packed lattice of solid solution of nitrogen in α -titanium does not influence on the solubility of aluminum and does not assist its diffusion. Releasing of lattice energy

and energy stability of system is achieved by the redistribution of other alloying elements. The similar selective redistribution, not so clear expressed, is observed for the systems, in which solubility and diffusion mobility of alloying elements differs significantly (for example, zirconium and molybdenum, tin and iron etc.). Near the interface gas (nitrogen) - metal and afterwards near nitride - gas-saturated layer the areas (clusters) with the high concentration of aluminum are formed (fig. 10). It is possible that the redistribution and coagulation of aluminum will be over by establishing of short range ordering completing by decomposition of solid solution with formation of superstructure of α_2 -phase (Ti_3Al) type.

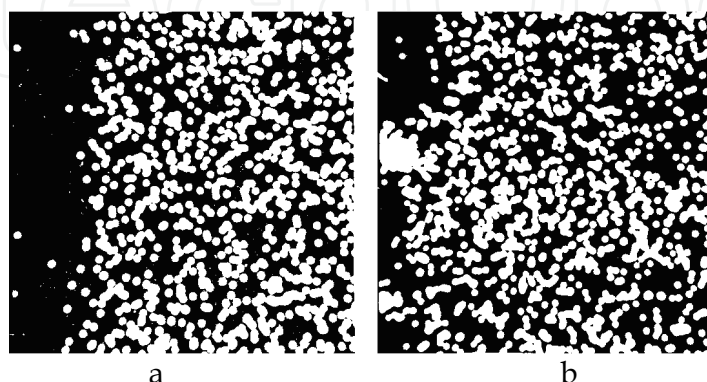


Fig. 10. Image of surface layers of OT4-1 alloy in the characteristic rays $K_{\alpha}\text{Al}$: a – 900°C, 100 h; b – 950 °C, 8 h.

With the rise of temperature of isothermal exposure the diffusion of alloying elements is activated because the diffusion coefficients increase. The active motion of alloying elements along grain boundaries leads to their loosening, nitrogen diffusion becomes accelerated and nitriding rate increases.

The morphology of gas-saturated layer of titanium alloys is connected with the redistribution of alloying elements in the surface layers. There is the active diffusion of alloying elements from the most enriched by nitrogen part of layer. In that part with nitrogen concentration the redistribution is negligible: alloying elements are redistributed between α - and β -phases of titanium. Aluminum (α -stabilizer) and, as a rule, the neutral reinforcers (zirconium, tin) are located in α -phase of titanium, β -stabilizers enrich β -phase.

Thus, the basic constituents of alloying elements redistribution at nitriding of titanium alloys are as follows: 1) separation of alloying elements from the hexagonal close-packed lattice of nitrogen solid solution in α -titanium; 2) diffusion of alloying elements from the surface into the alloy's matrix.

The first process is controlled by the solubility and the second – by the diffusion constants.

In result of alloying elements redistribution, as a rule: 1) a concentration of aluminum increases near the boundary nitride – gas-saturated areas; 2) the surface layers are depleted by β -stabilizing elements.

The redistribution of alloying elements causes the structural and phase changes in the surface layers of alloys, determining the morphology of the nitrided layer.

In spite of the fact that at the increase of temperature the degree of surface strengthening increases continuously (thickness of both nitrided layer and its constituents, surface

microhardness and gradient of nitrogen concentration on the cross section of surface layers increase), the use of temperature as the factor of intensification of saturation process has substantial limitations. In particular, the perceptible structural and concentration heterogeneity (on nitrogen and alloying elements) of surface layers caused by the active diffusion processes, and also the inconvertible grain growth of titanium matrix at the saturation temperatures of $(\alpha+\beta)$ - β - areas result in the substantial decrease of fatigue life, plasticity of the nitrided details. The heightened requirements to these characteristics cause the limitation on the saturation temperature (α -area) that does not always provides the provide level of surface strengthening ($H_{\mu}^s \geq 6...8$ GPa; $l \geq 100$ μm). Moreover, with the increase of temperature the brittleness of nitrided layer increases catastrophically. In the result of thick nitride film forming the surface quality of the nitrided layer becomes worse (surface roughness increases, imperfection and heterogeneity of nitride film grow because the effect of growth texture increases). It influences negatively on the wear- and corrosion resistance of the nitrided details.

At present, it is actual to find out other factors of intensification which allow to provide the effective surface strengthening at lower nitriding temperatures and exclude the negative consequences of the influence of high nitriding temperatures on surface quality and level of mechanical characteristics.

3. Nitriding of titanium alloys at thermocycling

One of the ways to weaken the negative consequences of the high-temperature nitriding is to decrease the time of processing at high temperatures. It can be attained by nitriding in the conditions of thermocycling.

As opposed to the standard methods of the chemical heat treatment there are the additional sources of the influence on the structure at thermocycling. They are inherent only to the process of continuous change of temperature: phase transformations, gradient of temperature, thermal (volume) and interphase tensions caused by the difference of thermophysical characteristics of the phases. The accumulation of structural changes in the material leads to forming, moving and annihilation of point and linear defects, redistribution of distributions, forming of low-angle boundaries, migration of low-angle boundaries with absorption of defects, migration of grain boundaries between recrystallized grains with their coarsening at the simultaneous decrease of grain boundary and surface energies, by the redistribution of alloying elements etc. It results to the increase of mobility of impurity atoms and the acceleration of diffusion processes.

For titanium alloys the thermocyclic treatment is considered as a way to achieve of such structural changes which improve the level of mechanical properties. To estimate the intensity of saturation process in these conditions is impossible due to the absence of such investigations for titanium, although the interaction of steels, aluminum and nickel alloys with gases (carbon, nitrogen) at the cyclic change of temperature, pressure and gas composition is well studied.

Let's consider the regularities of interaction of titanium alloys with nitrogen in the conditions of thermocycling.

Nitriding is intensified at the cyclic change of temperature. It influences on the rise of mass increase of the samples, surface microhardness and depth of the nitrided layer as compared to the isothermal exposure at the middle temperature of thermal cycle (fig. 11).

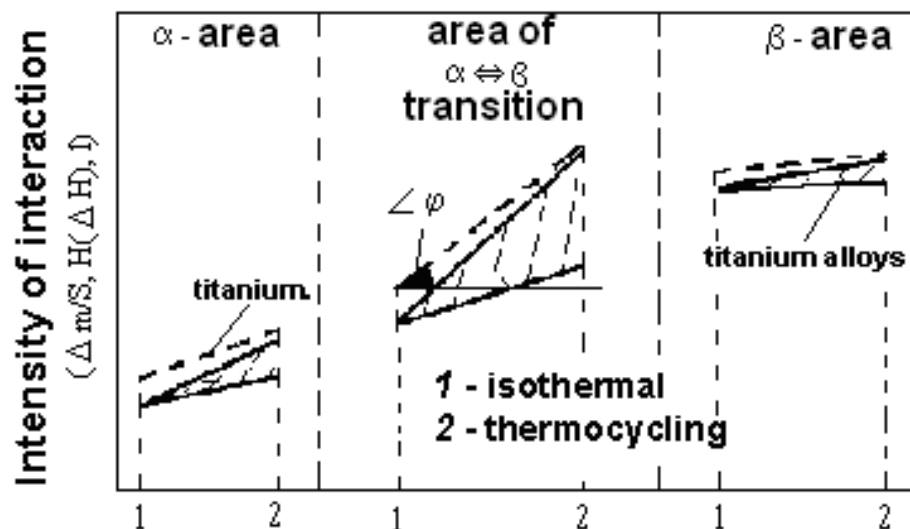


Fig. 11. Influence of thermocycling on intensity of interaction of titanium alloys with nitrogen in different temperature intervals.

The efficiency of thermocycling at nitriding depends on the parameters of thermocyclic treatment (amplitude of thermal cycle, frequency of thermocycling) and increases with their rising.

The maximal effect of thermocycling is proper for the temperature range of polymorphic transformation and correlates with the clear expressed effect of volume strengthening which increase at the rise of amplitude and frequency of thermocycling. Alloying, as a factor of intensification on interaction of titanium alloys with gas media, does not change generally the influence of thermocycling but changes only its intensity (slope of curves φ) depending on participating of certain alloying element in the forming of defect structure.

The morphology of nitrided layer thermocycling as well as after the isothermal conditions is the thick nitride film ($\geq 1 \mu\text{m}$) and gas-saturated area. The difference from the isothermal nitriding is that the increase of degree of imperfectness of surface layers at thermocycling leads to the forming of surface nitride films with considerable deviation from stoichiometry, mainly the deficit of nonmetal component. Therefore the lattice parameter of TiN after isothermal saturation with the rise of temperature is decreased significantly while the cyclic change of temperature assists to reach the reverse dependence: lattice parameter of TiN increases (fig. 12).

Taking into account the dependence of the lattice parameter of titanium mononitride on nitrogen content in the homogeneity region, the observed regularities allow to suppose that at nitriding in the conditions of thermocycling nitride with considerable deviation from stoichiometry with the deficit on nitrogen is formed on the surface. With displacement of temperature range of thermocycling into the range of lower temperatures the deviation from stoichiometry of surface nitride increases.

It should be noted that forming of these nitride layers gives new possibilities in surface engineering of titanium alloys, in particular, at the complex modification of surface layers by the interstitial elements (Pohreliuk et al., 2007; Pohrelyuk et al., 2009, 2011; Yaskiv et al., 2011; Fedirko et al., 2009).

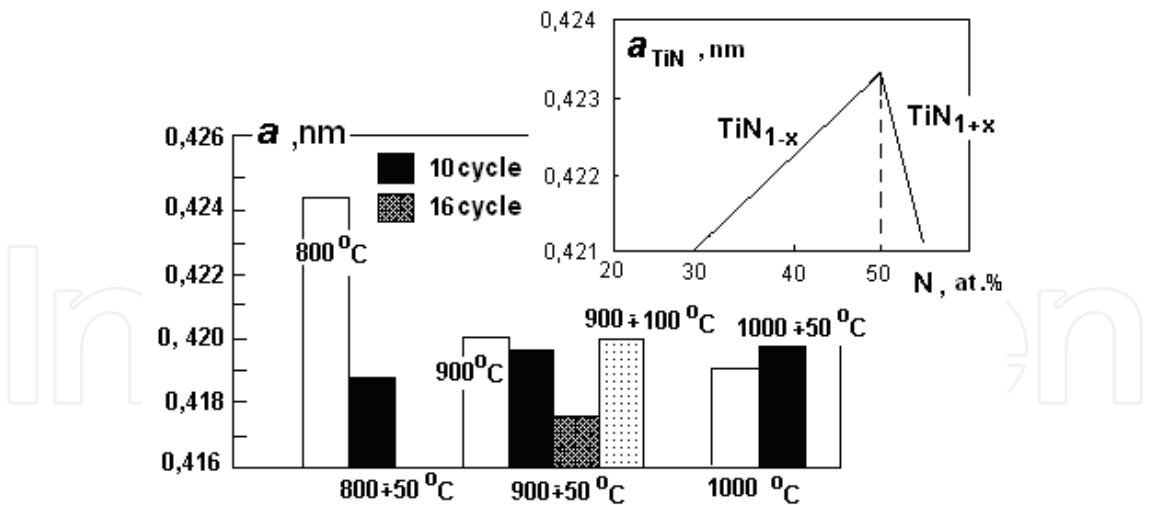


Fig. 12. Lattice parameters of TiN after the isothermal nitriding and nitriding in the conditions of thermocycling. Change of lattice parameter of TiN depending on the content of nitrogen in the homogeneity region (Goldschmidt, 1967).

Thus, at thermocycling the nitriding process of titanium is intensified and reaches the maximum during processing in area of $\alpha \leftrightarrow \beta$ transition. The efficiency of application of thermocycling at nitriding depends on the parameters of thermocyclic treatment and rises with their increase. The temperature range of thermocycling determines the character of the surface strengthening. The nonstoichiometric nitride films with the deficit of nonmetal component are formed on the titanium surface.

The strength characteristics of titanium are improved after nitriding at thermocycling. The highest strengthening effect is observed at cycling in the area of temperatures of polymorphic transformation of titanium alloys and enhances with the increase of both amplitude and frequency of thermocycling.

4. Influence of initial deformation texture on nitriding of titanium alloys

The intensification of nitriding at thermocycling is based on the structural changes in material. The same changes in the structure of material is possible to provide before thermal heat treatment, for example, using material with deformation texture. Such approach is based on the dependence of diffusion constants on predominating crystallographic orientation (texture).

In practice the metallic materials are used, as a rule, in the polycrystalline state. Although all grains in homogeneous metal have the identical crystalline structure, however they differ in the mutual crystallographic orientation of axes. The analogue of crystallographic orientation of plane in monocrystal for polycrystal is the predominating orientation of grains (texture). One of the basic technological processes causing the formation of crystallographic texture, is plastic deformation. Formation of texture at plastic deformation occurs in the result of crystallographic planes turning in the process of sliding and twinning. In titanium the deformation occurs by sliding on the systems $\{10\bar{1}0\} \langle 11\bar{2}0 \rangle$, $\{10\bar{1}1\} \langle 11\bar{2}0 \rangle$ and $(0001) \langle 11\bar{2}0 \rangle$ (critical shear stress is minimal for plane $\{10\bar{1}0\}$ and maximal for basal plane) and by twinning on planes $\{10\bar{1}2\}$, $\{11\bar{2}2\}$ and $\{11\bar{2}\}$ and causes corresponding deformation texture.

The crystallographic texture of titanium alloys depends on the chemical composition (alloying) of metal, degree of deformation, temperature and method of rolling, thickness of semi-finished rolled products, presence of gas-saturated layer etc. Heating of textured material also allows to change the texture (recrystallization, polygonization annealing, polymorphic transformation). Therefore in practice there is a great number of methods to operate the crystallographic texture of titanium alloys allowing to form texture with set-up parameters.

Having established the correlative dependences between crystallographic texture and processes of interaction of titanium alloys with gas media, it is possible to use the texture factor for operating of the intensity of physical and chemical processes in gas - metal system, and, consequently, to influence on improved characteristics of construction material.

Let's illustrate the influence of texture on the nitriding of titanium alloys.

At the gasing of samples with t_1 - "base" $(0001)[10\bar{1}0]$ (fraction of orientations 44 %) deformation texture (the plane of base of hexagonal close-packed lattice is parallel to the rolling plane) the rate of the increase of nitrogen concentration in titanium is higher than for samples with t_2 - "prismatic" $(10\bar{1}0)[11\bar{2}0]$ (fraction of orientations 50 %) texture that assists to form strengthened layers with different parameters (depth of area, surface hardness, gradient of hardness). During nitride formation with "base" texture the density of nucleation centers of nitride phases is larger and time to formation of continuous surface films is less than for the samples with "prismatic" texture (the plane of prism of hexagonal close-packed lattice is parallel to the rolling plane), that assists to form nitride films of different thickness. That is crystallographic texture of titanium alloys influences on the conditions of mass transfer on the gas - metal boundary and diffusion mobility of nitrogen. A schematically influence of crystallographic texture on the processes of interaction of titanium with nitrogen at different phase-boundary conditions on the boundary gas - metal is presented on fig. 13.

Thus, the application of texture factor allows to influence on the intensity of nitride formation and gasing, changing the relation between the dimensions of nitride and gas-saturated areas. Forming by preprocess of the primary crystallographic orientation ("base" or "prismatic" properly), it is possible to provide either higher level of surface strengthening or larger depth of nitrogen penetration in matrix.

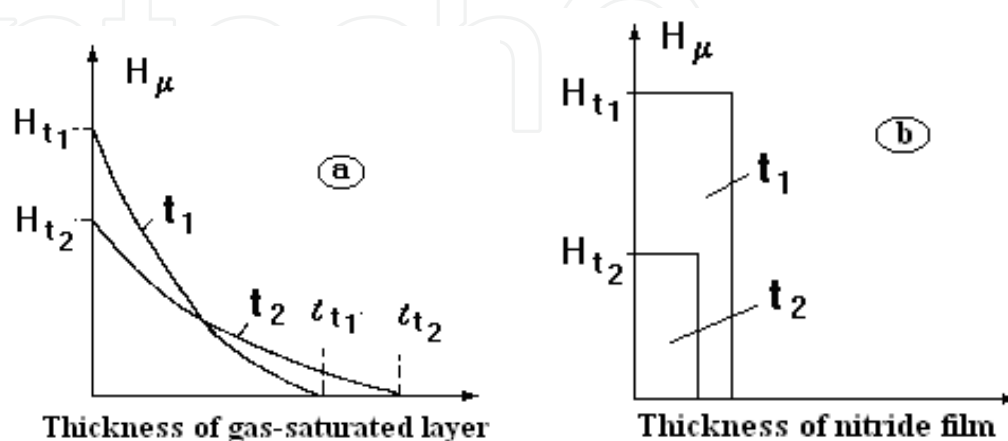


Fig. 13. Influence of crystallographic texture on the processes of interaction of titanium with nitrogen: a - at gasing; b - at nitride formation.

The intensification of process at the use of the considered approach allows to decrease the temperature of treatment, and, consequently, to weaken the negative consequences of the influence of high saturation temperatures on the quality of surface and level of mechanical characteristics.

5. Use of elements of vacuum technology at nitriding

The analysis of results of nitriding of titanium alloys at high temperatures showed that the major reason which decelerates the diffusion of nitrogen into the matrix is the forming of thick nitride film with nitrogen diffusion coefficient less on 2 - 4 orders of magnitude than in matrix ($D_{\text{TiN}^{\text{N}}} = 3,76 \times 10^{-12} \text{ cm}^2/\text{s}$; $D_{\alpha\text{-Ti}^{\text{N}}} = 1,29 \times 10^{-10} \text{ cm}^2/\text{s}$; $D_{\beta\text{-Ti}^{\text{N}}} = 3,92 \times 10^{-8} \text{ cm}^2/\text{s}$ at 950°C). Another reason is the presence of oxide films formed at technological operations of details' manufacturing and their heating to nitriding temperature due to the presence of oxygen impurities in nitrogen. Therefore, the possible ways of intensification of nitriding is to provide the corresponding conditions that allows to : 1) increase the nitrogen diffusion coefficient in nitride film or in general prevent its formation on the initial stages of nitriding; 2) favour the dissociation of existing oxide films and prevent the formation of new ones.

Let's consider some variants of realization of the above approaches.

5.1 Nitriding in rarefied dynamic nitrogen atmosphere

The parabolic character of kinetics of high-temperature interaction of titanium with nitrogen is caused by forming of nitride film on the surface. The amount of nitrogen diffused through nitride layer during its growth is decreased constantly preventing to penetration of nitrogen into the metal.

The calculated nitrogen diffusion rate in titanium and rate of nitrogen supply to the metal surface testify that under the certain conditions even all nitrogen molecules which get on surface can not be sufficient to provide the maximal flux of nitrogen atoms from surface into matrix. Except of it, not all nitrogen molecules, contacting with the surface of metal, interact with surface. In this case the processes connected with supply of nitrogen to the gas – metal reaction area become limiting. It allows to control the maximal nitrogen concentration on titanium surface and thus to provide the necessary nitrogen concentration for nitride formation. The absence of nitride film on the surface removes the diffusion barrier, and, consequently, penetration of nitrogen into titanium matrix intensifies. That is, the nitrogen partial pressure becomes the factor of intensification of nitriding process (fig. 14).

With the decrease of nitrogen partial pressure it is possible to provide the conditions when beginning of nitride film forming is shifted in time, that is at corresponding duration the nitride film is in general absent or its thickness is too thin. Thus, in the certain interval of nitrogen partial pressure the area of solid solution of nitrogen in α -titanium on the surface is formed, providing the more uniform distribution of hardness in the diffusion layer and increasing the depth of nitrogen penetration.

Let's consider the general tendencies in the processes of gasing and nitride formation at nitriding of titanium alloys in the rarefied dynamic nitrogen medium.

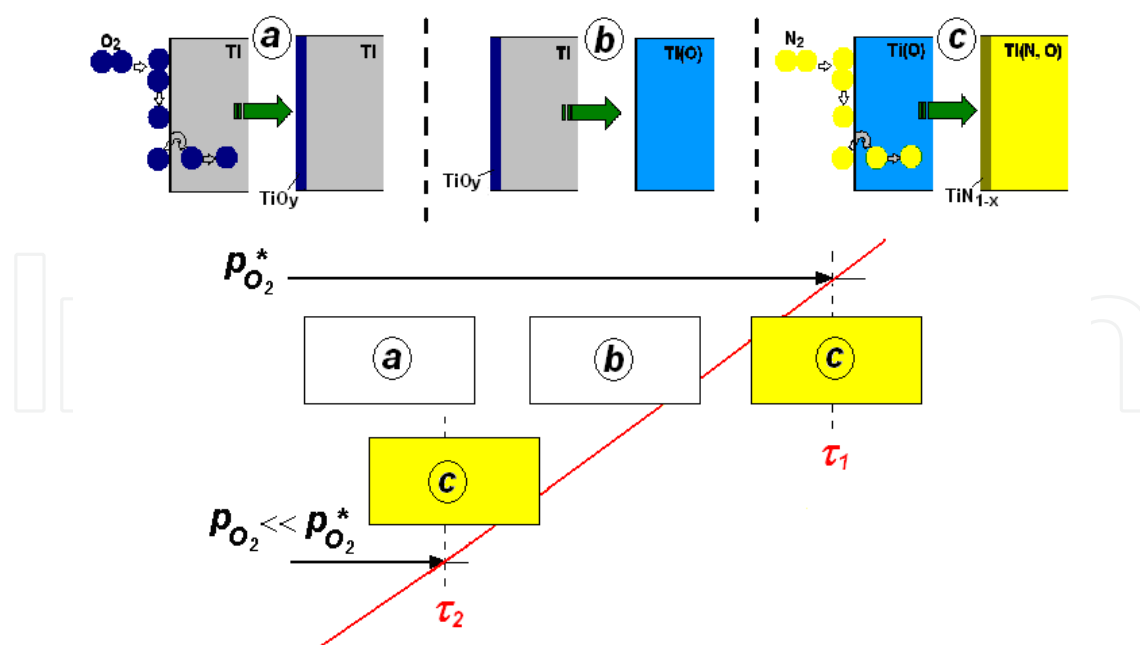


Fig. 14. Stages of nitriding of titanium alloys in nitrogen containing oxygen (a, b, c) and possibility of the intensification of process at the decrease of oxygen partial pressure.

The decrease of pressure from 10^5 to 100 Pa (gas flow rate 0,03 l/min) with the rise of mass increase of samples causes the increase of depth of nitrided layer and the significant decrease of thickness of nitride film. With the increase of gas rarefaction to 10 Pa the nitride thickness is stabilized and the depth of nitrogen penetration into titanium is decreased. With the decrease of gas flow rate on one order of magnitude, the mass increase and depth of nitrided layer increase, and thickness of nitride film decreases. This effect is similar to the decrease of gas partial pressure. At the decrease of pressure to 0,1...1 Pa in order to intensify the nitriding it is necessary to change the nitrogen flow rate. Thus, with the decrease of nitrogen flow rate in the range of 0,03...0,003 l/min the growth of depth of nitrided layer slows down.

The observed regularities and general tendencies in the processes of saturation of titanium alloys in the rarefied dynamic nitrogen medium indicate that in the interval of rarefaction 0,1...10 Pa at the gas flow rate 0,03..0,003 l/min (specific leakage rate $7 \times 10^{-2} \dots 7 \times 10^{-4} \text{ Pa} \times \text{s}^{-1}$) the kinetics of nitriding becomes receptive to the processes connected with supply of nitrogen to the gas - metal reaction area.

The analysis of the results on the influence of nitrogen partial pressure and nitrogen supply rate on the mass increase of samples, surface strengthening (surface microhardness), depth of nitrided layer testifies that the providing of the indicated gas-dynamic parameters of gas medium allows the dynamic equilibrium between adsorbed and diffused nitrogen into the titanium matrix to be maintained in certain time interval. In such conditions the nitride film is not formed on the surface and the strengthened area is the solid solution of nitrogen in α -titanium. In due course, in the result of forming of diffusion layer and increase of nitrogen concentration on the gas - metal boundary to the necessary level for nitride formation, that corresponds t^* , titanium nitride is fixed continually on titanium alloys (fig. 15).

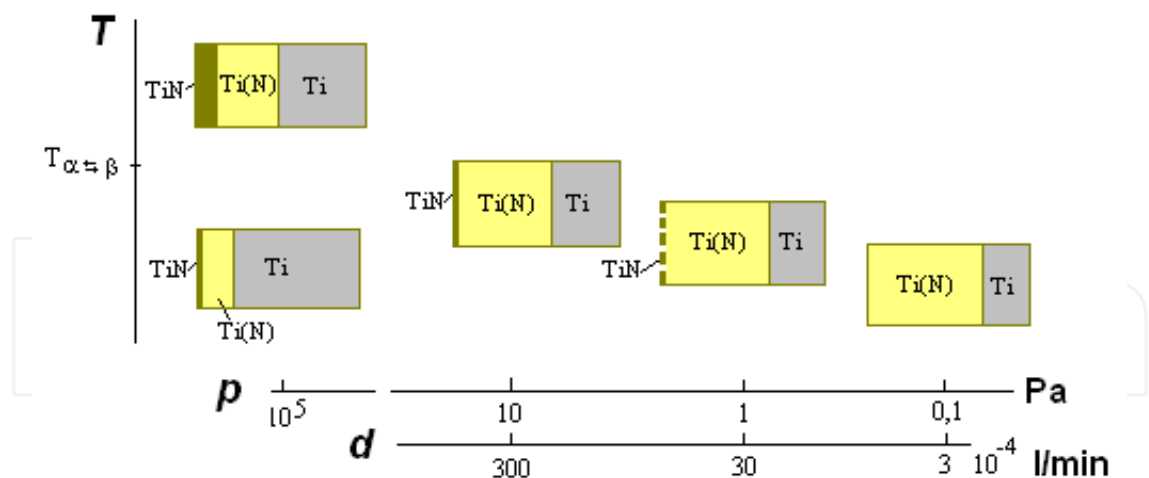


Fig. 15. Influence of temperature (T) and gas-dynamic parameters of nitrogen (p, d) on the phase-structural state of surface layers of titanium alloys.

At nitriding of titanium alloys with conservation of general tendencies the corresponding correctives in the process of saturation contributes the redistribution of alloying elements that influences on the absolute values of characteristics of the nitrided layers.

Nitriding in the rarefied nitrogen as compared to saturation in nitrogen of atmospheric pressure decreases the gradient of nitrogen concentration on the cross section of surface layers and increases the depth of penetration of nitrogen (in 1,3...2,3 time) and decreasing surface strengthening (fig. 16).

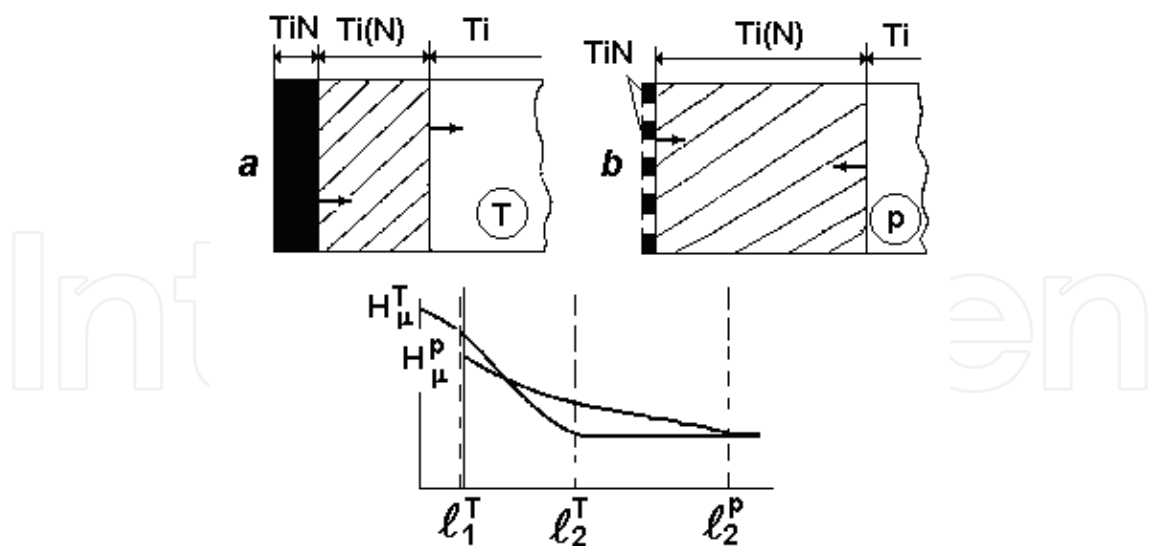


Fig. 16. Saturation temperature (a) and nitrogen partial pressure (b) as factors of the intensification of nitriding process of titanium alloys (arrows are direction of motion of phase boundaries in the areas of the identified parameters as factors of intensification).

As at lowering of nitrogen partial pressure the process of thermodiffusion saturation of titanium alloys intensifies, it makes possible to lower the nitriding temperature and decrease

the process duration. The possibility to provide the sufficient surface strengthening at the temperatures of α -area excludes the negative aspects connected with high saturation temperatures, that is the quality of surface rises and the level of mechanical characteristics increases.

Thus, with lowering of nitrogen partial pressure the nitride formation is suppressed. The absence of nitride film on the surface or substantially less its thickness weakens the diffusion barrier and penetration of nitrogen into titanium matrix intensifies. Nitriding in the rarefied dynamic nitrogen condition as compared to nitrogen of atmospheric pressure provides more uniform redistribution of hardness through the diffusion layer and more significant depth of nitrogen penetration.

5.2 Some methods of nitriding improving

The vacuum technology is widely used in practice of thermal heat treatment, including at nitriding. A brief annealing in vacuum (800 °C, 2 h) before nitriding and final treatment of detail surface is recommended to conduct for distressing and prevention of warping (Samsonov & Epik, 1973). To decrease the brittleness of diffusion layer and increase the plasticity of alloys after nitriding on 10...15 % regardless of method it is recommended to conduct the additional annealing of details in vacuum at rarefaction of 4×10^{-2} Pa during 2 h at 800 °C (Kiparisov & Levinskiy, 1972).

The vacuum annealing in this case is the separate technological process. However, such technological process can be used with better efficiency when applying the vacuum technology in nitriding, that is, realizing vacuum annealing not as the separate process but as the element of nitriding process. It allows to considerably shorten and simplify the treatment as in this case the additional processes of heating and cooling are not necessary (fig. 17a) and, consequently, to improve substantially its productivity.

The treatment of titanium alloys in vacuum of 0,1..10 mPa when oxygen partial pressure is about 0,001...0,01 mPa excludes the possibility of formation of surface oxide films. Moreover, at the such oxygen partial pressures and corresponding time and temperature parameters it is possible to provide the conditions for dissociation and dissolution of natural oxide films before nitriding. The surface is activated and, as a result, at the subsequent inflow of nitrogen the adsorption and diffusion processes have been intensified. The upper limit of pressure of residual gases in vacuum is caused by the intensive processes of sublimation, contributing vacuum embittering of alloys's surface, and the lower one - by the active processes of oxidation and oxygen saturation.

That is, providing before the nitrogen supply in the reaction furnace the pressure of the residual gases of 0,1...10 mPa provides the necessary conditions for the intensification of nitriding. At the rarefaction of 0,1...1 mPa and temperatures above 600..700 °C the dissolution of oxide films is began and the effective removal of internal tensions is occurred that determines the lower boundary of temperatures of vacuum treatment. To receive the optimal complex of the mechanical characteristics the use of temperatures above the temperature of polymorphic transformation is undesirable. This determines the upper boundary of temperatures range of vacuum treatment.

The use of vacuum technology elements before nitriding in above indicated temperatures interval assists in the increase of saturation of surface layers with nitrogen, depth of

strengthened area, surface quality and more higher temperature of exposure in vacuum. With the increase of temperature the more smooth redistribution of hardness throughout surface layers is achieved.

On this stage the heating in vacuum provides the conditions which exclude the additional oxidation of titanium surface and intensifies the nitriding. The vacuum medium (~ 1 mPa) during the heating activates the surface in the result of dissociation of oxide films. In result, the supply of nitrogen even of technical purity (with oxygen content to 0,01 % vol.) at the saturation temperatures of 750...850 °C allows to realize the quality nitriding. Providing of low pressure of residual gases of vacuum before supply of nitrogen into the reaction furnace does not require the long-duration isothermal exposure (≤ 2 h). Only heating in vacuum causes the positive result because it excludes the forming of oxide film at heating.

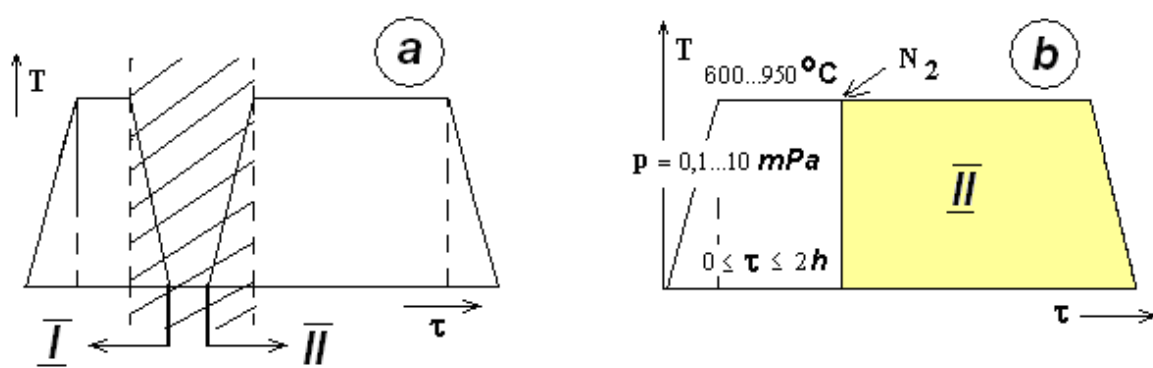


Fig. 17. Efficiency of the use of vacuum technology elements at nitriding of titanium alloys: I – vacuum treatment; II – nitriding.

Thus, the proposed vacuum technology before nitriding (fig. 17b) assists the intensification of thermodiffusion saturation of titanium alloys with nitrogen, allows to decrease the purity requirements to nitrogen for oxygen impurities at high-temperature treatment (> 850 °C) and to realize nitriding at the temperatures of 750..850 °C.

Thus, at the use of one or another intensification factor it is possible to influence on the constituents of nitriding process – nitride formation and gasing. At thermocycling as well as at the high saturation temperatures both nitride formation and gasing intensify. At the use of vacuum technology elements (lowering of nitrogen partial pressure, heating before nitriding and exposure in vacuum) the nitride formation is slowed down but gasing is activated.

At the same time the nitrided layers formed on titanium alloys are not limited by single variant of structure (thick nitride film (≥ 1 μm) and gas-saturated area). Depending on the conditions of nitriding by the control of intensity of physical and chemical processes on the boundary gas - metal it is possible to form various phase-structural states of surface layers of the nitrided titanium (fig. 18) which allows to change the level of surface strengthening (surface hardness, depth of penetration of nitrogen, distribution of microhardness on the cross section of surface layers) in the wide range, to control by thickness, continuity, composition stoichiometry and content of oxygen impurities, and, consequently, to realize the surface engineering of titanium alloys at nitriding according to the requirements of exploitation.

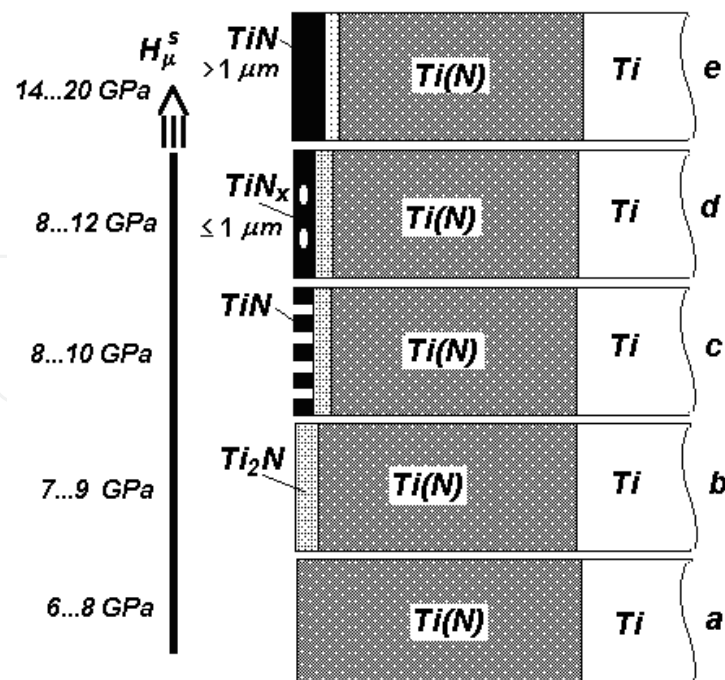


Fig. 18. The phase-structural state of surface layers of nitrided titanium alloys: a – gas-saturated area without nitride film; b, d – thin nitride film and gas-saturated area; c – nitride islands and gas-saturated area; e – thick nitride film and gas-saturated area.

Thus, the change of thermokinetic parameters of saturation, the use of vacuum technology elements and corresponding initial deformation texture allow to intensify the process of nitriding of titanium alloys in molecular nitrogen.

6. Surface engineering of titanium alloys by nitriding for corrosion protection in aqueous solutions of inorganic acids

Thermodiffusion coatings, including nitride ones, protect the titanium alloys against corrosion by combining of covering and electrochemical mechanisms (Chukalovskaya et al., 1993). The covering mechanism is being realized by making of barrier layer on the metal-medium border and thus it depends on its dimension. The electrochemical mechanism is defined by electrochemical characteristics of contacting surface and thus it causes the tendency of system to disturb the balance. In other words, it leads to reactions between surface layer ions and medium. Thus, protective properties of coatings depend on their dimension and structural characteristics (such as uniformity, relief, amount of oxygen impurities). In aggressive medium every mechanism brings in own contribution in protection. The effective combination of these mechanisms is mandatory criterion to ensure the high protective properties of nitride layers. The high saturation temperature (950 °C) provides the high-quality of nitriding in commercially pure nitrogen medium. However, the increasing of nitride coating saturation by nitrogen as well as the increasing of coating dimension due to saturation temperature rising do not lead to the improving of protective properties, but quite the contrary these processes lead to the decrease of these properties due to roughness and defectiveness raising. The saturation temperature determines the changes of surface relief. The nitride film forming at the temperature lower then the

temperature of polymorphic transformation, only follows the material's matrix geometry. Nevertheless, at the temperatures higher than polymorphic transformation temperature, the relief fragments, such as burrs, form a grid and thus a roughness has been developed. The roughness is in 0,2...0,3 μm more than after nitriding at 850 °C. The activity of nitride-forming on the grain boundaries at high temperatures assists the relief forming. Processes following $\alpha \leftrightarrow \beta$ transformation, such as deformation strengthening and three-dimensional changes, can only enhance the relief. It should be noted that the plastic deformation has certain influence. The plastic deformation is caused by significant residual stresses during the thick nitride film forming (Rolinski, 1988). The influence of temperature on the surface roughness is essential while the influence of isothermal duration is no significant because in this case the enhancing of surface relief is minimum. For instance, the roughness R_a after different durations (5 h and 10 h) is close: 1,06 and 1,09 μm .

The investigations of influence of temperature-time parameters of nitriding on the nitride coatings dimension reveal that their thickness rises when the temperature and isothermal duration increase. For instance, after nitriding at the 950 °C thickness increases up to 3...4 μm with duration change from 5 to 10 h as well as from 4 to 5 μm at the duration 5 h but with the temperature increasing (from 850 °C to 950 °C) and from 5 to 6 μm at duration 10 h.

At the same time low-temperature nitriding (lower than 950 °C) does not provide the forming of high quality phase composition since the surface becomes dark gold colors. XRD measurements show TiN and Ti₂N reflexes as well as rutile TiO₂ ones. It determines by high thermodynamic relationships between titanium and oxygen, because the active interaction each other begins at 200...300 °C while with nitrogen – at 500...600 °C. Thus the surface oxidation takes place before nitride-forming. Oxide films dissolve and dissociate only at the high temperature (upper than 850 °C).

Therefore, temperature-time and gaseous-dynamic parameters determine the dimension, quality and phase composition of nitride coating. The oxygen partial pressure and saturation temperature determine the purity of nitride coating. The roughness of nitride coating depends on saturation temperature. The thickness of nitride layer is grown with increasing of temperature and duration. Moreover the influence of temperature is more sufficient.

Since every part of nitride structure brings in own contribution in protection against corrosion, it can be possible to optimize the morphology of nitride coatings by manipulating of above-mentioned parameters to achieve the highest protective properties.

The aqueous solutions of inorganic acids dissolve the titanium and its alloys very actively (Kolotyrkin et al., 1982; Gorynin & Chechulin, 1990; Kelly, 1979). To prevent a significant corrosion losses the nitrides, carbides and borides coatings are formed, e.g. in chloric and sulphuric acids corrosion rate of nitrated titanium alloys decreases in hundred times (Kiparisov & Levinskiy, 1972; Tomashov et al., 1985; Fedirko et al., 1998). In the same time according to some studies, the corrosion mechanism has differences in chloric and sulphuric acids (Kolotyrkin et al., 1982; Brynza & Fedash, 1972; Sukhotin et al., 1990). It indicates that protective coatings must have a different structure and phase composition for use in these acids.

The corrosion of nitride coatings passes by the parabolic dependence. At first, the nitride layers are being dissolving and then the oxidation layers takes place. During the corrosion,

the corrosion cracking of nitride films has been occurred and then the oxidation and dissolution processes have being following.

Change of quality, morphology and phase composition of nitride coatings influence on their protective properties in chloric and sulphuric acids.

In 30 % HCl the increasing of thickness of nitride film improves the anticorrosion protection: kinetic curves of mass losses of nitrided specimens of significant thickness lie below. When thickness, caused by change of saturation temperature, increases the corrosion losses of light thin nitride films (5 μm) formed at 900 $^{\circ}\text{C}$ are less in 1,2-1,4 times. Another words, the thickenings of nitride films caused by longer isothermal duration improve their protective properties, whereas when it caused by increasing of temperature of saturation – decrease. Losses of nitride films have been increased in 1,5 times (Fig. 19). Obviously, it connected with forming of surface relief. To confirm this assumption the influence of coating thickness was excluded. For that the nitride coatings of different roughness but similar thickness (10 μm) have been forming. It has been achieved by nitriding at 950 $^{\circ}\text{C}$ for 10 h and at 1000 $^{\circ}\text{C}$ for 6 h. It was shown that increasing of roughness is been accompanied by increasing of corrosion rate near in 2 times (Fig. 20).

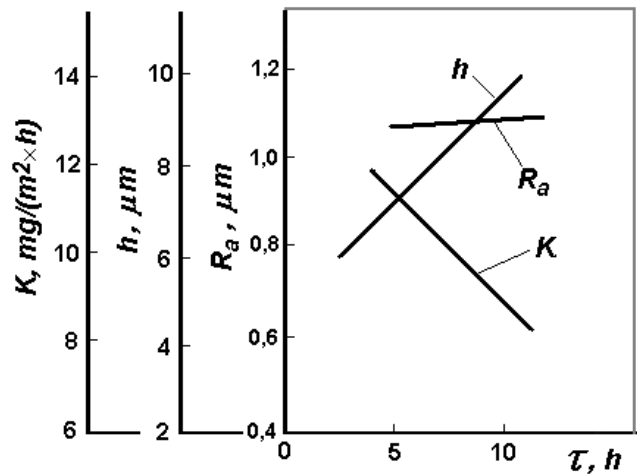


Fig. 19. Dependence of roughness ($R_a, \mu\text{m}$), nitride coating thickness ($h, \mu\text{m}$) and corrosion rate ($K, \text{mg}/\text{m}^2 \times h$) in 30% aqueous solution of chloric acid on nitriding duration at 950 $^{\circ}\text{C}$.

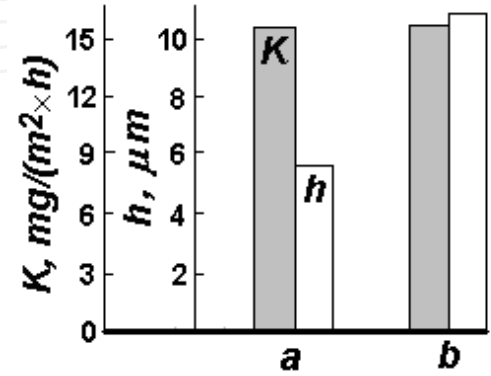


Fig. 20. Dependence of corrosion rate in 30% aqueous solution of chloric acid on the nitriding temperature and time parameters: a – 950 $^{\circ}\text{C}$, 10 h; b – 1000 $^{\circ}\text{C}$, 6h.

Electrochemical measurements in 30 % HCl confirm above-mentioned regularities. The forms of anodic curves of nitride coating are similar to the nontreated cases. Nevertheless, the electrochemical values of nitride coating with lower roughness are better: corrosion potential (E_{cor}) becomes higher (+0,08 V versus +0,06 V) and corrosion current density (i_{cor}) becomes lower from 1,0 up to 0,2 A/m² at the active dissolution and from 3,0 up to 0,8 A/m² at the passive state (fig. 21). Decreasing of the growth of corrosion current density on the different intervals of anodic curve is obviously connected with the forming of oxide films of different composition during the polarization (Gorbachov, 1983).

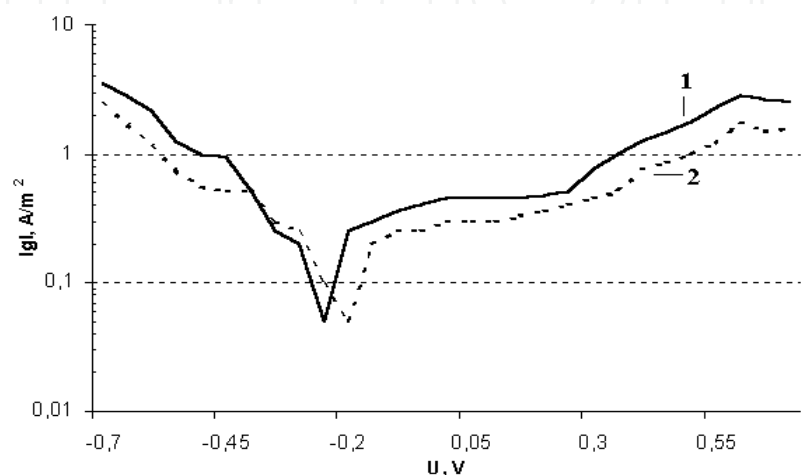


Fig. 21. Polarization curves of nitrided titanium in 30% aqueous solution of chloric acid (1 - 950 °C, 5 h; 2 - 850 °C, 5 h).

In 30% HCl the oxygen impurities or oxides including in nitride layers after the nitriding at 850 °C increase the corrosion rate (Table 4). For instance, the corrosion potential of free of oxygen nitride coating is more positive than oxynitride coating ones (Fig. 21). The corrosion current density decreases up to 10⁻¹ A/m². The decreasing of anodic current density on the nitride coating in comparison with oxynitride ones indicates about a big braking of dissolution processes and confirms their advantage in protective properties. Cathode polarization passes by the hydrogen polarization mechanism. At the cathode polarization the nitride coating has lower current densities of cathode hydrogen depolarization. It indicates about the increasing of protection against electron conduction at the cathode depolarization of hydrogen. It is obviously that the hydrogen pickup of nitride coating is decrease sufficiently at that it decreases the hydrogen degradation of ones.

Coating technique	Morphology of coating	Corrosion rate, K, <i>mg/m² × h</i>	
		30% HCl	80% H ₂ SO ₄
Heating and cooling in nitrogen, 950 °C, 5 h	Nitride coating with large surface relief	5,2	12,0
Heating and cooling in nitrogen, 850 °C, 5 h	Multiphase coating (mixture of nitrides and oxides or oxynitrides)	9,7	7,0

Table 4. Corrosion rate of nitride coatings of different morphology in aqueous solutions of inorganic acids

The mass losses investigations of corrosion processes confirm the high protective properties of nitride coating without oxygen impurities (Table 4).

In 80% H_2SO_4 protective properties of nitride coating are changed: nitride layer without oxygen impurities is characterized by the lower corrosion resistance than oxynitride layer, e.g. more negative corrosion potential and higher current density at anodic dissolution (Fig. 22). Since the values of overstresses in both cases are similar the increasing of anodic characteristics of oxynitride coating should be related to addition modification of nitride coating by oxygen.

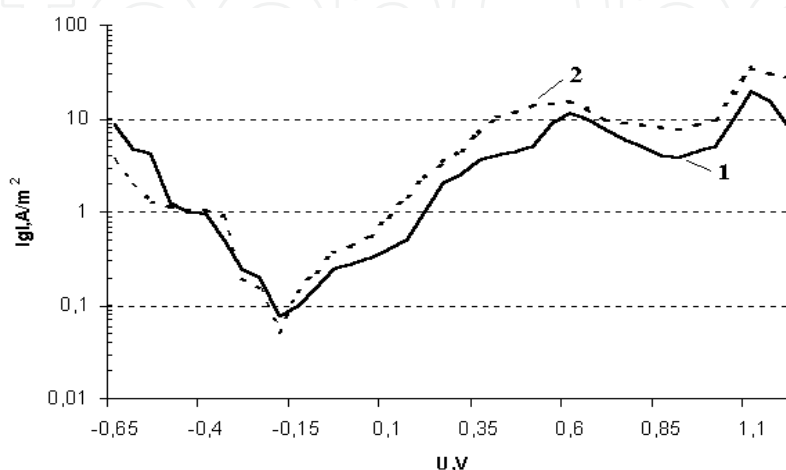


Fig. 22. Polarization curves of oxynitride (1) and nitride (2) coatings on the titanium surface in 80% aqueous solution of sulphuric acid.

Indeed, the kinetic curves of mass losses of nitride coating without oxygen impurities are situated higher and corrosion rate is in 3...10 times bigger than the oxynitride layer ones. It indicates about the good protection properties of oxynitride coatings. The positive role of oxygen impurities at the providing of protective properties of nitride coatings in sulphuric acid should be explained by different activity of chlorine- and sulphate-ions in passivation processes.

Differences in protective properties of nitride coatings in aqueous solutions of sulphuric and chloric acids indicate about necessity of differential approach to a protection against corrosion of titanium. Nitride coatings are more effective for use in chloric acid whereas oxynitride coatings are more effective in sulphuric acid.

Oxygen impurities in nitride coatings increase the corrosion losses in chloric acid whereas it decreases the corrosion dissolution in sulphuric acid.

Decreasing of nitride surface roughness at the simultaneous retaining of big thickness improves the protection properties in inorganic acids. More effective way to decrease the roughness is the decreasing of temperature of saturation. Increasing of thickness due to the large duration increases the protection properties but due to higher temperature – decreases ones.

7. Influence of nitriding and oxidation on the wear of titanium alloys

The methods of thermodiffusion surface hardening of titanium alloys and, specifically, the procedures of thermal oxidation and nitriding have serious advantages over the other

available methods under service conditions excluding the application of high contact stresses (>4 MPa) (Gorynin & Chechulin, 1990; Nazarenko et al., 1998). They are technologically simple, guarantee the reliable physical and chemical characteristics of treated surfaces, and do not require any additional technological procedures. Unlike the application of coatings, in this case, we have no problems connected with the adhesion between the hardened layers and the matrix, porosity, and, hence, with the sensitivity to aggressive media.

Let's analyze the wear resistance of titanium after thermal oxidation and nitriding.

To increase the output and efficiency of the technological processes of surface hardening, it is necessary to find out the ways of their intensification because the procedure of thermodiffusion saturation of titanium alloys, e.g., with interstitial impurities (oxygen, nitrogen, carbon, and boron), requires high temperatures and long duration. At present, the problem of intensification of the thermodiffusion saturation of titanium alloys with oxygen finds its solution in new technologies of thermal oxidation. Both the duration of process of getting the desired thickness and degree of hardening of the diffusion layer and its temperature can be decreased by applying of the procedures of boiling-bed and vacuum oxidation.

The thermodiffusion saturation of titanium alloys with oxygen from the boiling bed (650-800 °C, 4-7 h) is accelerated due to the activation of the surface of workpieces in contact (friction) with sand particles, which intensifies the processes of absorption and adsorption (Zavarov et al., 1985). In this case, we observe the formation of a hard (with a surface microhardness of 6.0-8.5 GPa depending on the alloy) wear-resistant diffusion layer consisting of a 3-7- μ m-thick film of titanium dioxide (in the rutile modification) and an interstitial solid solution of oxygen in titanium with a thickness of 20-70 μ m.

However, the non-uniform boiling of sand, its insufficient degree of dispersion and deviations from the required temperature conditions quite often lead to the formation of cavities on the titanium surface and exfoliation of the surface layer, which means that the corresponding workpieces must be rejected.

More stable results are attained in the process of thermal oxidation (700-1050 °C, 0.3-7 h) of titanium alloys in a vacuum ($\sim 0,1$ Pa). In this case, the surface of workpieces is saturated with residual gases of vacuum media (oxygen, nitrogen, and carbon), which results in the formation of a hard wear-resistant layer consisting of two areas: a complex compound of titanium oxides, nitrides, and carbides and an interstitial solid solution of these elements in the matrix.

The procedure of nitriding of titanium alloys is carried out at temperatures of about 950 °C for 15-30 h either under the atmospheric pressure (10^5 Pa) or in rarefied nitrogen ($\leq 10^2$ Pa) (Gorynin & Chechulin, 1990). Long periods of holding at high temperatures result in the irreversible growth of grains in the titanium matrix accompanied by the formation of brittle surface layers and, hence, in a pronounced deterioration of the mechanical characteristics of nitrided workpieces. The characteristics of plasticity and fatigue life of the material prove to be especially sensitive to high-temperature treatment (Table 5). Thus, after nitriding in the indicated mode, the plasticity of unalloyed VT1-0 titanium becomes in 2.3 times lower than

after oxidation in a vacuum. At the same time, its fatigue life decreases by a factor of 3-6 depending on the level of strains (Table 5, rows 2 and 3).

No	Treatment	Alloy	σ_B , MPa	δ , %	Fatigue life, cycles	
					$\varepsilon = 1,0$ %	$\varepsilon = 1,5$ %
1	No treatment	VT1-0	450	34,5	2500	900
		OT4-1	790	19,3	10100	2200
		BT6s	1040	15,3	33700	6500
2	Oxidation	VT1-0	374	21,7	1000	300
		OT4-1	729	5,9	2600	250
		BT6s	975	7,2	11700	2000
3	Nitriding	VT1-0	395	9,3	300	50
		OT4-1	735	5,1	2700	230
		BT6s	950	4,8	4200	1500
4	Nitriding in rarefied nitrogen	VT1-0	369	32,9	4000	770
		OT4-1	740	18,4	3700	670
		VT6s	943	14,2	13200	3100

Table 5. Mechanical characteristics of titanium alloys.

Thus, the energy consumption, productivity, and the general level of the attained mechanical characteristics of workpieces for the procedure of oxidation are better than for nitriding. At the same time, the process of nitriding enables to set the higher degrees of surface hardening than oxidation due to the difference between the ionic radii of the interstitial elements (0,148 nm for nitrogen and 0,136 nm for oxygen). Moreover, titanium nitrides are characterized by much smaller Pilling-Bedworth ratios (1,1 for TiN and 1,7 for TiO₂), coefficients of thermal expansion and residual stresses in the surface layer of nitrides, which excludes the possibility of violation of the continuity of the formed film (Strafford, 1979). In addition, the corrosion resistance of nitrided layer is higher than the corrosion resistance of the oxidized layer. Thus, the intensification of nitriding makes it possible to decrease the temperature and time of treatment and preserve the characteristics of toughness of the base material. This enables us to recommend this type of treatment as an efficient and cost-effective method of surface hardening.

The diffusion coefficient of nitrogen in titanium nitride is in 2-4 times lower than in titanium. Indeed, at 850 °C we have $D^{N_{TiN}} = 3,95 \cdot 10^{-13} \text{ cm}^2 \times \text{s}^{-1}$, $D^{N_{\alpha-Ti}} = 1,81 \cdot 10^{-11} \text{ cm}^2 \times \text{s}^{-1}$, and $D^{N_{\beta-Ti}} = 9,03 \cdot 10^{-9} \text{ cm}^2 \times \text{s}^{-1}$.

As the nitrogen partial pressure decreases due to the weakening of the barrier effect of the nitride film or its complete vanishing, the process of nitriding intensifies. However, a vacuum of 10² Pa is insufficient for a positive effect attained only if the pressure of the dynamic atmosphere of nitrogen is as low as 0,1-1 Pa for a feed rate of the gas of 0,003 l/min (Fedirko & Pohrel'yuk, 1995). The elements of vacuum technology (heating in a vacuum and preliminary vacuum annealing) also intensify the thermodynamic saturation of titanium with nitrogen.

The low pressure of residual gases of rarefied atmosphere (~ 10 mPa) prior to the delivery of nitrogen in the stage of heating and, for a short period of time (≤ 2 h) at the saturation temperature, activates the titanium surface and promotes the dissociation of oxide films.

These technological procedures decrease temperature and time of treatment down to 800-900 °C and 5-10 h and, hence, significantly improve the mechanical characteristics of nitrided samples (Table 5, rows 2 and 4). Thus, the plasticity and fatigue life of nitrided VT1-0 (c.p. titanium) are, respectively, in 1,5 and 2,6-4,0 (depending on the level of strains) times higher than in the case of oxidation.

The outlined procedure of nitriding leads to the formation of a hardened layer consisting of a TiN + Ti₂N nitride film ($\leq 1 \mu\text{m}$) and a deep diffusion layer (100-180 μm).

Let's compare the wear resistance of the oxidized (in a vacuum of 0,1 Pa at 850 °C for 5 h) and nitrided [heating to 850 °C in a vacuum of 10 mPa, creation and maintenance of a dynamic atmosphere of nitrogen (1 Pa, 0.003 l/min) for 5 h, and cooling in nitrogen] titanium. The surface microhardness of nitrided and oxidized layers was 7,9 and 5,1 GPa and the thickness of hardened layer was 100 and 55 μm , respectively.

Wear tests were carried out for the case of boundary sliding friction with lubrication with a AMG-10 hydraulic fluid in an SMTs-2 friction-testing machine by using the disk-shoe mating scheme. The contact load was as large as 1 and 2 MPa. The counter body was made of bronze. The sliding velocity was equal to 0,6 m/s. The friction path was equal to 10 km. To make the contact area of the mating bodies not lower than 90%, the friction couple was run in on a path of 200 m. We analyzed the mass losses of the treated specimens and counter bodies, the friction coefficients, and wear depending on the lengths of the basic friction paths (1, 2, 2, 2, and 3 km).

It was discovered that the wear resistance of nitrided titanium is quite high. After testing, the mass losses of the disk for the indicated contact loads did not exceed 1 mg (Fig. 23, curves 1 and 2). The influence of the load is noticeable (i.e., for 2 MPa, the mass losses are higher) only for the first 1.5 h of operation of the friction couple (this corresponds to a friction path of about 3 km). After this, the mass losses under loads of 1 and 2 MPa are practically equal.

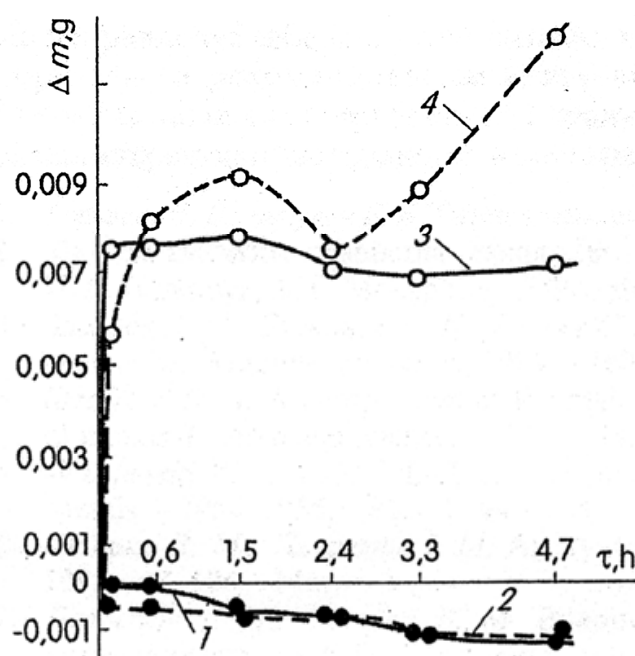


Fig. 23. Kinetics of mass changes of nitrided (1, 2) and oxidized (3, 4) disks of VT1-0 titanium in the process of friction with BrAZh9-4l bronze: 1, 3 – 1 MPa; 2, 4 – 2 MPa.

The process nitriding of titanium alloys is accompanied by the formation of a typical surface pattern, which worsens the quality of the surfaces of the workpieces (the parameter R_a increases by 0,4-0,7 mm). During the friction, the microproasperities (elements of the pattern) are separated, move into the contact zone, and finally, penetrate into the relatively soft counterbody. These hard particles of nitrides play the role of an abrasive substance and make scratches of relatively small depth in the nitrided surface. Thus, to enhance the characteristics of wear resistance, it is necessary to improve the quality of the nitrided surface, which, in turn, depends on the temperature of nitriding (the lower is the saturation temperature, the lower the roughness of the surface) (Fedirko & Pohrelyuk, 1995).

The nitriding noticeably increases the antifriction characteristics of titanium in a friction couple with bronze. The friction coefficient equal to 0,18 is stable and independent of contact pressure.

The process of friction of the oxidized disk is accompanied both by the wear of its surface layers and the process of transfer of small pieces of soft bronze to the oxidized surface. This is connected with the adhesion of bronze particles to the disk leading to the formation of unstable secondary structures, which are destroyed and removed in the course of friction, and the process is repeated again. As a result, the time dependence of the mass of the oxidized disk is not monotonic (Fig. 23, curves 3 and 4). Under a load of 1 MPa, the processes of mass transfer of bronze and its fracture are practically balanced. As a result of fitting of the mating surfaces, the friction coefficient decreases from 0,23 to 0,14 and then stabilizes. Under a load of 2 MPa, the mass transfer of bronze is predominant and, in the course of time, the oxidized surface is more and more intensely rubbed with bronze. The friction coefficient is unstable and varies from 0,24 in the stage of fitting to 0,22-0,21 in the stationary mode. In aggressive media, the appearance of bronze on the oxidized titanium surface leads to the formation of galvanic couples and, thus, promotes the corrosion processes.

The mass increment of the oxidized disk exceeds the degree of wear of the nitrided surface by one or even two orders of magnitude and the wear of the counterbodies is of the same order. Moreover, the wear of the counterbody is more intense in couples with the nitrided and oxidized disks and, thus, determines the wear of the friction couples.

In the friction couple of nitrided titanium with bronze, the wear of bronze exceeds the wear of the nitrided disk by more than three orders of magnitude. Under a load of 1 MPa, the mass loss of the shoe is a monotonically increasing function of time (Fig. 24, curve 1). Under a load of 2 MPa, this process becomes in 1,4-1,6 times more intense (curve 2). For a friction couple of oxidized titanium with bronze, the increase in the load leads to a more pronounced increase in the wear of the shoe (by a factor of 3,4-3,8) (Fig. 24, curves 3 and 4). Moreover, under a contact pressure of 1 MPa, the mass losses of the shoe in the process of friction with the nitrided disk are in 1,9 times greater than for the oxidized disk but, under a pressure of 2 MPa, the situation changes and the mass losses of the shoe coupled with the oxidized disk are in 1,6 times greater than for the nitrided disk.

The mass losses of the friction couples and their elements after different parts of the basic friction path have their own regularities. Let's now consider the wear of the counterbody in the process of friction against the nitrided and oxidized disks.

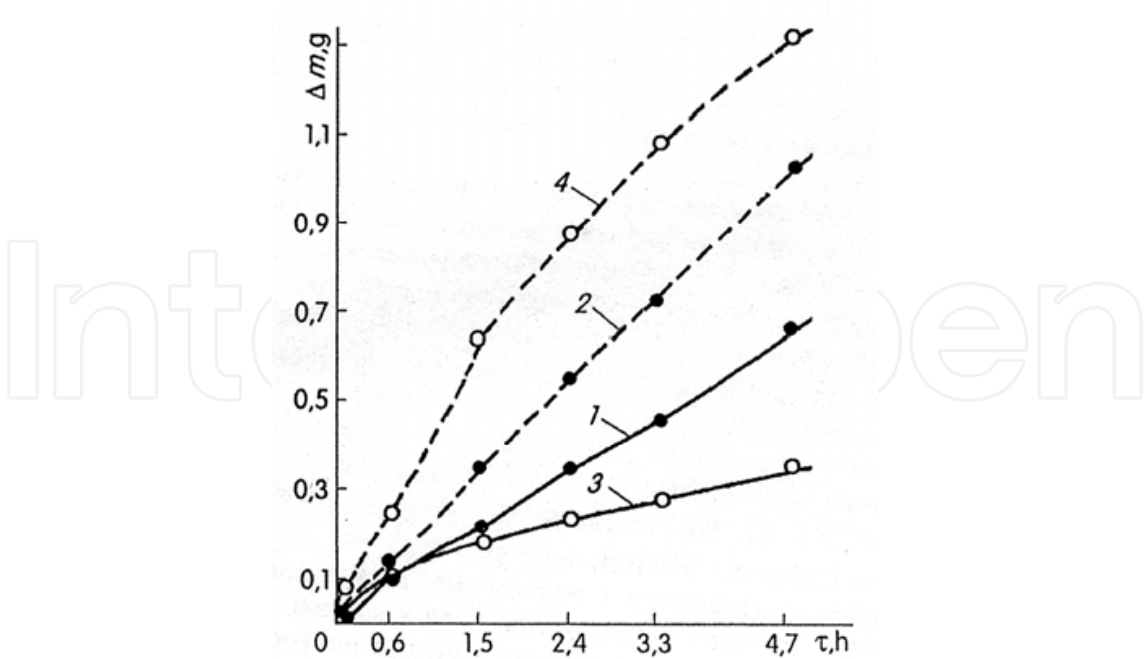


Fig. 24. Kinetics of the mass losses of the counterbody of BrAZh9-4l bronze in the process of friction with nitrided (1, 2) and oxidized (3, 4) disks of VT1-0 titanium: 1, 3 – 1 MPa; 2, 4 – 2 MPa.

In the former case, the wear of the bronze shoe after fitting and the first reference section (200 and 1000 m) first increases, then stabilizes at a level of 0,12 g (0,21 g) under a contact load of 1 MPa (2 MPa) and, finally, begins to increase again. In the latter case, the wear of the bronze is different for different sections of the friction path and under different stresses. Thus, under a load of 1 MPa, the mass loss of the bronze shoe slightly increases after fitting and then stabilizes. Only at the very end of the tests, we observe a weak tendency to increase in the mass losses. Under a load of 2 MPa, the wear of bronze significantly increases after fitting, then decreases and, finally, stabilizes.

It seems possible that the intense wear of the counterbody in the process of friction against the nitrided or oxidized titanium surface is explained by the hydrogenation of bronze as a result of tribodestruction of the lubricant (Goldfain et al., 1977). This observation is confirmed by the formation of bronze powder, which may be caused by the dispersion of hydrated bronze.

Thus, as compared with recommended nitriding, the application of oxidation as a method for increasing the wear resistance of titanium alloys is reasonable only under low contact stresses (≤ 1 MPa). Under higher contact stresses, the processes of oxidation and nitriding are characterized by practically equal levels of energy consumption and productivity but the tribological and mechanical characteristics of nitrided titanium are better than the corresponding characteristics of oxidized titanium.

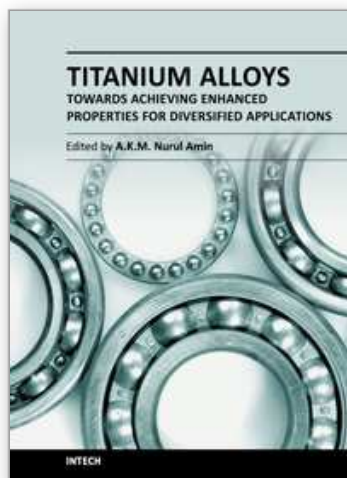
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Titanium Alloys - Towards Achieving Enhanced Properties for Diversified Applications

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The first section of the book includes the following topics: fusion-based additive manufacturing (AM) processes of titanium alloys and their numerical modelling, mechanism of β -case formation mechanism during investment casting of titanium, genesis of gas-containing defects in cast titanium products. Second section includes topics on behavior of the $(\alpha + \beta)$ titanium alloys under extreme pressure and temperature conditions, hot and super plasticity of titanium $(\alpha + \beta)$ alloys and some machinability aspects of titanium alloys in drilling. Finally, the third section includes topics on different surface treatment methods including nanotube-anodic layer formation on two phase titanium alloys in phosphoric acid for biomedical applications, chemico-thermal treatment of titanium alloys applying nitriding process for improving corrosion resistance of titanium alloys.

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