

KINETIC ASPECTS OF HIGH-TEMPERATURE INTERACTION OF TITANIUM ALLOYS WITH GASEOUS MEDIUMS

V.S. Trush^{1*}, I.N. Pohrelyuk¹, A.H. Luk'yanenko¹

¹Department of high temperature strength of structural materials in gas and liquid metal media, Karpenko Physico-Mechanical institute of the National Academy of Sciences of Ukraine, Lviv, Ukraine

Abstract. The kinetic regularities of an interaction of α -, pseudo- α - and ($\alpha + \beta$)- titanium alloys with oxygen- and nitrogen-containing gas environments depending on the temperature-time and gas-dynamic parameters of the saturation have been determined. It has been shown that by increasing saturation duration the parameters of gas-saturated layers H_{μ}^{surface} , $\Delta H_{\mu}^{\text{surface}}$ and l increase under the same parameters of pressure and temperature. By increasing saturation temperature the depth of gas-saturated zone l increases and the relative increment of surface hardness K decrease. The alloys with a high content of β -phase are less sensitive to change of the interaction conditions with rarefied gas oxygen-containing environment compared to α - and pseudo- α - titanium alloys. Nitriding of titanium alloy at temperatures of 850...950°C at the pressure of nitrogen 0.1...10 Pa provides a high intensity of diffusion processes at inhibited nitride formation. The quality of nitrided surface improves, surface micro hardness decreases and depth of diffusion layer increases under these conditions.

Keywords: titanium alloys, oxygen, nitrogen, hardened surface layer.

Corresponding Author: Vasyl Trush, Department of high temperature strength of structural materials in gas and liquid metal media, Karpenko Physico-Mechanical institute of the National Academy of Sciences of Ukraine, Lviv, 79060, Ukraine, e-mail: trushvasyl@gmail.com

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1. Introduction

One of the important areas of modern materials science titanium and alloys based on it is to ensure the maximum level of performance characteristics of products through the creation of new processing methods, as well as optimization of existing ones. In recent years, there has been a significant increase in interest in modifying the surface layer of metal in order to improve the operational properties of articles made of titanium alloys, which is associated with the appearance of new technologies for processing titanium alloys and expanding the scope of their use (Lutjering & Williams, 2007; Moiseyev, 2007). A separate place is occupied by modifying the interstitial elements, since the classical ideas about the negative effect of the gas-saturated layer, in particular on fatigue (Ebrahimi, 2008; Fukai, 2005), were revised with the appearance of results on the possibility of increasing a number of physical-mechanical properties (corrosion, antifriction, fatigue, etc.) of titanium alloys by solid-solution hardening of the surface layer of metal (Ostash & Fedirko, 2007; Pichugin, 2009; Zhecheva *et al.*, 2005). To varying degrees, scientists from different countries have been involved in this problem in different years, but the views on the role of the elements of implementation remain ambiguous (Bloyce *et al.*, 1998; Ebrahimi *et al.*, 2008; Fukai *et al.*, 2005; Zhecheva *et al.*, 2005).

At the end of the last century, a direction has emerged to use the positive effect of oxygen gas saturation on the mechanical properties of titanium alloys (Fedirko, 1996; Kolomenskii *et al.*, 1992), which eventually consolidated and developed (Fedirko *et al.*, 2009; Kolomenskiy, 2003; Kolomenskiy, 2007; Ostash & Fedirko 2007; Peshkov *et al.*, 2006; Pichugin *et al.*, 2009). For solid-solution hardening of the surface of titanium, other insertion elements, for example, nitrogen, are also used.

The required level of solid-solution hardening of surface layers of titanium by admixture impurities depends on the phase structural state of the metal and on the relative depth of the hardened zone. In this connection, there arises the problem of purposefully controlling the intensity of physical and chemical processes in the system «titanium (titanium alloy) - gas medium» to form the necessary phase structural state of the near-surface layer. In turn, this implies the study of the kinetic regularities of the interaction of titanium with the gaseous medium.

2. Kinetics of interaction of titanium alloys with an oxygen-containing gas medium

The influence of temperature-time and gas-dynamic parameters ($T = 650, 700, 750^\circ \text{C}$, $\tau = 1,3,5$ hours, $P = 6.6 \cdot 10^{-3}, 1.33 \cdot 10^{-2}, 6.6 \cdot 10^{-2}$ Pa) of thermal diffusion saturation from a controlled gas medium on the regularities of the change in the mass of titanium alloys VT1-0, VT5, OT4-1 and VT16 (Table 1).

According to the obtained results for titanium alloys (VT1-0, VT5), the gas saturation process intensifies with increasing interaction temperature and pressure of the gaseous medium (partial pressure of oxygen). Under all conditions, the maximum rate of interaction with a rarefied gas oxygen-containing medium is inherent in BT1-0 (Table 1). Titanium alloying with 5% Al (VT5 alloy) somewhat slows the rate of increase in the mass of the samples.

Table 1. Specific increase mass samples and titanium alloys as a result of interaction with rarefied oxygen-containing gas medium

$T, ^\circ\text{C}$			650	700	750		650	700	750
$\Delta M/S$ (mg/cm^2) at the residual pressure of the gaseous medium	$P = 6.6 \cdot 10^{-3}$ Pa	1 h.	3.46	8.109	17.42	VT6	2.24	5.62	12.83
		3 h.	9.91	22.96	48.83		6.53	16.2	36.64
		5 h.	15.98	36.82	77.85		10.65	26.29	59.07
	$P = 1.33 \cdot 10^{-2}$ Pa	1 h.	4.58	10.67	22.82		2.57	6.43	14.64
		3 h.	12.90	29.68	62.68		7.44	18.42	41.49
		5 h.	20.61	47.07	98.64		12.10	29.27	66.60
	$P = 6.6 \cdot 10^{-2}$ Pa	1 h.	7.95	18.25	38.45		3.31	8.24	18.68
		3 h.	21.34	48.11	99.49		9.48	23.31	52.14
		5 h.	33.14	73.9	151.2		15.31	37.36	82.86
	$P = 6.6 \cdot 10^{-3}$ Pa	1 h.	-0.10	-0.16	-0.24	VT16	2.00	2.32	2.80
		3 h.	-0.31	-0.49	-0.73		6.00	7.00	8.50
		5 h.	-0.52	-0.82	-1.23		9.66	11.60	13.29
	$P = 1.33 \cdot 10^{-2}$ Pa	1 h.	3.18	4.98	7.47		2.50	2.80	3.20
		3 h.	9.55	15.00	22.00		7.80	8.80	9.75
		5 h.	16.00	25.00	37.00		13.00	14.20	16.60
	$P = 6.6 \cdot 10^{-2}$ Pa	1 h.	7.25	11.50	17.25		3.50	4.10	5.30
		3 h.	22.00	34.75	52.00		10.60	12.60	16.70
		5 h.	36.75	57.75	86.50		17.80	22.50	27.40

For pseudo- α -alloy OT4-1 (2% β -phase at room temperature) under certain conditions of interaction with the allowed medium, a mass loss is possible (Table 1), which is associated with an intensification of sublimation of the alloying elements Mn. For this alloy there is a parity of the parameters T and p , at which the rates of gas saturation and sublimation processes become commensurable. To make the gas saturation prevailing, it is necessary to increase the oxygen partial pressure or reduce the interaction temperature.

With an increase in the amount of the β -phase in alloys (OT4-1 \rightarrow VT16), the gas saturation rate in the rarefied gas medium is significantly slowed down, which is associated with decrease of the maximum solubility of oxygen in the β -phase of titanium (6 at.%), compared with α -phase (33 at.%). A more significant difference is manifested with an increase in the interaction temperature and the pressure of the rarefied medium. This allows us to conclude that alloys with a large content of β -phase are less sensitive to changes in the conditions of interaction with a rarefied oxygen-containing gas medium.

According to the data on the change in the mass of titanium samples in a rarefied oxygen-containing gas medium, the kinetic parameters are calculated as a function of the interaction temperature.

All kinetic relationships in the 5-hour interval at a residual pressure $p = 1.33 \cdot 10^{-2}$ Pa are satisfactorily described by the linear dependence (1). This indicates that control over processes lies on surface reactions at the metal-gas interface (Ostash & Fedirko, 2007):

$$\Delta m/S = (K^p \times \tau \pm A) \cdot 10^{-2}, \text{ [g/m}^2\text{]} \quad (1)$$

where K^p is the coefficient of linear velocity at constant pressure; A is a confidence interval with a probability of 0.98.

The linear velocity coefficient in accordance with the isobaric conditions of the thermally activated process depends on the absolute temperature T in accordance with the Arrhenius equation:

$$K^p(T) = B \times \exp(-E_{\text{ekc}}/RT) \pm C, \text{ [g} \cdot \text{m}^{-2} \cdot \text{hour}^{-1}\text{]} \quad (2)$$

where B is a constant, does not depend on temperature; E_{ekc} is the total activation energy of the process; C is a confidence interval with a probability of 0.98.

Table 2. Kinetic parameters of gas saturation of titanium alloys under isobaric conditions

Alloy		VT1-0			VT5			VT16			OT4-1			
$T, ^\circ\text{C}$		650	700	750	650	700	750	650	700	750	650	700	750	
at $P = 1.33 \cdot 10^{-2}$ Pa	by the formula (1)	$K^p, \text{ g} \cdot \text{m}^{-2} \cdot \text{hour}^{-1}$	3.23	7.46	15.80	2.44	6.02	13.49	2.60	2.86	3.30	3.20	5.00	7.38
		$A, \text{ g} \cdot \text{m}^{-2}$	1.67	3.53	4.21	0.59	2.96	4.10	0.10	0.87	1.10	0.20	1.41	2.87
	by the formula (2)	$B, \text{ g} \cdot \text{m}^{-2} \cdot \text{hour}^{-1}$	4 $\cdot 10^7$			1 $\cdot 10^8$			29.21			16585.2		
		$E_{\text{ekc}}, \text{ J} \cdot \text{mol}^{-1}$	7477.6			8140.6			1350.8			4148		
		$C, \text{ g} \cdot \text{m}^{-2} \cdot \text{hour}^{-1}$	4.66			3.91			1.07			6.34		

Constants formulas (1) and (2) and the experimental activation energy of the process are given in Table 2.

According to thermogravimetry under isothermal conditions at various pressures, all kinetic regularities are satisfactorily described by linear dependences:

$$\Delta m/S = (K^T \times \tau \pm F) \times 10^{-2}, [\text{g}/\text{m}^2] \quad (3)$$

where K^T - coefficient of linear velocity at a constant temperature ($T = 700^\circ\text{C}$); F is a confidence interval with a probability of 0.98.

The dependence of the linear velocity coefficient on isothermal conditions on the residual pressure of the medium is satisfactorily approximated by the logarithmic dependence

$$K^T(p) = [H + J \cdot \ln(p)] \pm K, [\text{g} \times \text{m}^2 \times \text{hour}^{-1}] \quad (4)$$

where H and J are constants not depending on pressure; K is a confidence interval with a probability of 0.98.

The coefficients of formulas (3) and (4) are given in Table 3.

Table 3. Kinetic parameters of gas saturation of titanium alloys under isothermal conditions

Alloy		VT1-0			VT5			VT16			OT4-1			
$P \cdot 10^2 \text{Pa}$		0.66	1.33	6.60	0.66	1.33	6.60	0.66	1.33	6.60	0.66	1.33	6.60	
at $T = 700^\circ\text{C}$	by the formula (3)	$K^p, \text{g} \times \text{m}^{-2} \cdot \text{hour}^{-1}$	7.46	9.57	15.20	5.30	6.02	7.57	2.32	2.86	4.41	-0.16	5.00	11.56
		$F, \text{g} \times \text{m}^{-2}$	1.25	1.53	2.24	0.64	0.90	1.68	0.24	0.74	1.05	0.063	0.41	0.77
	by the formula (4)	$H, \text{g} \times \text{m}^{-2} \cdot \text{hour}^{-1}$	24.357			10.243			6.8862			25.189		
		$J, \text{g} \times \text{m}^2$	3.3804			0.98			0.9116			4.8973		
		$K, \text{g} \times \text{m}^{-2} \cdot \text{hour}^{-1}$	1.05			0.77			0.37			5.11		

The formation of solid solutions in the metal during the diffusion saturation of titanium alloys with gases (oxygen) is associated with a significant increase in the hardness of the metal.

Table 4 shows the experimentally obtained results on the effect of the parameters of thermal diffusion saturation on the relative increase in the surface hardness of the investigated titanium alloys $K(K = ((H_{\mu}^{surface} - H_{\mu}^{core}) / H_{\mu}^{core}) \times 100 \%$, where: $H_{\mu}^{surface}$ is the hardness of the metal surface, H_{μ}^{core} is the hardness of its core) and the depth of the gas-saturated zone l .

The analysis of the obtained durometric results allows to reveal the regularities of thermal diffusion saturation characteristic for all investigated alloys, namely:

- with increasing duration of saturation, at the same pressure of the gas medium and temperature, the parameters of the gas-saturated layer: $H_{\mu}^{surface}$ is $\Delta H_{\mu}^{surface}$ l grow;
- with increasing saturation temperature in the range $T = 650 \dots 750^\circ\text{C}$, the depth of the gas-saturated zone l increases and the value of the relative increase in the surface hardness $\Delta H_{\mu}^{surface}$ decreases.

Table 4. Changes in the (*K* - relative surface hardness / *l* - size of gas-saturated layer) of titanium and its alloys as a result of interaction with a rarefied oxygen-containing gas medium at different pressure and temperature

<i>T</i> , °C			650	700	750		650	700	750
<i>ΔM/S</i> (mg/cm ²) at the residual pressure of the gaseous medium	<i>P</i> = 6.6 · 10 ⁻³ Pa	1 h.	41/6	37/10	22/19	VT5	30/5	28/7	605/8
		3 h.	66/13	61/22	37/38		47/11	45/17	11/22
		5 h.	81/18	75/30	47/53		58/16	56/25	15/32
	<i>P</i> = 1.33 · 10 ⁻² Pa	1 h.	56/7	49/11	30/21		37/6	35/9	10/12
		3 h.	84/14	78/24	48/41		58/12	56/20	18/28
		5 h.	103/20	96/33	60/57		70/18	67/28	22/40
	<i>P</i> = 6.6 · 10 ⁻² Pa	1 h.	80/8	74/13	45/24		52/7	50/11	20/17
		3 h.	121/16	116/27	72/46		78/14	75/22	32/35
		5 h.	143/22	134/36	88/62		92/20	89/31	40/49
	<i>P</i> = 6.6 · 10 ⁻³ Pa	1 h.	38/13	17/20	9/30	VT16	25/19	5/3	045/2
		3 h.	66/22	30/35	17/52		47/48	8/10	0.77/5
		5 h.	86/29	38/45	22/67		60/71	12/33	1/40
	<i>P</i> = 1.33 · 10 ⁻² Pa	1 h.	33/26	28/33	8/40		24/22	3/5	0.4/1
		3 h.	58/45	50/57	15/70		41/53	5/40	0.8/55
		5 h.	75/58	64/73	19/90		54/76	6.7/70	0.8/100
	<i>P</i> = 6.6 · 10 ⁻² Pa	1 h.	11/36	26/45	13/54		22/26	1/27	0.4/37
		3 h.	18/62	45/77	23/93		38/60	2/73	0.8/108
		5 h.	24/80	59/100	29/120		48.8/85	2.5/109	1/163

The first regularity is associated with an increase in the concentration of the impurity with time in the surface layer of the metal and its penetration to a greater depth. The second regularity can be explained by the acceleration of the removal from the impurity surface by introduction due to an increase in their diffusion coefficient in α - and β -titanium with an increase in temperature (Ostash & Fedirko, 2007). Under such conditions, the flow of oxygen from the medium to the surface of the metal becomes less than the outflow stream due to diffusion from the surface into the interior of the metal.

3. Kinetics of interaction of titanium alloys with a nitrogen-containing gas medium

Nitride film, which is formed on the surface of titanium alloys during nitriding under atmospheric gas pressure, slows the diffusion of nitrogen into the depth of the metal and prevents the formation of deep fortified layers. The achievement of a technologically satisfactory depth of nitrided layers (> 100 μm) in the presence of a nitride film requires the use of high temperatures and long exposures in the process of chemical heat treatment, which, in turn, negatively affects the performance characteristics of the nitrided material. That is, the limiting link of the nitration process of titanium and its alloys under normal conditions (the nitrogen pressure is close to atmospheric, temperature $T = 700...1500^{\circ}\text{C}$) is diffuse processes through the nitride into the chemical reaction zone. At low partial nitrogen pressures, the kinetics of nitriding can change. Based on the statistical theory of gases, the rate of nitrogen supply to the metal surface and compared with the rate of diffusion of nitrogen in titanium (Fedirko & Pogrelyuk, 1995) showed that under certain conditions, even all nitrogen molecules entering the surface may not be sufficient to provide the maximum flow of nitrogen atoms from surface in the depth of titanium. Moreover, in fact, not all nitrogen

molecules, collided with the surface of the metal, interact with it. At the same time, the processes associated with the supply of nitrogen to the gas-metal reaction zone become limiting, and in this period the maximum concentration will not be created on the surface and there may be no nitride layer, although under the given conditions it would be thermodynamically stable.

Thus, under certain conditions, the gas pressure can influence the whole process of nitriding of titanium and its alloys. With a decrease in the partial pressure of nitrogen during nitriding, it is possible to prevent the formation of a nitride film on the surface or to substantially reduce its thickness. In a certain range of nitrogen partial pressure values, a hardened zone is formed on the basis of a solid solution of nitrogen in α -titanium in the absence of a brittle substance on the surface, providing a more even distribution of hardness in the diffusion layer and increasing the depth of nitrogen penetration.

Let us dwell in more detail on the kinetics of nitriding of titanium alloys in a rarefied to $p = 10 \dots 10^{-1}$ Pa dynamical nitrogen atmosphere (Maksimovich *et al.*, 1987; Maksimovich *et al.*, 1992; Pohrelyuk & Fedirko, 2012; Raychenko, 1981). Let us consider the process of nitrogen saturation at a temperature of 950°C on a 25-hour base of titanium alloys VT1-0, OT4-1 and VT6C. The increase in the mass of the samples of the investigated alloys (Fig. 1) at a nitrogen pressure of 1 Pa to 5 h exposure is slightly less than the increase in the mass of the samples nitrided at a vacuum of 10 Pa.

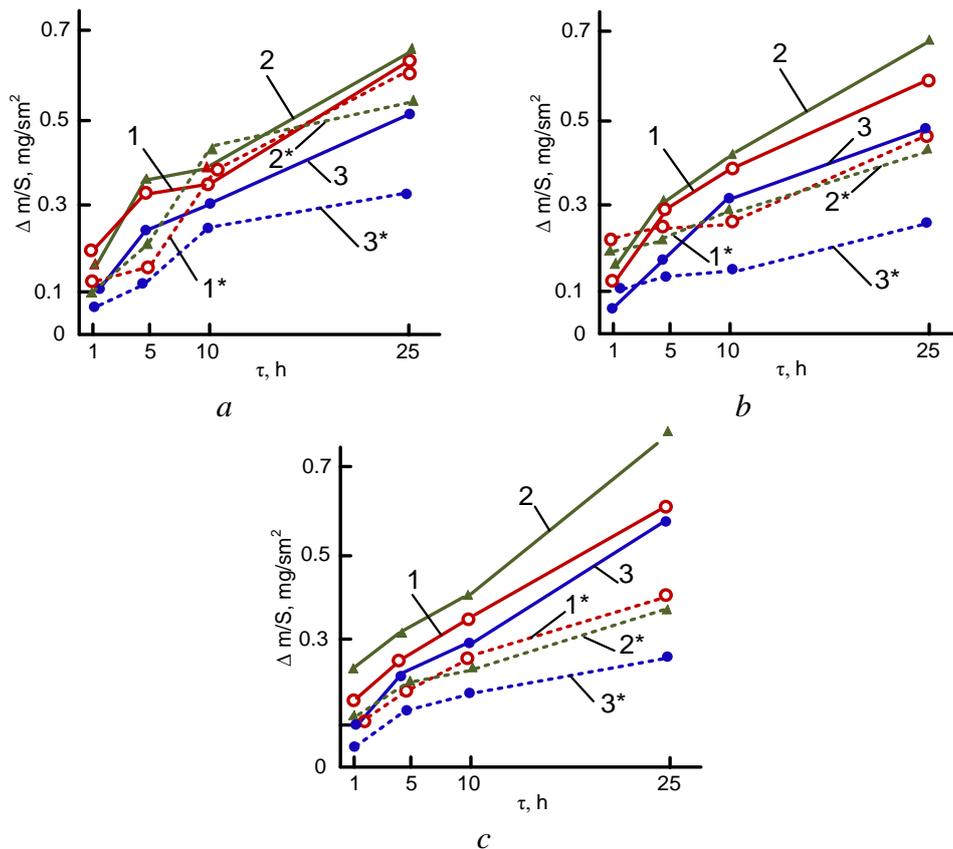


Figure 1. Kinetics of nitriding of titanium alloys VT1-0 (1, 1*), OT4-1 (2, 2*) and BT6c (3, 3*) for nitrogen pressures of $p = 10$ Pa (a), $p = 1$ Pa (b) and $p = 0,1$ Pa (c) and temperatures of 850°C (1*, 2*, 3*) and 950°C (1, 2, 3). The gas flow rate is 0.003 l/min.

However, an increase in the duration of isothermal exposure to 10 hours or more activates the saturation process and the increase in mass of the samples, if not exceeding, is not inferior to the same value obtained at a nitrogen pressure of 10 Pa. Active absorption of nitrogen is observed in the pseudo- α -alloy OT4-1, in the ($\alpha + \beta$) - alloy BT6C this process is rather passive. At a pressure of 10 Pa, the kinetic curves of nitrogen absorption by alloys are characterized by three clearly pronounced regions: a sharp increase in the mass of the samples is observed until 5-hour exposure, a further slowing down of the process occurs, and then further intensification after 10-hour exposure. The rate of nitrogen absorption by the investigated alloys at a pressure of 1 Pa to 10-hour saturation is practically equal to the absorption rate at a pressure of 10 Pa to 5-hour exposure. After a 10-hour exposure, the rate of nitrogen absorption by the alloys is somewhat slowed down and for the OT4-1 alloy, it basically corresponds to the velocity at a pressure of 10 Pa, for BT1-0 and BT6C it is inferior to it. Reducing the nitrogen pressure to 10^{-1} Pa promotes a smoother change in the mass gain during the nitriding process. At the same time, the increase in the mass of nitrated samples of the OT4-1 and BT6C alloys at a 1- and 25-hour exposure is longer, and at a 5- and 10-hour time, corresponds to a gain in the mass of samples nitrated at 1 Pa. For unalloyed titanium, VT1-0, a smaller increase in the mass of nitrated samples is observed in the entire investigated time range at a gas pressure of $p = 10^{-1}$ Pa, than at a pressure of $p = 1$ Pa.

The surface microhardness of the samples with a change in the nitrogen pressure from 10 to 10^{-1} Pa significantly decreases, indicating a decrease in the nitrogen concentration in the near-surface layers of nitrated alloys.

At a pressure of 10 Pa, an increase in the isothermal aging contributes to the continuous growth of the surface microhardness of technically pure titanium BT1-0 and the most significant in a 10-hour exposure ($H_{\mu}^{surface}_{0.96}$ (1h) = 10.5 GPa; $H_{\mu}^{surface}_{0.96}$ (10h) = 12.3 GPa). With an increase in the duration of nitriding, an insignificant change in the surface microhardness of the alloy is observed ($H_{\mu}^{surface}_{0.96}$ (25h) = 12.7 GPa). Decrease in pressure to 1 Pa, and even more to 10^{-1} Pa, is accompanied by a perceptible increase in the surface microhardness of the alloy up to a 10-hour exposure: $\Delta H_{\mu}^{surface}_{0.96} = H_{\mu}^{surface}_{0.96}$ (10h) - $H_{\mu}^{surface}_{0.96}$ (1 hour) is 4.1 and 4.5 GPa at 1 and 10^{-1} Pa, respectively. However, with an increase in the duration of nitriding up to 25 hours, the surface microhardness of the alloy decreases somewhat and the more noticeable the greater the rarefaction of the dynamic nitrogen atmosphere.

The nature of the change in the surface microhardness of the alloy VT1-0 in time after nitriding at the saturation temperature of $T = 950^{\circ}\text{C}$ suggests that during the nitriding of the alloy at a nitrogen pressure of $p = 10$ Pa, a thin nitride film on the surface forms and grows. The surface microhardness of the alloy corresponds to the hardness of the strengthened layers with a nitride film, the thickness of which continuously increases in time, which causes an increase in the surface microhardness, respectively. The decrease in pressure significantly slows down this process: only a nitrogen saturation of the solid solution passes through the 10-hour exposure, and only then begins the nitride-titration (the formation of a thin nitride film), which at a lower nitrogen pressure is faster. Since the film is very thin, the integral hardness of the surface is lower than the microhardness of the saturated solid solution and corresponds to the hardness of the surface of the alloy with a film of a certain thickness.

For alloys OT4-1 and VT6C, an increase in the surface microhardness in time over the entire investigated range of rarefactions of the dynamic atmosphere of the gas

is characteristic. However, the rate of change in surface hardness after 10-hour exposure at nitrogen underpressures of 1 and $p = 10^{-1}$ Pa is much less than at $p = 10$ Pa. A slight (by 0,4 ... 0,6 GPa) increase in the surface microhardness at a vacuum of 10^{-1} Pa with respect to the pressure of $p = 1$ Pa after a 25-hour exposure for the BT6C alloy obviously indicates the saturation of only the solid solution without forming a dense thin nitride film on a surface. That is, the 25-hour saturation of the BT6C alloy at 10^{-1} Pa is carried out with practically no formation of nitride films on the surface, and visual observations of the alloy samples confirm, fixing only a weak golden glow. Thus, a decrease in pressure during nitriding significantly slows the saturation of the near-surface layers of alloys with nitrogen, and therefore reduces the rate of nitride-titration.

The depth of the gas-saturated zone of the alloys at a pressure of $p = 10$ Pa significantly exceeds the analogous value at nitrogen rarefactions of 1 and $p = 10^{-1}$ Pa. This is especially pronounced in alloys OT4-1 and VT6C: the depth of the gas-saturated zone of the OT4-1 alloy at a vacuum of $p = 10$ Pa and the exposure of 5 and more hours exceeds the depth of the zone is formed at pressures of 1 and $p = 10^{-1}$ Pa by 20 ... 30 μm , for the alloy BT6C - by 15...20 μm , respectively. The difference in the values of the zones formed at the rarefactions of the dynamic atmosphere of nitrogen $p = 1$ and $p = 10^{-1}$ Pa is insignificant and amounts to about 10 ... 15 μm .

The microhardness distribution over the section of the nitrated layers of the VT1-0 alloy at a pressure of $p = 10$ Pa is smooth, without a pronounced gradient, as was observed in nitriding under atmospheric gas pressure conditions. Curves corresponding to a longer holding time, located in the region of high values of hardness. For OT4-1 and VT6C alloys, with a noticeable difference in the magnitude of the zones with increased microhardness at various exposures, practically no difference in their saturation with nitrogen is observed. The pressure of a rarefied nitrogen atmosphere of 1 Pa is characterized by a pronounced gradient of microhardness over the cross section of near-surface layers with a noticeable difference in nitrogen saturation of gas-saturated zones formed at different exposures. When the pressure drops to $p = 10^{-1}$ Pa, the microhardness gradient decreases noticeably.

Let us consider the kinetics of the nitration process of titanium alloys in the indicated range of nitrogen rarefaction at a temperature of $T = 850^\circ\text{C}$.

The decrease in temperature significantly changes the rate of the nitrogen process. At a pressure of $p = 10$ Pa and an exposure time of up to 10 hours, there is acceleration in the change in the increase in the mass of the nitrated samples, which, with an increase in the duration of nitriding, slows down considerably. For a pressure of a rarefied dynamic nitrogen atmosphere equal to $p = 1$ Pa, for a clock exposure, the mass gain of samples is much larger than the mass gain at a saturation temperature of $T = 950^\circ\text{C}$ and a similar rarefaction. But further in the process of saturation, there is an almost uniform increase in the mass gain by a minimum value for all the alloys under study. For liquefaction of 10^{-1} Pa nitrogen, the rate of nitrogen absorption is typically slow in the time interval under study.

The decrease in temperature helps to reduce the surface microhardness of nitrated alloys. The pressure of a tenuous dynamic nitrogen atmosphere of $p = 10$ Pa is characterized by a sharp change in surface hardness up to 10-hour exposure ($\Delta H_\mu^{surface}$ relative to the initial one is 4 ... 6 GPa), after which an intense thin nitride film begins to form on the surface. Over time, the hardness of the surface remains practically unchanged and stabilizes at a level of 10 ... 12 GPa, depending on the alloy, reflecting the growth of the existing nitride film. Nitriding in nitrogen, the partial pressure of

which is $p = 1$ Pa, slows down the nitride adherence, which causes a smooth increase in the surface microhardness. The hardness of the surface is somewhat inferior to that obtained by nitriding at a nitrogen pressure of $p = 10$ Pa with an exposure time of more than 5 hours.

The microhardness of the samples of alloys under study is changed in a rarefied way, under a nitrogen atmosphere of $p = 10^{-1}$ Pa: it rapidly increases in the case of a 5-hour exposure to 10 ... 12 GPa, and then decreases to a value close to that obtained at 1-hour endurance. Subsequently, at 25-hour exposure, the microhardness again increases, but, as a rule, does not exceed the hardness of the samples nitrided at lower vacuum pressures (in the alloy BT6C it is more indicated values).

The regularities of the change in the depth of the gas-saturated zone with time, depending on the magnitude of nitrogen dilution at $T = 850^{\circ}\text{C}$, differ radically from those observed at $T = 950^{\circ}\text{C}$. While at $T = 950^{\circ}\text{C}$ the maximum depth of the zone is formed at the slightest rarefaction in the pressure range is considered, then at $T = 850^{\circ}\text{C}$ the maximum depth of the gas-saturated zone is formed at a pressure of $p = 10^{-1}$ Pa and substantially exceeds the depth of the zones formed at a lower pressure (at 25 hours the exposure time is 30 ... 70 μm). For alloys VT1-0 and OT4-1, the magnitude of the zones formed at nitrogen pressures of $p = 10$ and $p = 1$ Pa differs little throughout the entire time base. The difference in the magnitude of the zones of the VT6C alloy at the indicated vacuum is 10 ... 30 μm , the zone being formed at a pressure of $p = 10$ Pa, larger than the zone formed at a vacuum of 1 Pa. At a nitrogen partial pressure of $p = 10^{-1}$ Pa, up to a 5-hour exposure, the zone with an increased microhardness of the alloy does not exceed 30 μm , but with an increase in the duration of nitriding the growth of the zone becomes noticeably more active and its value at a 25-hour exposure is already about 130 μm .

At $T = 850^{\circ}\text{C}$, nitriding of commercially pure titanium occurs in the α - phase. Since the diffusion coefficient of nitrogen in α -titanium is smaller than that of the β phase ($D_{[\text{N}]\alpha\text{-Ti}} = 1,817 \cdot 10^{-11}$ cm^2/s , $D_{[\text{N}]\beta\text{-Ti}} = 9,037 \cdot 10^{-9}$ cm^2/s at $T = 850^{\circ}\text{C}$ (Pohrelyuk & Fedirko, 2012), then with such an amount of nitrogen coming to the surface and being absorbed by it, which exceeds the possibility of diffusion of nitrogen to the depth of the alloy, a critical concentration of nitrogen is reached rather soon on the surface of the samples and a nitride film is formed. This complicates the diffusion of nitrogen ($D_{[\text{N}]\text{TiN}} = 3.957 \cdot 10^{-13}$ cm^2/s at $T = 850^{\circ}\text{C}$ (Pohrelyuk & Fedirko, 2012), which is two orders of magnitude smaller than in α -Ti) to the matrix and, as a consequence, contributes to a sharp decrease in the depth of the gas-saturated layers. The described physicochemical situation is evidently formed at a nitrogen pressure of ~ 10 Pa. Reducing the pressure to 1 ... 10^{-1} Pa, adequate to reduce the amount of nitrogen arriving at the surface, leads to the establishment of a dynamic equilibrium between the amount of adsorbed and diffusion-depleted matrix of the nitrogen alloy. The result of this is the formation of deep fortified layers at the indicated rarefactions. After a certain exposure (10...15h), the nitrogen concentration in the near-surface layers of α -titanium increases to critical, a nitride film is formed and the diffusion saturation process slows down (Fig. 1). At temperatures of the β -region ($T = 950^{\circ}\text{C}$), due to the difference in the diffusion coefficients of nitrogen in the α and β phases of titanium, the dynamic equilibrium between the adsorbed and diffusedly removed into the depth of the titanium matrix by nitrogen shifts toward lower values of the rarefaction of the active gas ($p = 10$ Pa) rarefaction $p = 1 \dots 10^{-1}$ Pa diffuse branch.

4. Conclusion

Thus, the maximum intensification of the process of saturation of titanium and nitrogen-based alloys in the range of rarefactions of the active gas $10 \dots 10^{-1}$ Pa is observed when a dynamic equilibrium is established between the adsorbed and diffusively removed into the depth of the titanium matrix by nitrogen, which is achieved at a nitriding temperature corresponding to the value nitrogen pressure and its consumption and depends on the chemical composition of the nitrided material, since, depending on the temperature range of polymorphic transformation, the alloy The temperature is nitrogen in α -, $\alpha + \beta$ - or β -phases. With a decrease in the partial pressure of nitrogen to 0.1 Pa, the nitride-titration is inhibited. The absence of a nitride film on the surface or substantially less than its thickness substantially attenuates the diffuse barrier, and then the penetration of nitrogen into the titanium matrix intensifies. Nitrogenation in rarefied nitrogen in comparison with saturation in nitrogen of atmospheric pressure provides a uniform distribution of hardness over the depth of the diffusion layer, increases the depth of nitrogen penetration (by 1.3 ... 2.3 times).

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