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Low-temperature plasma nitriding of titanium alloy Ti-6Al-4V

Низкотемпературное плазменное азотирование титанового сплава Ti-6Al-4V

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ABSTRACT
Reports on the results of two-stage-experiments of low-temperature plasma nitriding of the Ti-6Al-4V titanium alloy in a non-self-sustained high-current arc discharge. The diffusion of nitrogen into the interior of the material was determined by the thickness of the layer being modified. It was established that the depth of the nitrided layer greatly depends on temperature, pressure of the working medium, as well as on process duration. When treated in non-self-sustained high-current arc discharge, the depth of the nitrided layer increases from 19 to 33 μm.

KEYWORDS
Plasma nitriding; titanium alloys; non-self-sustained high-current arc discharge; surface microhardness.

АННОТАЦИЯ
Представлены результаты двухэтапных экспериментов низкотемпературного плазменного азотирования титанового сплава Ti-6Al-4V в несамостоятельном сильноточном дуговом разряде в различных условиях. Диффузия азота в материал определялась толщиной модифицированного слоя. Установлено, что глубина азотированного слоя сильно зависит от температуры, давления рабочей газовой смеси, а также от продолжительности процесса. При обработке в несамостоятельном сильноточном дуговом разряде глубина азотированного слоя увеличивается с 19 до 33 мкм.

КЛЮЧЕВЫЕ СЛОВА
Плазменное азотирование; титановые сплавы; несамостоятельный сильноточный дуговой разряд; микротвердость поверхности.

Introduction

Nowadays, titanium alloys are widely used as a structural material in the aviation and aerospace industries due to such material properties as excellent corrosion resistance, high specific strength, low modulus of elasticity, non-magnetic properties, and low coefficient of thermal expansion [1–4]. However, its application is limited because of the low hardness and poor tribological properties. There exist many hardening methods aimed to improve the mechanical properties of the surface of titanium alloys. The most common and effective ones are the methods of surface modification, in particular nitriding. Usually, traditional gas nitriding of titanium alloys is carried out at high temperatures (above the polymorphic transformation temperature) ranging from 850 to 1050 °C. This method also requires longer holding period, i.e. over 30 hours [2, 3]. During nitriding, a nitride zone consisting of titanium mononitride TiN (δ-phase) with the hardness of about 1500 HV and the sublayer of diffusion zone (solid solution of nitrogen in titanium) with its maximum hardness of 700 HV is formed on the surface of titanium and titanium alloys. Sometimes a dark band consisting of α+Ti2N or Ti2N+TiN is observed between them [4]. The nitride zone slows down the diffusion of nitrogen deep into the material [5–9]. Besides, high processing temperature adversely affects the mechanical properties of titanium alloys due to the fact that the material undergoes structural-phase transformations. Thus, a greater decomposition of titanium mononitride occurs and a significant grain growth takes place under the process of cooling [1].

Due to this fact the low-temperature plasma nitriding is regarded as a promising hardening method of titanium alloys and has the following advantages over the traditional gas nitriding [1–11]:

– higher saturation speed, which makes it possible to decrease the temperature and to make the pro-cessing time shorter;

– wider range of process parameters aimed to achieve specified characteristics of the surface layer;

– insignificant deformations of parts due to low temperature of the process and uniform heating;

– possibility of titanium alloys nitriding without additional depassivating treatment.

It should be noted that according to the studies [12] an extended hardened layer is formed after plasma ni-triding at the temperatures below the polymorphic transformation. In this case, a large diffusion zone is formed under the thin nitride layer, consisting of δ-phase and ε+α phases. The presence of an extended diffusion zone favorably affects the fatigue characteristics. Thus, in the opinion of the authors [13–16] the large thickness of the nitride layer and the insignificant extension of the diffusion zone during high-temperature gas nitriding negatively affect the fatigue characteristics of the alloy. This leads to the enhanced cracking caused by the extended nitride layer, as well as their rapid spread caused by the large-sized grains. The influence of low-temperature plasma nitriding modes on the structure, phase composition, and mechanical properties of the titanium alloy Ti-6Al-4V is investigated in this paper.

1. Materials and methods

The research was carried out using a two-phase titanium alloy Ti-6Al-4V widely applied in industry (6.5% Al, 5.1% V, 0.1% Fe, 0.03% Si, 0.02% C, 0.01% N).

Several experiments on low-temperature plasma nitriding of the titanium alloy Ti-6Al-4V were performed in non-self-sustained high-current arc discharge (NNV-6,6-I1 installation) (fig. 1) [8].

The influence of process parameters such as temperature (T=450–600°C) and duration of treatment on both microhardness and depth of the nitrided layer was studied in this work. The modes of low-temperature plasma nitriding of titanium alloys are presented in tables 1. The nitriding was carried out at a constant pumping of gas medium 80%N2+20%Ar. Anhydrous nitriding is due to the fact that, when diffusing into the surface layer, hydrogen dramatically increases the brittleness of the layer. This fact is confirmed by different authors in their papers [15].

Microhardness measurements along the depth of the nitrided layer were carried out applying the method of reconstructed imprint in accordance with the Russian State Standard GOST 9450-76 using the Struers Duramin-1/-2 microhardness tester. The static load applied to the diamond indenter for the period of 10 s was 490.3 mN (50 g). The depth of a hardened layer was determined from the hardness distribution curve to the value of the hardness of the basic material.

The microstructure of a hardened layer was studied using optical microscope Olympus GX-51. Thin section was etched with the etching agent 10% HF–15% HNO_3–75% H_20 in order to determine the structure of the titanium alloy.

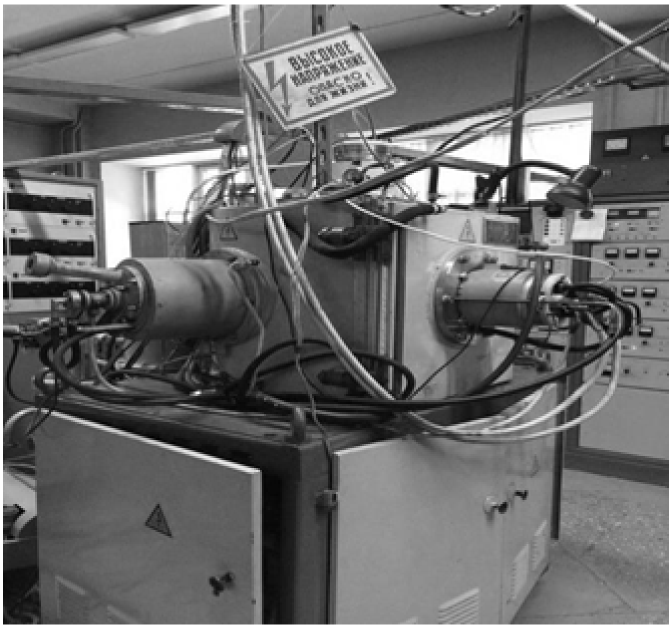


Fig. 1. Appearance of installation NNV-6,6-I1

Рис. 1. Внешний вид установки ННВ-6,6-И1

Table 1

Таблица 1

Nitriding modes in non-self-sustaining high-current arc discharge

Режимы азотирования в несамостоятельном сильноточном дуговом разряде

No. samples	Temperature, °C	Duration *t, h*
1	600±10	1
2	550±10	1
3	500±10	3
4	500±10	1
5	450±10	1

2. Results and discussions

The initial structure after annealing at 800°C is presented by small equiaxial and elongated α-phase crystallites with boundary separation of drop-, acicular, and prolate shape β-phase. The hardness of the initial structure is 350 $HV_{0.05}$.

The microstructure of samples after various surface treatment modes is mainly presented by equiaxial α-phase grains [11] with boundary separation of β-phase of drop-, acicular, and prolate shape (fig. 2).

Treatment at 450°C does not change the microstructural parameters of samples and the grain phases remain equiaxial. There is no sharp boundary between the diffusion zone and the material base.

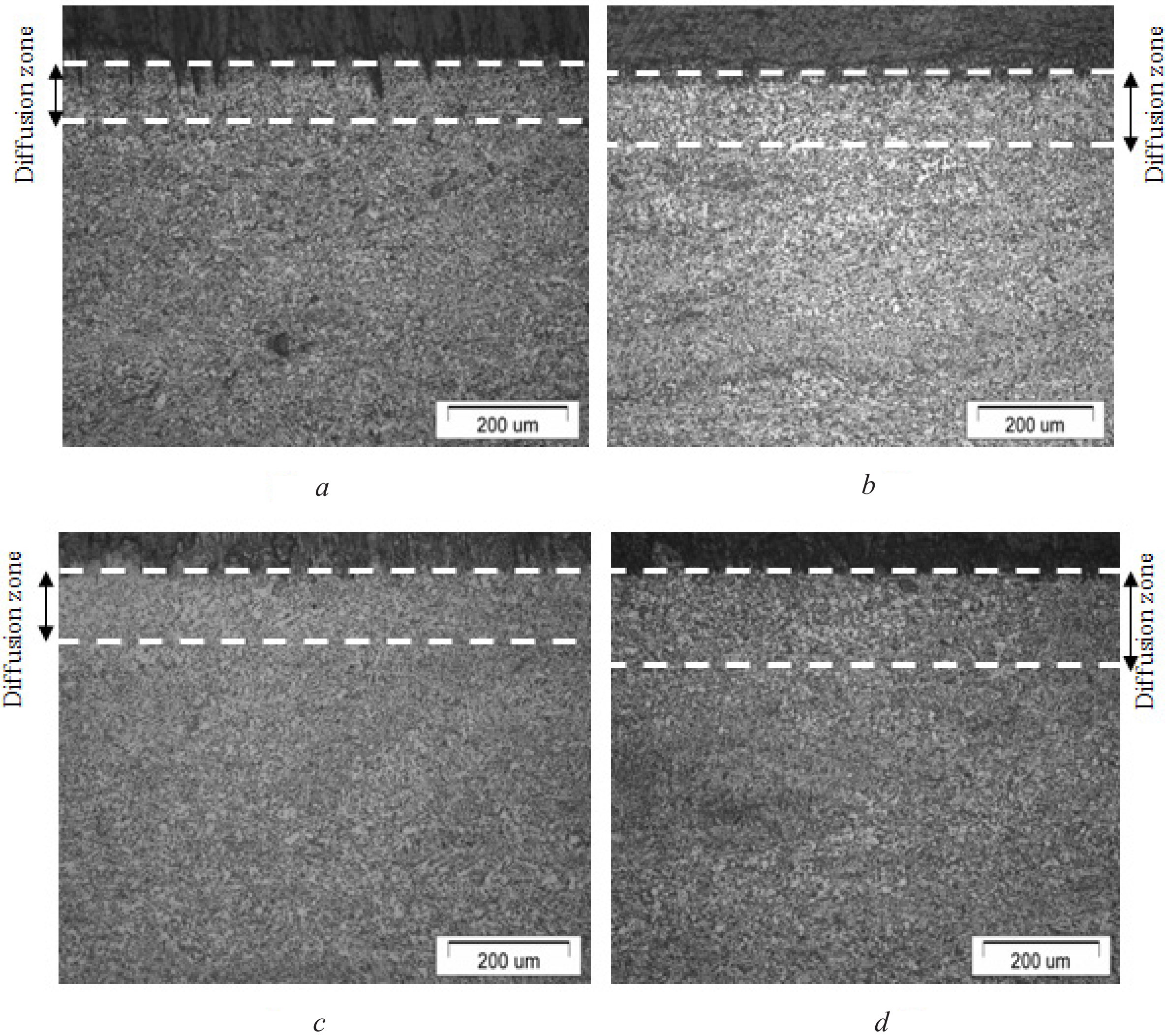


Fig. 2. Microstructure of the Ti-6Al-4V alloy after low-temperature plasma nitriding by non-self-sustaining high-current discharge at *t* = 1 h: *a* – 450 °C; *b* – 500 °C; *c* – 550 °C; *d* – 600 °C

Рис. 2. Микроструктура сплава Ti-6Al-4V после низкотемпературного ионного азотирования несамостоятельным сильноточным разрядом при *t* = 1 ч: *a* – 450 °C; *b* – 500 °C; *c* – 550 °C; *d* – 600 °C

At 600 °C there is a growth of separate crystallites which illustrates the beginning of secondary recrys-tallization. Microstructural parameters in the near-surface layer are similar to the parameters in the volume of material.

Microhardness measurements along the depth showed that after the nitriding, an increase in the surface microhardness is observed, which is associated with the formation of a nitride layer on the sample surface having golden hue and a diffusion zone [16]. Fig. 3 demonstrates the hardness distribution curves for different temperatures along the depth of a modified layer.

The dependence analysis (fig. 3) showed that the microhardness along the depth of the samples de-creases gradually, which indicates the presence of an extended layer with the increased hardness. Besides, as the treatment temperature increases, the thickness of the modified layer increases as well.

Dependences of microhardness of the depth of the nitrided layer show that the temperature of plasma nitriding, both in non-self-sustained high-current arc discharge, has a significant effect on the nature of nitrogen diffusion into the interior of titanium alloy during low-temperature nitriding. That is one of the most important parameters that control the properties of nitrided parts is their temperature during processing.

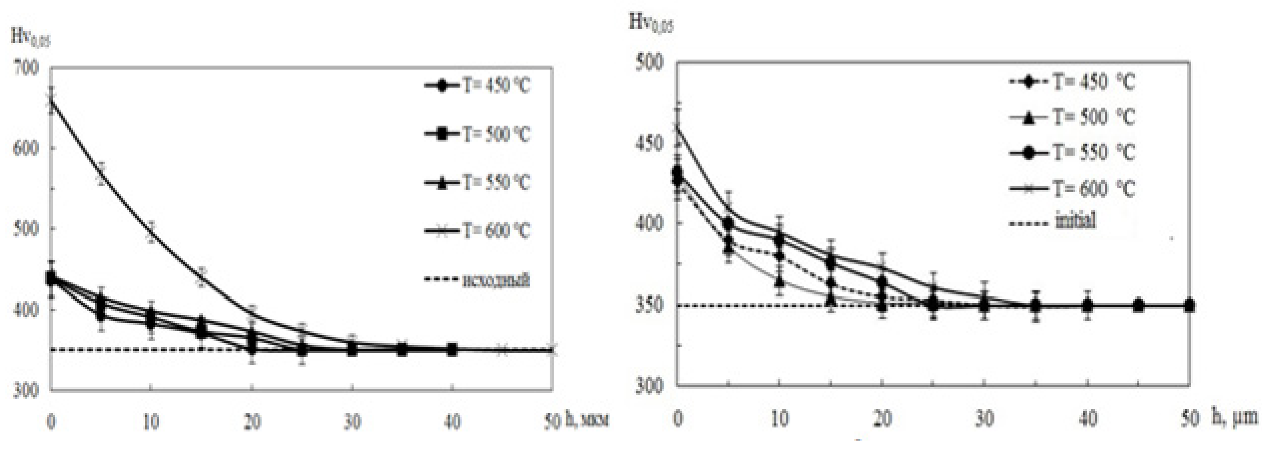
The results, which are shown in fig. 3, confirm the presence of diffusion at relatively low temperatures used in this work. For example an increase in temperature from 450 to 600 °C leads to an increase of the nitrided layer depth from 19 to 33 μm. Thus, when temperatures rise to 150° C leads to an increase in the depth of the diffusion layer in 1.73 times.

This is explained by the fact that the nitriding is a thermally activated diffusion process [3, 12, 16]. This regularity is observed in the paper [17] where the authors show that the nitrided layer thickness depends on the temperature (exponential law) and the plasma nitriding kinetics of titanium alloys is described with the help of quadratic parabolic dependence, since the process is controlled by the diffusion of nitrogen in the metal.

The time of ion nitriding at a constant temperature has a significant effect on the thickness of the diffusion layer. The graphs show (fig. 4) that increas ion nitriding unit time dramatically increases the depth of diffusion. For example, the increase of the nitriding process duration from 1 to 3 hours at a temperature of 500 °C leads to an increase of the depth of the nitrided layer from 23 to 33 μm.

The diagram of microhardness (fig. 5) dynamics along the depth of the nitrided layer shows that the microhardness of the sample surfaces decreases smoothly away from the surface, which indicates the presence of an extended layer.

Analysis of the dependence further showed that the depth of the strengthened layer after nitriding was 27 μm. However, the surface microhardness of the sample located parallel to the plasma flow was 1.5 times higher that of the sample that was placed perpendicular to the plasma flow and made 660HV$_{0,05}$. This is due to the fact that titanium nitride of high hardness is formed on the surface of the sample [17–20].



a *b*

Fig. 3. Dependences of microhardness variation of the nitrided layer depth of titanium alloy Ti-6Al-4V

Рис. 3. Зависимости изменения микротвердости по глубине азотированного слоя титанового сплава Ti-6Al-4V

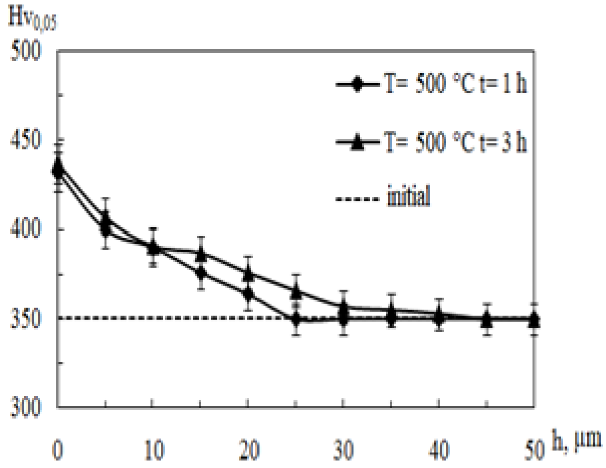


Fig. 4. Microhardness distribution along the depth of a hardened layer depending on the nitriding time

Рис. 4. Распределение микротвердости по глубине упрочненного слоя в зависимости от времени азотирования

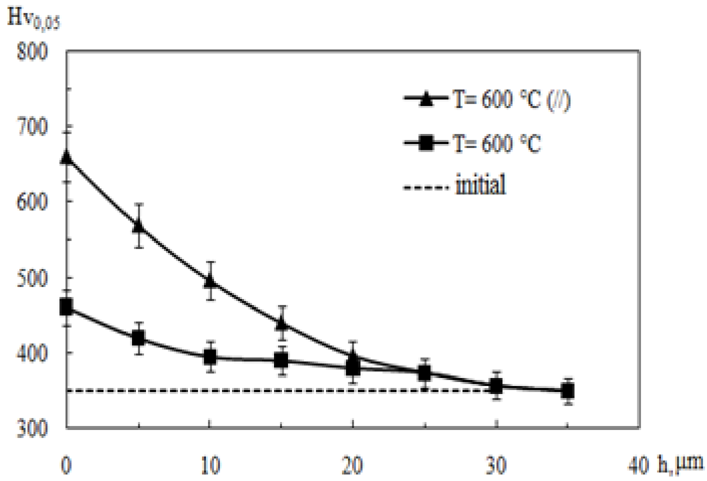


Fig. 5. Dependance of microhardness dynamics along the depth of the nitrided layer

Рис. 5. Зависимость распределения микротвердости по глубине азотированного слоя

Conclusion

As a result of the study of the effect of low-temperature plasma nitriding modes on the structure and properties of Ti-6Al-4V titanium alloy the following was established:

1) The nitriding at 450 and 500°C does not result in the change of sample microstructural parameters, and at 550°C and above a slight grain growth is observed in the samples due to the processes of recrystallization.

2) The depth of a modified layer significantly depends on the treatment temperature and duration. Thus, the temperature increase from 450 to 600°C leads to the increase in the depth of a nitrided layer from 20 to 33 μm. Besides, when the holding time is increased, the increase in the depth of a nitrided layer is observed.

4) The surface microhardness of the sample located parallel to the plasma flow has been 1.5 times higher that of the sample that was placed perpendicular to the plasma flow and made 660HV0,05. This should be attributed to the fact that titanium nitride is formed on the surface. The depth of the nitrided layer in both cases has been similar and reached 27 μm.

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