

## ПОВЕРХНОСТНЫЕ СВОЙСТВА СПЛАВА VT 6 ПОСЛЕ ПЛАЗМО-ЭЛЕКТРОЛИТИЧЕСКОЙ ОБРАБОТКИ

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*Методом плазменно-электролитической обработки проведена поверхностная модификация титанового сплава VT 6 в водном растворе, содержащем 5 мас. % гидрата аммония и 10 мас. % хлорида аммония в температурном интервале 650-900 °С. Характеристика поверхностных слоев сплава после плазменной электролитической обработки проводилась с помощью инфракрасной спектроскопии Фурье (FTIR) и порошковой рентгеновской дифракции (XRD). Спектры FTIR регистрировали на спектрометре BrukerVertex80 при комнатной температуре в диапазоне 7500-350 см<sup>-1</sup>. Спектры показывают наличие фазы рутила на поверхности сплава после плазменной электролитической обработки в растворе электролита указанного состава. Интенсивные пики при 654-643 см<sup>-1</sup>, слабые пики около 560 см<sup>-1</sup> и пики при 425-416 см<sup>-1</sup> могут быть отнесены к рутилу. Пики при 466-462 см<sup>-1</sup> связаны с валентными колебаниями Ti-O-Ti. С ростом температуры относительная интенсивность пиков, относящихся к рутилу, возрастает. Плазменно-электролитическая обработка приводит к появлению пиков, свидетельствующих об обогащении поверхности сплава азотом: пики при 1634-1622 см<sup>-1</sup> могут быть отнесены к асимметричной деформации NH<sub>4</sub><sup>+</sup>; пики около 1539 см<sup>-1</sup> относятся к деформации N-H или симметричной деформации NH<sub>4</sub><sup>+</sup>. Пики около 1428-1426 см<sup>-1</sup> также могут быть отнесены к*

*деформационным колебаниям  $\text{NH}_4^+$ . Плазменно-электролитическая обработка в температурном диапазоне 650-750 °C приводит к появлению пиков при 1069-1064  $\text{см}^{-1}$ . Согласно литературным данным, пики могут быть отнесены к колебаниям Ti-O-N. Рентгеноструктурный анализ позволил установить кристаллическую структуру и фазовую идентификацию титанового сплава VT 6 после плазменно-электролитической обработки. Измерения проводились с использованием дифрактометра Bruker D8 Advance с излучением Mo K $\alpha$  ( $\lambda = 0,07107$  нм). Анализ образцов XRD показал, что оксид титана в образцах присутствует как фаза хонгевита ( $\gamma$ -моноклинная сингония), и как фаза «magnesium» (гексагональная сингония). Кроме пиков TiO наблюдались пики, характерные для хамрабевита TiC в фазе галита (кубическая сингония) и Ti<sub>2</sub>O<sub>3</sub> в фазе корунда (тригональная сингония).*

**Key words:** плазменно-электролитическая обработка, титановый сплав, поверхностная модификация, фаза рутила

## SURFACE PROPERTIES OF TITANIUM ALLOY VT 6 AFTER PLASMA ELECTROLYTIC TREATMENT

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*Surface modification of titanium alloy VT 6 in aqueous solution containing 5 wt% of ammonium hydrate and 10 wt% of ammonium chloride in a temperature range of 650- 900 °C by plasma electrolytic treatment was carried out. Characterization of surface layers of the alloy after plasma electrolytic treatment was done by Fourier Transform Infrared spectroscopy (FTIR) and powder X-ray diffraction (XRD). The FTIR spectra were recorded on a spectrometer BrukerVertex80 at room temperature in the range of 7500-350  $\text{см}^{-1}$ . The spectra show the presence of rutile phase on the alloy surface after the plasma electrolytic treatment in the electrolyte solution of the indicated composition. The intensive bands at 654-643  $\text{см}^{-1}$ , the weak bands near 560  $\text{см}^{-1}$  and the bands at 425-416  $\text{см}^{-1}$  can be assigned to rutile. The bands at 466-462  $\text{см}^{-1}$  are related to Ti-O-Ti stretching vibrations. With increasing temperature the relative intensity of the bands assigned to rutile increase. The plasma electrolytic treatment leads to appearance of the bands testifying en-*

*richment of the alloy surface by nitrogen: the bands at 1634-1622  $\text{cm}^{-1}$  can be assigned to asymmetric bending of  $\text{NH}_4^+$ ; the bands about 1539  $\text{cm}^{-1}$  are related to N-H bending or symmetric bending of  $\text{NH}_4^+$ . The bands about 1428-1426  $\text{cm}^{-1}$  can be also assigned to  $\text{NH}_4^+$  bending vibrations. The plasma electrolytic treatment in the temperature range of 650-750 °C results in appearance of the bands at 1069-1064  $\text{cm}^{-1}$ . According to literature data, the bands can be assigned to vibrations of Ti-O-N. X-ray diffraction analysis allowed to ascertain crystal structure, phase identification of the titanium alloy VT 6 after its plasma electrolytic treatment. The measurements were performed using a Bruker D8 Advance diffractometer with Mo K $\alpha$  radiation ( $\lambda=0.07107$  nm). Analysis of XRD patterns showed that titanium oxide in the samples is present as hongquite phase ( $\gamma$ - monoclinic singony) and «magnesium» phase (hexagonal singony). Besides the peaks of TiO, the peaks which are characteristic for hamrabevit TiC in halite phase (cubic singony) and  $\text{Ti}_2\text{O}_3$  in corundum phase (trigonal singony) were observed.*

**Key words:** plasma electrolytic treatment, titanium alloy, surface modification, rutile phase

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## INTRODUCTION

Titanium alloys are very attractive materials for many industrial areas such as aeronautic engineering, automobile industry, shipbuilding, chemical, power generation, etc. They are widely used for manufacturing components of various technical equipment which work under fretting-initiated damage conditions. Hence, an improvement in the fretting damage resistance of titanium alloys is very important problem [1,2]. As fretting damage of titanium alloys is surface dependent, surface modification treatment is a promising approach for improving fretting fatigue resistance of the alloys. One of efficient methods of the improvement of the surface properties of titanium and titanium alloys is plasma electrolytic saturation (PES) of the alloy surface with interstitial elements. The PES including carburizing, nitriding or carbonitriding is rapid and inexpensive method which allows to increase significantly the wear and corrosion resistance, decrease the coefficient of friction of titanium and titanium alloys [3-5].

The aim of this work is to study anodic PES of titanium alloy VT 6 with interstitial elements in electrolytes containing ammonia and ammonium chloride. The characterization of surface layers of the alloy before and after plasma electrolytic treatment was done by Fourier Transform Infrared spectroscopy (FTIR) and powder X-ray diffraction (XRD). The effect of the processing temperature on chemical and phase composition of VT 6 alloy was evaluated.

## EXPERIMENTAL

Cylindrical samples ( $\varnothing 10 \times 15$  mm) of titanium alloy VT 6 ( $\text{Ti}_6\text{Al}_4\text{V}$  alloy) were nitrided in a cylindrical electrolyzer with an axially symmetric electrolyte flow supplied through a nozzle located at the bottom of the electrolyzer [6]. Prior to the surface treatment, each specimen was ground with SiC abrasive paper grit size P320 to  $R_a \sim 1.0 \mu\text{m}$  and ultrasonically cleaned with acetone. In the upper part of the electrolyzer, the electrolyte was overflowing into the sump and was further pumped through a heat exchanger at a rate of 3 L/min. The volume flow rate was measured with a RMF-0.16 GUZ flowmeter (accuracy of  $\pm 2.5\%$ ). The solution temperature was measured using thermocouple placed at the bottom of the chamber. The electrolyte temperature was maintained at  $20 \pm 1$  °C. The samples were connected as the positive output and the electrolyzer was connected as the negative output of the DC power supply.

After switching the voltage, the samples were immersed in the electrolyte at a depth equal to their height. The voltage was measured using an LM-1 voltmeter (accuracy  $\pm 0.5\%$ ). The current was probed with an MS8221 multimeter. The sample temperature was measured with another MS8221 multimeter and M89-K1 thermocouple accuracy to 2% over a temperature range of 400-1000 °C. Temperature measurements were performed using thermocouple fixed in a hole made in the samples at a distance of 2 mm from the heated surface. The treatment time was 5 min. The

treatment temperature varied from 650 to 900 °C. After PEN samples were quenched in the electrolyte (hardening). Aqueous solution of ammonia NH<sub>3</sub> (5 wt.%) and ammonium chloride NH<sub>4</sub>Cl (10 wt.%) was used as the working electrolyte.

The FTIR spectra were recorded on a spectrometer BrukerVertex80 at room temperature in the range 7500-350 cm<sup>-1</sup>. The scrapes of surface layers of the titanium alloy after plasma electrolytic treatment were carefully milled and mixed with dried KBr. The samples were examined as KBr disks

*X-ray diffraction (XRD) analysis*

The phase composition of the surface layers after PES treatment was performed using a Bruker D8 Advance diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.07107$  nm). Phase identification was done using JCPDS (Join Committee on Powder Diffraction Standards) database [7].

RESULTS AND DISCUSSION

The FTIR spectroscopic study of VT 6 alloy surface layers can give an information about its modification after plasma electrolytic treatment. Fig. 1 shows the FTIR spectra of VT 6 alloy surface layers after the alloy treatment in a solution of ammonia (5%) and ammonium chloride (10%) in a temperature range of 650-900 °C.

The anodic plasma electrolytic treatment in aqueous electrolytes led to oxidation of the samples' surface with formation of oxide layer. As can be seen from Fig. 1, titanium dioxide with rutile structure is formed on the titanium surface after the treatment at all the studied temperatures. The intensive peaks at 654-643 cm<sup>-1</sup>, the weak peaks about 560 cm<sup>-1</sup> and the peaks at 425-416 cm<sup>-1</sup> can be assigned to rutile [8]. The peaks at 466-462 cm<sup>-1</sup> are related to Ti-O-Ti stretching vibrations [9,10]. The surface layer of the sample becomes enriched with rutile phase with increasing temperature. Fig. 1 also demonstrates that the plasma electrolytic treatment led to appearance of the peaks testifying about enrichment of the alloy surface by nitrogen: the peaks at 1634-1622 cm<sup>-1</sup> can be assigned to asymmetric bending of NH<sub>4</sub><sup>+</sup>; the peaks about 1539 cm<sup>-1</sup> are related to N-H bending or symmetric bending of NH<sub>4</sub><sup>+</sup> [11]. The peaks about 1428-1426 cm<sup>-1</sup> can be also assigned to NH<sub>4</sub><sup>+</sup> bending vibrations [11]. At the treatment in a temperature range of 650-750 °C the peaks at 1069-1064 cm<sup>-1</sup> appear. According to literature data, the peaks can be assigned to vibrations of Ti-O-N [12]. At 900 °C the surface layer of VT 6 alloy consists of a rutile.

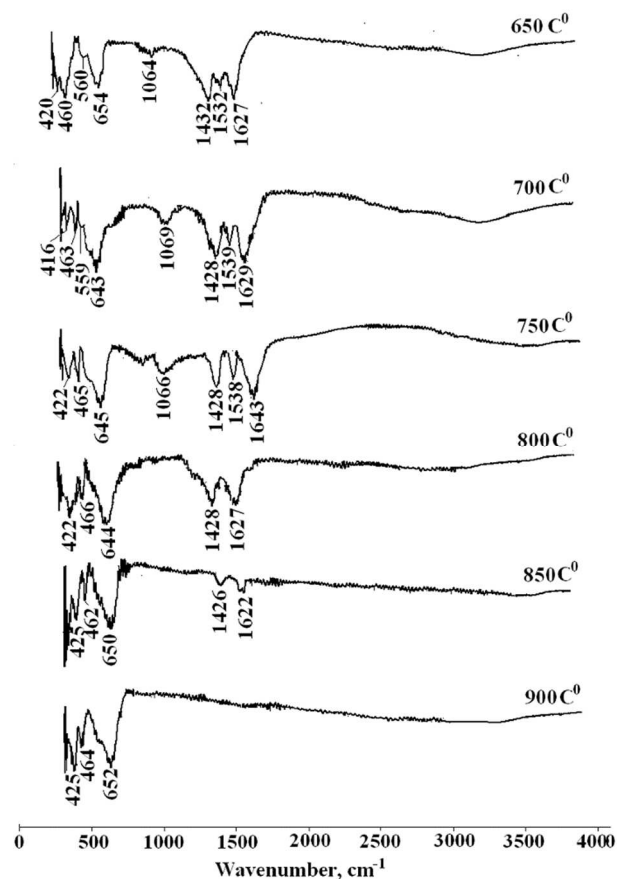


Fig. 1. FTIR spectra of surface layers of titanium alloy VT 6 after plasma treatment in an aqueous solution containing ammonia (5%) and ammonium chloride (10%) in a temperature range of 650- 900 °C

Рис. 1. ИК-Фурье спектры образцов титанового сплава VT 6 после электролитно-плазменной обработки в водном электролите, содержащем 5% аммиака и 10% хлорида аммония, при температурах 650-900 °C

Thus, the FTIR study showed that the plasma treatment of VT 6 alloy in an aqueous solution containing ammonia (5%) and ammonium chloride (10%) led to surface layer modification.

X-ray diffraction analysis allowed to ascertain crystal structure, phase identification of the titanium alloy VT 6 after its plasma electrolytic treatment. The XRD spectra of VT 6 sample before and after the plasma electrolytic treatment at different temperatures are presented in Fig. 2.

As can be seen from Fig. 2, the plasma electrolytic treatment led to structural alterations of the alloy surface layer. In the XRD pattern of the sample before the treatment (Fig. 2 a) the reflections assigned to Ti (“magnesium”, hexagonal system), TiO (“Pm-hong-quitte”, monoclinic-gamma system) and Ti<sub>2</sub>O<sub>3</sub> (“corundum”, trigonal system) are observed. The plasma electrolytic treatment at increasing temperature leads to oxidation of the alloy surface and formation of titanium oxides. Therefore, the reflections associated with

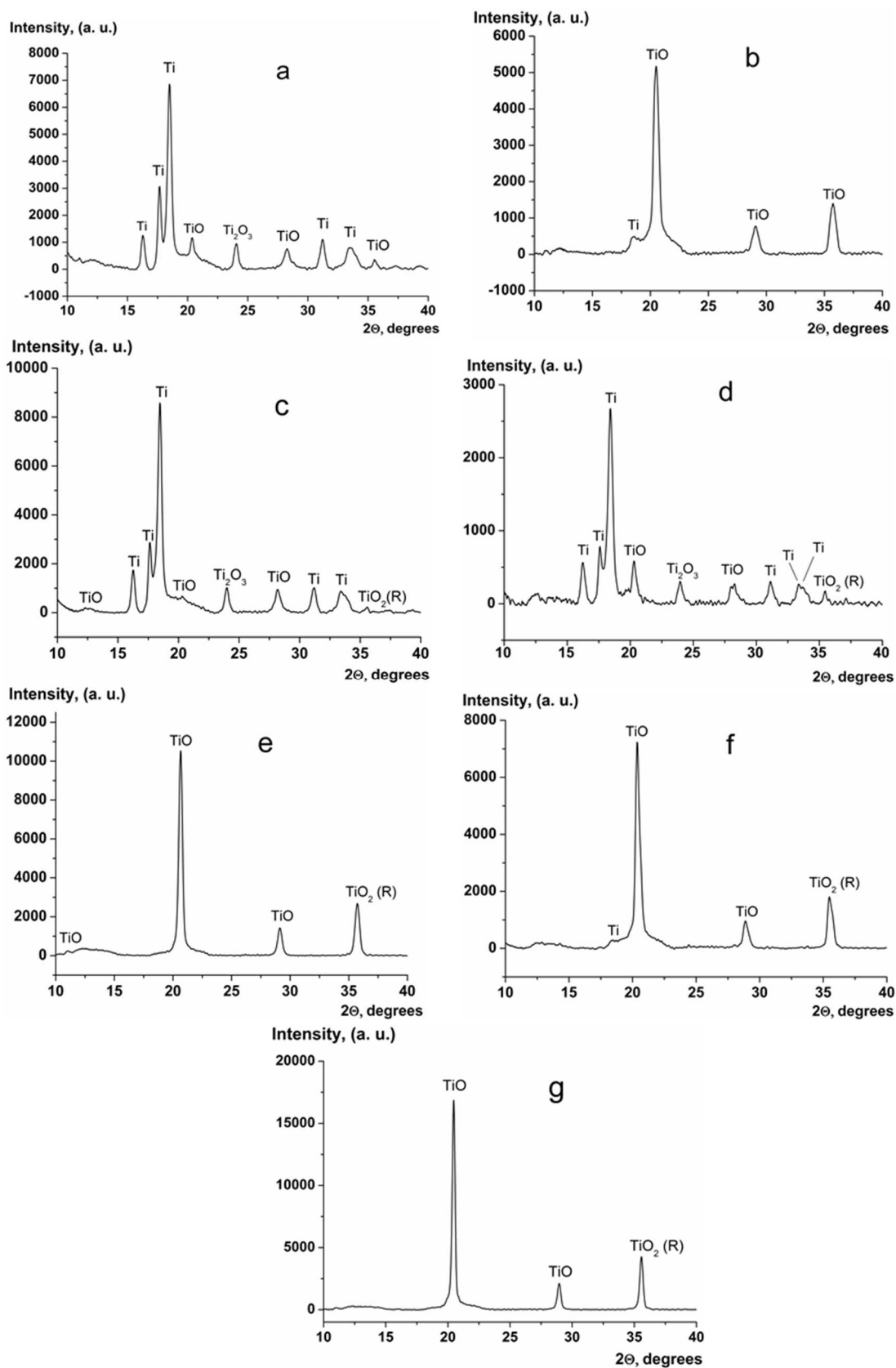


Fig. 2. XRD patterns of VT 6 alloy samples before (a) and after plasma treatment in aqueous solution of 5%  $NH_4OH$  and 10%  $NH_4Cl$  at different temperatures: (b) 650 °C; (c) 700 °C; (d) 750 °C; (e) 800 °C; (f) 850 °C; (g) 900 °C

Рис. 2. Рентгенограммы образцов титановых сплавов ВТ 6 после электролитно-плазменной обработки в водном электролите, содержащем 5% аммиака и 10% хлорида аммония, при различных температурах: (b) 650 °C; (c) 700 °C; (d) 750 °C; (e) 800 °C; (f) 850 °C; (g) 900 °C

titanium disappear, and the XRD patterns of VT 6 after the treatment at 800-900 °C demonstrate the reflections of titanium oxides only (Fig. 2 e-g). Fig. 2 also shows that the surface layer of the sample becomes enriched with rutile phase with increasing temperature. This fact is in agreement with the data obtained by FTIR spectroscopy. It should be noted that XRD method does not allow determination of nitrogen binding to the titanium alloy surface through non-covalent interactions.

#### CONCLUSION

The obtained results showed that the plasma electrolytic treatment of titanium alloy VT6 in the aqueous solution of ammonia and ammonium chloride promotes modification of surface layer of the alloy. The surface layer of the sample becomes enriched with nitrogen compounds and titanium oxides. The increasing temperature of the plasma treatment results in the formation of a surface layer saturated with rutile phase.

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