Dynamics of titanium surface characteristics after its treatment by runaway electron preionized diffuse discharge

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Abstract. Ageing changes of the elementary composition of titanium surface (VT-1) treated by runaway electron preionized diffuse discharge in nitrogen at atmospheric pressure have been studied. Dependence of the elementary composition of titanium surface layers on surface free energy has been shown.

1. Introduction
Runaway electron preionized diffuse discharge (REP DD) has some distinguished properties such as the possibilities to uniformly generate discharges in different gases and their mixtures in a wide range of pressures without contraction [1,2] as well as short duration and low discharge input power which allows to modify near-surface layers (several tens of nanometers [3]) of the materials placed into discharge plasma. The possibility of thin surface layer modification without damages [3,4] is very important for nanotechnology.

The main types of metal surface modification by REP DD are oxidizing and cleaning from the carbon contaminations [5,6]. Oxidizing of the metal near-surface layers forms the protective coating against the influence of the ambient environment. Due to that fact titanium is the corrosion resistive metal. It is also a known method of the titanium surface hardening due to increasing the thickness of the oxidized layer by titanium heating in oxygen atmosphere. The main disadvantage of this method is a difficulty to control growth of the oxidized layer because of the changes of the oxygen diffusion rate with the titanium heating. Moreover, increasing the oxidized layer leads to corrosive cracking under mechanical action, destruction of the surface layer, and propagation of the oxidizer into the metal depth with time, that is why the formation of the thin protective coating on the titanium surface is an important task.

In this paper we present the ageing results of the titanium surface, which was modified by cold plasma of REP DD. Four titanium alloy (VT-1) specimens were used to determine the datum point of the elementary composition changes with time. Before the diffuse discharge treatment all specimens had been polished until mirror surface (roughness Ra = 0.079 µm) and cleaned in ultrasonic bath with alcohol.

2. Experimental setup and methods of measurements
In the experiments, we used a voltage pulse generator GIN-100-1 (Antares Ltd., Russia) with voltage amplitude of 50 kV and pulse repetition frequency (PRF) up to 800 Hz. The REP DD was generated into interelectrode gap 1 (Figure 1a) by applying voltage pulse to a sharp-end cathode 2. A treated specimen was placed on a plane anode 3, the number of discharge shots was 80000. The distance...
between the cathode and anode was 12 mm. REP DD was initiated in nitrogen flow rate of 2 sl/min. Figure 2b shows the photograph of the REP DD at PRF of 40 Hz.

The changes in concentration of the main chemical elements in the surface layers were measured with Auger-electron spectrometer Shkhuna-2 (NPO “Electron”, Russia) on 2, 27 and 63 days after treatment. The specimens were stored in the ambient environment covered from dust.

Figure 1. Scheme of the discharge chamber. a: 1-interelectrode gap, 2 – sharp-end cathode, 3- plane anode; b: photograph of the REP DD

3. Results and discussion

Figure 2 shows the results of the elementary composition on the titanium surface specimens.

![Figure 2](image)

It is seen from the figure that the surface cleaning (figure 2b) after plasma treatment allows the oxygen from the ambient air intensively to diffuse into surface layers of the specimens even during the treatment process (figure 2c). As can be seen from figure 2c, in the treated specimen after 2 days, the oxygen concentration in the top surface layer at the depth up to 30 nm is 10 at. % higher than that in
the untreated specimen. The changes of the carbon concentration (figure 2b) show that top surface layers were cleaned from the carbon-contained contaminants during ultrasonic cleaning, but at a depth larger than 5 nm specimen was cleaned by REP DD.

During the next 27 days, oxygen concentration in the surface layers was practically unchanged due to all chemical bonds occupied by oxygen. Nevertheless, oxygen atoms continue to diffuse into the metal bulk, while carbon concentration remains unchanged.

However, the significant changes occurred after 63 days after treatment. Impurities concentration reached 90 at. % on the surface, and at the depth less than 10 nm, the main share of the impurities are carbon-contained compounds. At a depth larger than 10 nm, more than 60 at. % belongs to the oxygen. Carbon concentration deeper than 120 nm also increased and reached 15 at. % at the depth of 5 nm.

In addition, surface free energy (SFE) of the titanium alloy VT-1 before and after discharge treatment at different moments of time was evaluated through water contact angle measurements according to the Owens-Wendt method [7] from equation (1) and (2):

\[
\gamma_{L1} = 2(\gamma_{L1} - \gamma_{S})1/2 + 2(\gamma_{L2} - \gamma_{S})1/2 \tag{1}
\]

\[
\gamma_{L2} = 2(\gamma_{L2} - \gamma_{S})1/2 + 2(\gamma_{L1} - \gamma_{S})1/2 \tag{2}
\]

where \(\theta_{L1}\) and \(\theta_{L2}\) – water contact angles of control liquids, \(\gamma_{L1}\), \(\gamma_{L2}\) – dispersive SFE of control liquids, \(\gamma_{L1}\), \(\gamma_{L2}\) – polar SFE of control liquids, \(\gamma_1\), \(\gamma_2\) – overall SFE of control liquids, \(\gamma_{S}\) and \(\gamma_{S}\) – dispersive and polar SFE of titanium specimen. Deionized water and glycerine was used as the control liquids.

Figures 3 and 4 show the dependences of SFE, polar and dispersive components from the number of discharge pulses and ageing time.

![Figure 3. Titanium alloy VT-1 surface free energy and its components versus number of REP DD pulses.](image1)

![Figure 4. Titanium alloy VT-1 surface free energy and its components versus ageing at the ambient air.](image2)

Experiments of SFE measurements have shown activation of titanium surface under the REP DD treatment. As can be seen from figure 3, SFE increased 2 times after the treatment by 20000 discharge pulses. Herewith dispersive component of the SFE increased constantly while polar component after 20000 pulses decreased. As it is known, dispersive component includes van der Waals force and others unspecific interactions (for instance, Coulomb interaction); polar component includes strong interaction and hydrogen bonds. The increase of the dispersion component of SFE can be explained by increasing the oxygen adsorption into titanium bulk along with increasing the surface temperature under discharge action. Decreasing the hydrogen adsorption due to increasing surface temperature [8] and formation of titanium oxide in the top surface layers lead to a decrease in the polar component. However, titanium SFE decreased 1.5 times in 24 hours after plasma treatment (figure 4). It should be noted that the value of dispersive component drops is faster than that of the polar component. Oxide layer formed under the REP DD action does not allow oxygen to penetrate into the depth of titanium, while it cannot protect the titanium surface from the hydrogen penetration.

Formation on the surface of the big amount of carbon-contained compounds can be explained by interaction of CO and CO\(_2\) from the air atmosphere with water film formed in reaction of oxygen with
hydrogen on the titanium surface. At room temperature, CO$_2$ is adsorbed by water with formation of carboxylic acid H$_2$CO$_3$ [9], which is unstable in the water solutions, and dissociates to hydrocarbonate HCO$_3^-$ due to reverse hydrolysis. In the end, on the metal surface at room temperature in the ambient air, the formation of the complex equilibrium system could be possible:

$$\begin{align*}
\text{CO}_2 \uparrow & \rightleftharpoons \text{CO}_2 \cdot \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}_2\text{CO}_3^- \rightleftharpoons \text{CO}_3^{2-}
\end{align*}$$

Unfortunately, Auger-electron spectroscopy (AES) method does not detect hydrogen at a depth up to hundreds of nanometers, nevertheless, the presence of such reaction on the surface of the titanium alloy referenced in [10], which described well the obtained experimental results.

4. Conclusion
This, the formation of the protective oxide film with thickness of 20 nm under the action of REP DD was confirmed by the AES depth profiles. This film protects titanium from the oxygen adsorption into the bulk depth at least during the month after plasma treatment. Experimental results of surface free energy before and after REP DD action show physical-chemical processes of titanium ageing.

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