Mechanism of Ti99.2 titanium unconventional ion nitriding

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Various surface engineering methods are used to form the mechanical and exploitation properties of the metallic materials surface layer. Currently, the fastest developing surface engineering methods include: nitriding, vacuum and low-temperature plasma heat treatment and thermochemical treatment and plasma or laser methods [1].

The modification of titanium and titanium alloys surface layer by gas nitriding process considerably inhibits their passivation. Compact TiO_2 oxide layers form, which hamper the diffusion of the atoms into the substrate. Therefore, a costly operation of oxide film removal is used before gas nitriding of these materials to preliminarily activate the surface [2]. The ion nitriding process in compare to gas nitriding allows to form superior quality layers [3].

Moreover ion nitriding enables the oxide films to be removed already at the initial stage of the process, while eliminating the need for preliminary surface activation [4]. Surface activation by cathode sputtering involves the bombardment of the surface with low-energy ions. However energy level of these ions must be higher than the threshold energy value of surface atom sputtering [5]. The present study concerns the effect of an unconventional Grade 2 titanium nitriding method using an active screen in different glow discharge areas. The analysis of the investigation results has enabled to study the development of a model for the ion nitriding process.

Titanium, Grade 2, was ion nitrided in a temperature range of $803 \div 863$ K for a duration from t = 18 ks to t = 61,2 ks, in an atmosphere of 25 % H_2 + 75 % N_2, at pressure of 150 Pa. Four variants of positioning the nitrided elements in the ion nitriding device chamber were assumed, either:

- directly on the cathode,
- in the plasma potential – area isolated from the anode and the cathode,
- on the cathode using an active screen,
- in the plasma potential using an active screen.

The active screens used had the purpose of intensify the surface phenomena due to the local temperature increase and the increase in the energy of active plasma components.

The XRD analysis was performed on a DRON-2 X-ray diffractometer using filtered cobalt anode tube radiation.The element distribution analysis was made on a GDS GD PROFILER HR glow-discharge optical emission spectrometer. The observation of the obtained structures was performed on specimens, either etched or not etched, using a Carl-Zeiss Jena Axiovert 25 metallographic microscope.

The analysis of the investigation results has shown that the previously established and adopted conventional ion nitriding process models might not be appropriate for active screen nitriding. The earliest model developed by Kölbel [7] assumes that the transfer of nitrogen requires iron atoms to be sprayed from the cathode surface and then passed to the plasma. In that case, the iron atoms react with the nitrogen to form FeN nitrides that are sprayed onto the substrate surface. The FeN nitrides are metastable and transform to $Fe_{2 \div 3}N$ and Fe_4N nitrides on the steel substrate surface. At the same time nitrogen atoms diffuse into the substrate material.

Study has found that the active screen changes to a considerable extent the course of phenomena under glow discharge conditions [9]. The Kölbel model does not fully allow for the characteristics of the physical phenomena occurring in this process. It only considers the sputtering and redeposition phenomena. Therefore, a different model of nitriding under an active screen has been proposed, especially for the initial process stage, which takes into

account the following phenomena: cathode sputtering, physical desorption (releasing atoms, ions or molecules), diffusion and spraying. In addition, study [10] has assumed that the cathode sputtering and then re-spraying play the most important role in nitriding using the active screen. The remaining phenomena need also to be taken into account.

The analysis of literature data shows that the conventional glow discharge nitriding process is adequately characterized in many studies. However, this is only true for individual phenomena and their effect on the process kinetics, but there is no comprehensive analysis of the process.

The results of our investigation into active screen glow discharge nitriding of titanium and its alloys enable us to claim that:

- the use of the active screen intensifies the nitriding process and increases its temperature;
- the active screen changes primarily the voltage characteristics, both quantitative and qualitative ones (Figure 1). Additional voltage pulses form under the active screen. The values of those voltages are greater by several times than the voltage values occurring during cathode nitriding. The time of these voltage pulses causes the ions and other active plasma components to gain a high velocity. This velocity corresponds to a high kinetic energy of the order of several hundred electron volts. The active plasma components are implanted into the substrate material. They form a disequilibrium nitrogen-supersaturated zone in the surface layer. The high nitrogen concentration facilitates the nitrogen diffusion into the substrate;
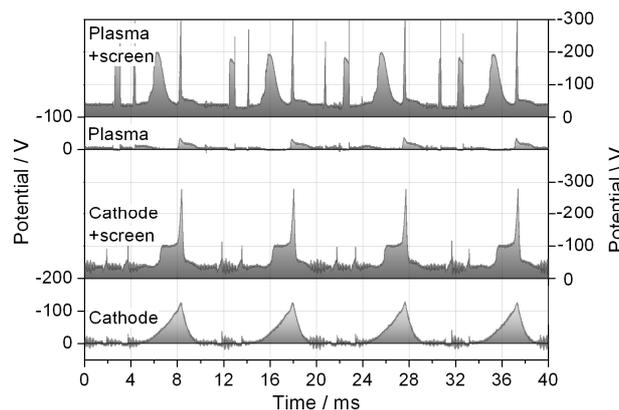
Figure 1. Oscilloscopic potential curves for different glow discharge regions

- increasing the temperature of titanium and titanium-alloy substrates in the active screen cathode nitriding process causes the nitrided layer to form both on the surface in the plasma environment and on the surface adjacent to the cathode. This indicates the presence of molecular nitrogen, despite the low-temperature nature of this nitriding process;
- the ion bombardment and cathode sputtering phenomena have a great effect on the nitriding process kinetics, the phase composition and the morphology of the microstructure phase constituents of the layers forming; hence, in the nitriding process as effected either on the cathode and using the active screen, nitride zones form in the surface layer, which have a high nitrogen concentration compared to the plasma potential nitriding process resulting in the formation of a layer composed solely of a diffusion layer;
- the process of nitriding in the nitrogen and hydrogen mixture atmosphere proceeds involving NH radicals capable of bonding hydrogen to form active NH_2 radicals. Reducing the nitrogen concentration in the mixture reduces the quantity of NH radicals. Therefore, with a low nitrogen content, no cathode nitriding effect is found, but the cathode sputtering intensity increases.

The presented investigation results provide a basis for developing a new model for glow discharge nitriding of Grade 2 titanium, depending on the position in the direct current glow discharge region, while allowing for the active screen effect (Figure 2). It has been found that the TiN nitride, formed at the initial stage of the Grade 2 titanium nitriding process under glow discharge conditions, undergoes transformation to the Ti_2N nitride and a free nitrogen atom diffusing into the substrate material. At the further stage of the process, the nitride decomposes following the reaction:

$$2TiN \rightarrow Ti_2N + N\downarrow \qquad (1)$$
$$Ti_2N \rightarrow 2Ti + N\downarrow \qquad (2)$$
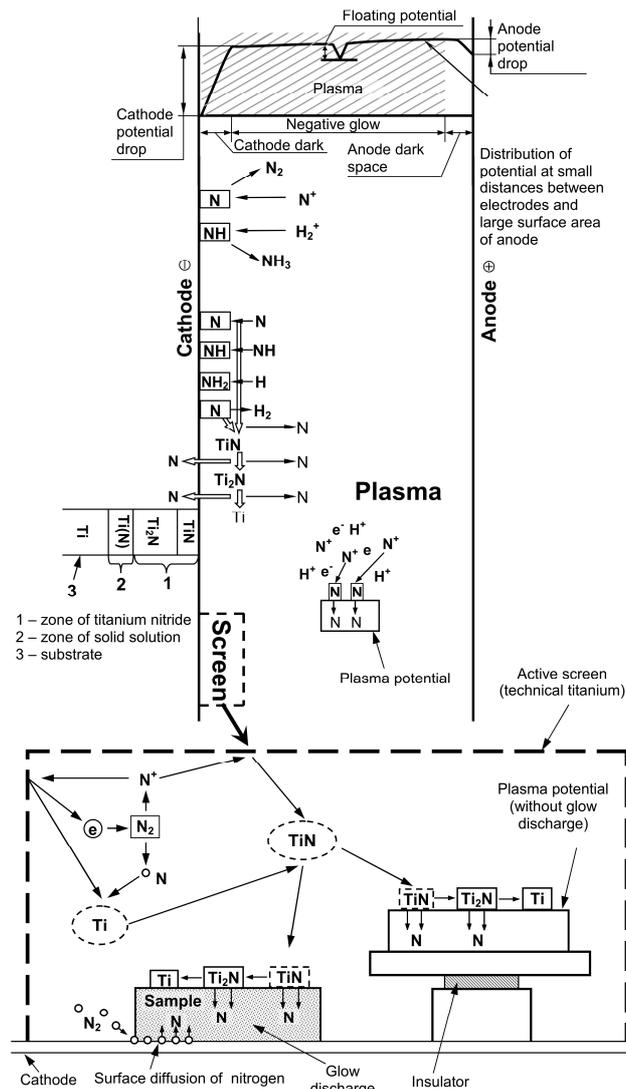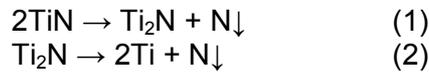
Figure 2. The model of Grade 2 technical titanium ion nitriding in different glow discharge regions

The nitrided layer on the substrate of titanium and its alloys, in the following glow discharge plasma regions: I – the cathode, II – the plasma potential + the active screen, III – the cathode + the active screen, has a zonal structure (Figure 4a). The following zones are distinguished: the TiN nitride zone; the Ti_2N nitride zone; and the deepest positioned zone of grains of the solid solution of nitrogen in α titanium, $Ti\alpha(N)$.

In contrast, in the case of the substrate isolated from the cathode and the anode – nitriding in the plasma potential – no presence of nitrides was found. In that case, grains of the solid solution of nitrogen in titanium, $Ti\alpha(N)$, occur in the microstructure. The reason for this is the low energy of ions for the given process conditions. Moreover, these ions are

characterized by a negative polarization relative to the plasma – approx. 20 V (Figure 1 – plasma). Hence the small effect of the sputtering phenomenon [3]. The low ion energy is also insufficient for driving metal atoms out from the base, which would then react with nitrogen atoms to form nitrides. For these conditions, only the nitrogen ion desorption phenomenon occurs, whereby the nitrogen ions diffuse to the iron crystal lattice to form grains of the solid solution of nitrogen in titanium, Tiα(N).

Noteworthy is the fact that the process of nitriding on the cathode with the use of the active screen, even for such a low temperature as the one used in the experiment, results in the formation of a nitrided layer on the surface screened from the glow discharge on the surface adjacent to the cathode - the bottom of the element being nitrided (Figure 4b). Literature data suggests that it is possible to produce a nitrided layer on such a surface at a temperature much higher than the temperature used in the experiment under consideration. In that case, titanium nitrides form as a result of reaction between the base titanium and the molecular nitrogen [11].

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