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A MODEL FOR UNCONVENTIONAL GLOW DISCHARGE NITRIDING OF GRADE 2 TITANIUM

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Preliminary Note – Prethodno priopćenje

An analysis of the influence of different parameters of the ion nitriding process conducted in a $H_2 + N_2$ atmosphere on the properties of the surface layer of Grade 2 titanium was carried out in the study. This allowed a model for ion nitriding of technical titanium to be developed. The equipment used in the experimental work included a JON-600 current glow-discharge furnace. It was found that the process of cathode nitriding with the use of the active screen led to an increase in the concentration of nitrogen in the surface layer and in the relative volume of nitrides. A factor which determines the qualitative and quantitative characteristics of phenomena that occur in the presence of the active screen is the high concentration and high energy level of nitrogen ions which interact with base material during nitriding.

Key words: technical titanium, glow discharge nitriding, active screen

INTRODUCTION

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

The modification of the surface layer of titanium and its alloys in the gas nitriding process considerably inhibits their tendency to passivation. Compact TiO_2 oxide layers form, which hamper the diffusion of the atoms of other elements into the layer. Therefore, a costly operation of oxide film removal is used in the process of gas nitriding of these materials to preliminarily activate the surface [2]. The glow-discharge nitriding process allows layers to be produced, which are of superior quality compared to gas nitriding [3]. Moreover, glow discharge nitriding enables the nitrogen diffusion hampering 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. The 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 regions. The analysis of the investigation results has enabled the development of a model for the process of glow discharge nitriding of the metallic material under study.

TEST MATERIAL AND THE SCOPE OF TESTS CARRIED OUT

Titanium, Grade 2, was subjected to glow discharge nitriding processes in a temperature range of 803 ÷ 863 K for a duration from t = 18 ks to t = 61,2 ks, in a reactive atmosphere composed of 25 % H_2 + 75 % N_2, at an atmosphere pressure of 150 Pa.

Four variants of positioning the elements to be nitrided in the glow-discharge chamber were assumed, either:

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

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

The X-ray phase 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 crosscut metallographic specimens, either etched or not etched, using a Carl-Zeiss Jena Axiovert 25 metallographic microscope.

The obtained examination results are more extensively discussed in study [6]. The analysis of these results made it possible to propose a model for glow discharge nitriding of Grade 2 titanium in different direct current glow-discharge regions with reference to the iron glow discharge nitriding model.

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INVESTIGATION RESULTS AND THEIR DISCUSSION

The analysis of the investigation results has shown that the previously established and adopted conventional glow discharge nitriding process models might not be appropriate for nitriding with the use of the active screen. 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 are transformed to $Fe_{2\div3}N$ and then Fe_4N nitrides on the steel substrate surface. At the same time, forming free nitrogen atoms diffuse into the substrate material. Figure 1 illustrates the model of iron nitriding in direct current glow-discharge plasma in gas under a reduced pressure according to Keller [8] (Figure 1a) and Michalski [3] (Figure 1b).

Study [9] has found that the active screen changes to a considerable extent the course of phenomena occurring under glow discharge conditions. 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.

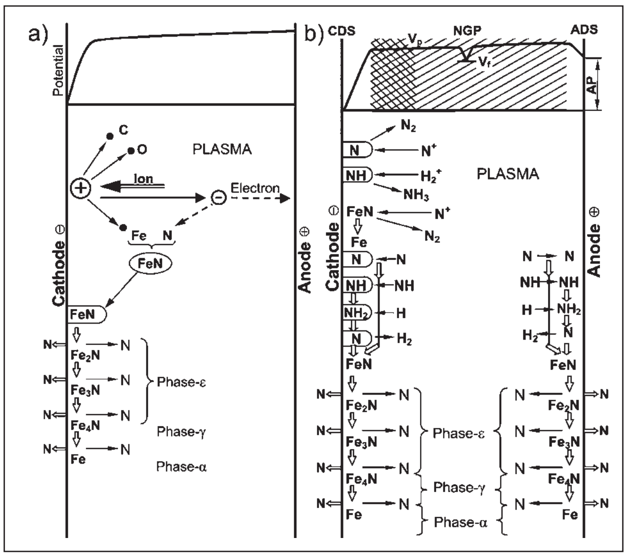

Figure 1 The model of iron nitriding in direct current glow-discharge plasma in gas under a reduced pressure: a) by Keller [1]; b) by Michalski [2]

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 2). 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;
- 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 mix-

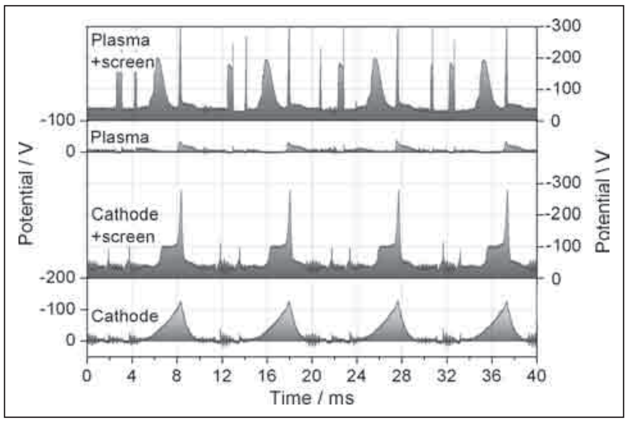

Figure 2 Oscilloscopic potential curves as recorded for different glow discharge regions

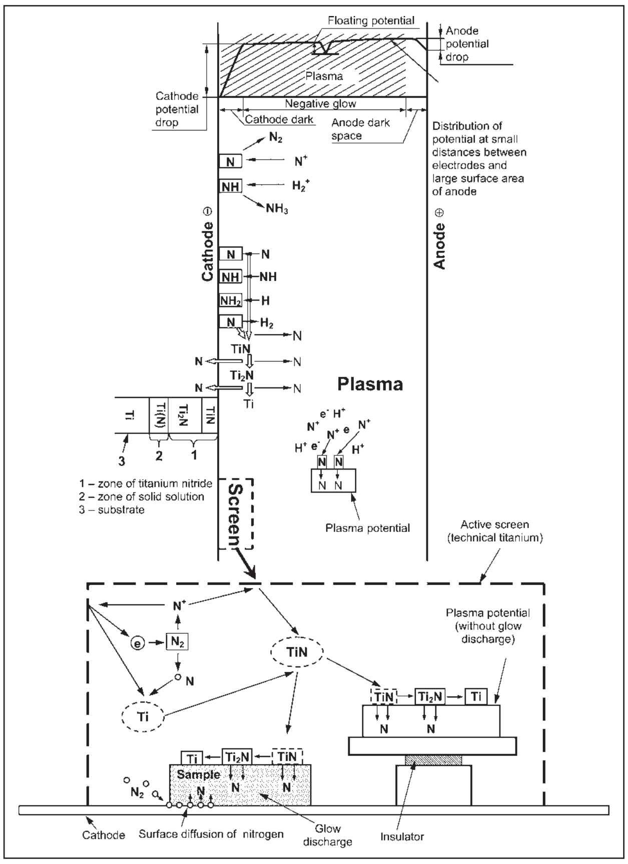

Figure 3 The model of Grade 2 technical titanium ion nitriding in different glow discharge regions

ture 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 3).

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:

$$2TiN \rightarrow Ti_2N + N\downarrow \qquad (1)$$

$$Ti_2N \rightarrow 2Ti + N\downarrow \qquad (2)$$

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, Tiα(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, Tiα(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 2 – 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).

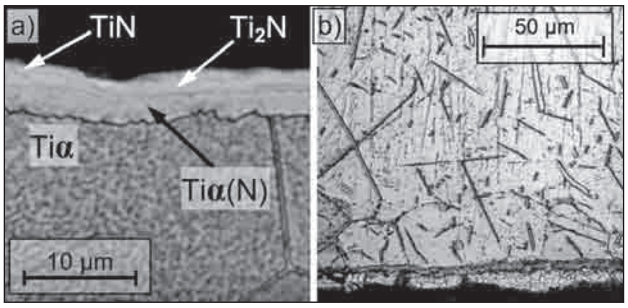

Figure 4 Structure of the surface layer after glow discharge nitriding with the use of the active screen. The sample: a) top; b) bottom

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].

The zonal structure, as mentioned above, was confirmed by the performed X-ray phase analysis examination (Figure 5).

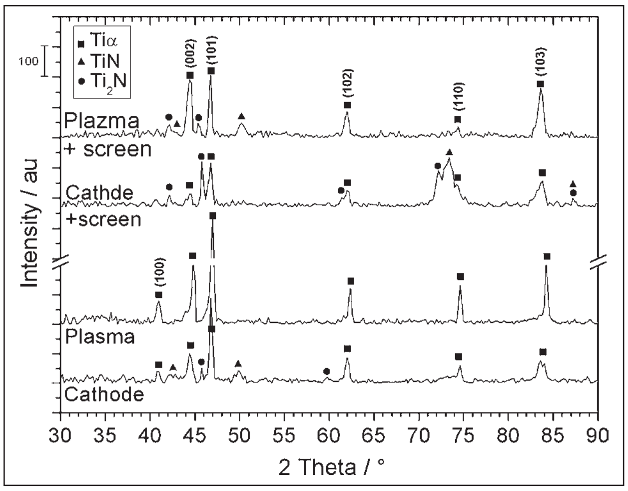

Figure 5 X-ray diffractograms of the surface layer after different variants of glow discharge nitriding

SUMMARY

- Achieving a higher ion energy due to the introduction of the active screen is a decisive factor intensifying the glow discharge plasma interaction in Grade 2 titanium nitriding processes.
- Introducing the active screen results in changes to the quantitative and qualitative voltage characteristics. The voltage value increases thus increasing the density and velocity of ions that gain a kinetic energy of approx. 300 eV. The high-energy ions are implanted into the substrate material to form a strongly disequilibrium nitrogen-supersaturated zone in the surface layer, which in turn favours the diffusion of nitrogen into the titanium being nitrided.
- The use of the active screen leads to an increase in plasma temperature, which simultaneously results in a reduction in the plasma density and an increase in the mean free path of electrons, thus increasing the energy of ions bombarding the surface being nitrided.

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Note: The responsible translator for English language is Czesław Grochowina, Częstochowa, Poland