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THE ROLE OF COMPLEMENTARY POTENTIAL IN PLASMA NITRIDING PROCESSES OF TECHNICAL TITANIUM

This article deals with the testing of surface layers produced on technical titanium Ti99.2 under glow discharge conditions. In order to determine the effect of process temperature on the produced surface layers, nitriding processes were carried out at 700°C and 800°C and for 3 and 5 hours. The research results on evaluating the properties of the obtained surface layers and the characterization of their morphology were presented. The impact of the adopted nitriding process variant on the quality of the obtained layers was evaluated. It was demonstrated that the use of the supplementary potential during the ion nitriding process reduces the unwanted edge effect, which results in a significant increase in the homogeneity of the nitrided layers and improves the functional properties of the technical titanium Ti99.2.

Keywords: plasma nitriding; active screen; titanium; ion nitriding

1. Introduction

Due to the specific physical and mechanical properties (high specific strength, high corrosion resistance, etc.) of pure titanium and titanium alloys, they are widely used in the manufacture of critical mechanical engineering parts, aerospace applications, many corrosive environments, sport equipment and medicine [1-3]. Titanium is neutral to the human body and is frequently used in the medical field to replace heart valves, joints and bones. The biocompatibility and strength of titanium make it an ideal material for dental posts and other oral prosthetics [3-5]. However, titanium alloys exhibit poor tribological properties including high and unstable friction coefficient and adhesive wear [6,7]. A series of surface modification processes, including physical vapor deposition, laser cladding, thermal oxidation and thermal spraying, chemical vapor deposition, plasma and laser nitriding as well as ion implantation have been proven to improve the tribological properties of titanium alloy [6]. Nitriding is a surface hardening process in which nitrogen atoms are utilized for surface modification and has been practiced for wear improvement in titanium alloys for many years. In conventional nitriding techniques such as salt bath treatments or gas nitriding, nitrogen atoms are provided by liquid, gas, or solid media. The modification of titanium and titanium alloys surface layer by gas nitriding process considerably inhibits their passivation. Ion nitriding enables the oxide films to be removed already at the initial stage of the process, while eliminating the need for preliminary surface with low-energy ions [8]. In plasma nitriding, also known as ion nitriding and glow discharge nitriding, active nitrogen is provided by an ionized nitrogen-containing atmosphere [9]. Plasma nitriding improves the tribological properties of titanium alloys through the formation of a thin surface layer mainly consisting of TiN and Ti_2N, that is, the compound layer [10]. The nitrided microstructure also consists of a region of nitrogen-stabilized α-titanium, that is, the α-case, and a nitrogen diffusion zone (typically 15-25 µm deep) underneath the compound layer. The plasma-nitrided microstructure is strongly correlated with the composition of the titanium substrate and the nitriding process parameters such as duration, temperature, pressure, and composition of the nitriding medium, among which temperature has the most significant influence [6]. A method of modifying glow processing can be to use an active screen and to apply additional polarization of the nitrided elements, using the so-called complementary potential [11-13]. This method involves the use of two independent power sources. By means of the first (AC or DC power supply) an abnormal glow discharge is generated on the active screen, which is the source of thermal radiation and inter-electron plasma, while the second power supply (AC or DC, bias voltages) is used to generate an arcing on the workpieces. The main role of using an additional power supply is to give extra energy to the molecules in the inter-electrode space [14]. Active screen plasma nitriding can achieve a similar hardening effect to that of cathodic plasma nitriding, but without the common problems as arcing surface damage, hollow-cathode effect or edging effect [15]. Previous literature data did not clearly identify the impact of the applied additional complementary potential on the formation of nitride layers on the sample surfaces during the nitriding process while simultaneously using the active screen.

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2. Experimental procedure

Ion nitriding processes were carried out on the technical titanium Ti99.2 according to EN10204-3.1 (Grade 2 by ASTM) with the chemical composition presented in Table 1.

Chemical composition of titanium Ti99.2

Element	O	C	N	H	Fe	Σ others	Ti
wt. %	0,12	0,02	0,004	0,007	0,14	<0,1	rest
Chemical composition according to EN10204-3.1.							

The sample surfaces intended to be nitrided were mechanically activated through polishing with the use of abrasive papers, and then polished with colloidal suspension of silicon oxide with a grain size of 0.04 μm. The samples were degreased with acetone immediately before loading them into the furnace chamber.

Ion nitriding processes were carried out in a JON-600 glow discharge treatment device with cooled anode, powered by a switching-mode power supply – Dora Electric Power System. For nitriding processes with complementary potential, an additional multi-range stabilized IZS-5/71 power supply was used. In order to intensify the process of ion nitriding, an active screen was placed on the cathode. The active screen has a cylindrical shape with 140 mm diameter and 100 mm height, made of 0.7 mm thick titanium Grade 2 perforated sheet which had equally distributed round holes of 5 mm diameter. The sample distance from the upper surface of the active screen was 50 mm.

The parameters of ion nitriding are presented in the Table 2.

Graphic representation of the process variants and sample arrangement in the furnace chamber are presented in Figure 1.

X-ray analyses were carried out using a Seifert 3003TT X-ray diffractometer. In the experiment, radiation coming from a cobalt anode X-ray tube was used; it emits radiation of wavelength $\lambda_{Co} = 0.1789$ nm. During the analyses the voltage powering

Parameters of ion nitriding titanium Ti99.2 processes

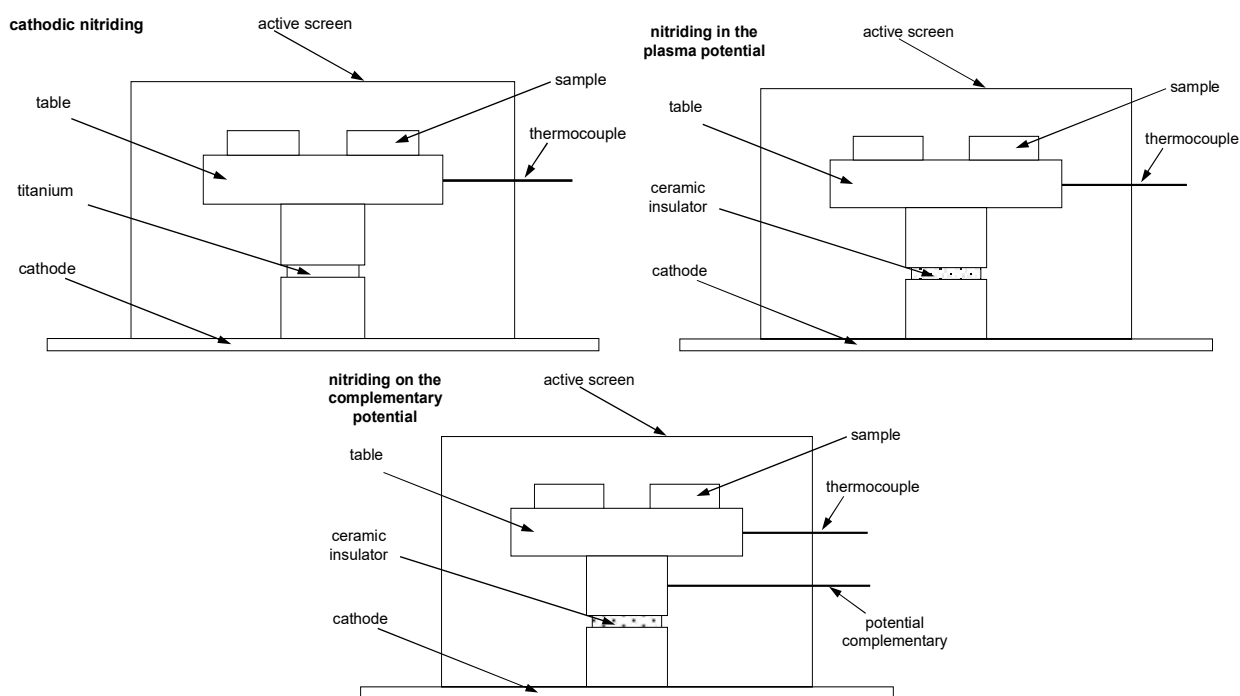| Variant of the process	Temperature, °C	Time, h	Value of complementary potential, V	Pressure, Pa	Composition of the atmosphere, %
Cathodic nitriding	700	3	0	150	N$_2$ 95 H$_2$ 5
		5			
	800	3			
		5			
Nitriding in the plasma potential	700	3	0		
		5			
	800	3			
		5			
Nitriding on the complementary potential	700	3	100		
		5			
	800	3			
		5			

Fig. 1. Schematic arrangement of samples in working chamber of furnace during nitridation

the tube was 30 kV. However, the current in the tube network was 40 mA. The XRD analyses, which are used for general identification of the phases occurring in nitrided surface layers, were carried out in the range of diffraction angles $2\Theta = 30 \div 95°$. The obtained diffraction patterns were approximated by the pseudo-Voigt function in order to determine the location of the diffraction reflections with the help of Match 3 software. Element distribution profile analysis was carried out on a GDS GD PROFILER HR glow-discharge optical emission spectrometer with excitation voltage $U = 700\ V = const$ and current $I = 20\ mA = const$. The anode diameter was 4 mm.

3. Results

On the basis of macroscopic observations of the nitrided samples – Fig. 2, it was found that the temperature of the process determines the color of the nitrided layer, whereas the occurrence of the edge effect and its size is determined by the complementary potential value. The samples nitrided at 700°C were characterized by a reddish brown color, but those nitrided at 800°C were yellow (yellowish brown).

According to literature [16,17], the type of color produced indicates that the nitride phase (TiN, Ti_2N) is present in the superficial zone. The variation in color of the surface of the nitrided samples may depend, among others, on the damage, impurities, the presence of oxygen, carbon and nitrite mixtures used.

Microscopic studies as well as studies of the element distribution profile in the surface layer (Fig. 3) show that during the nitriding process of technical ion titanium, a nitrided diffusion layer is made from the area of TiN nitrides, under which a Ti_2N zone phase occurs, at a lower nitrogen concentration, solid solution nitrogen grains occur in titanium α-$Ti\alpha$ (N). The $Ti\alpha$ phase occurs beyond the diffusion range of nitrogen into the nitrided
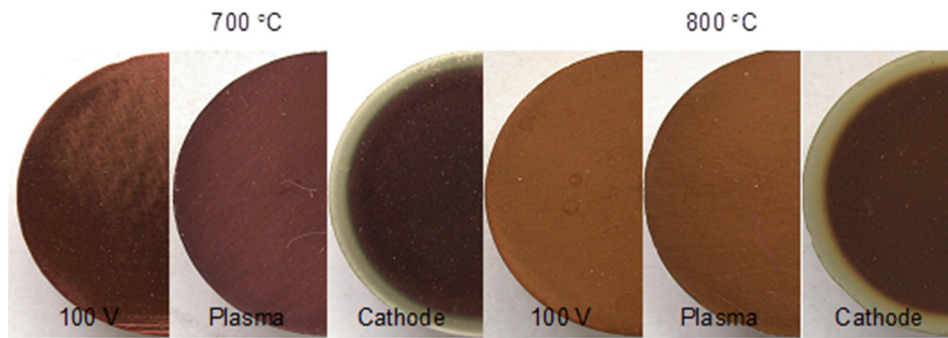

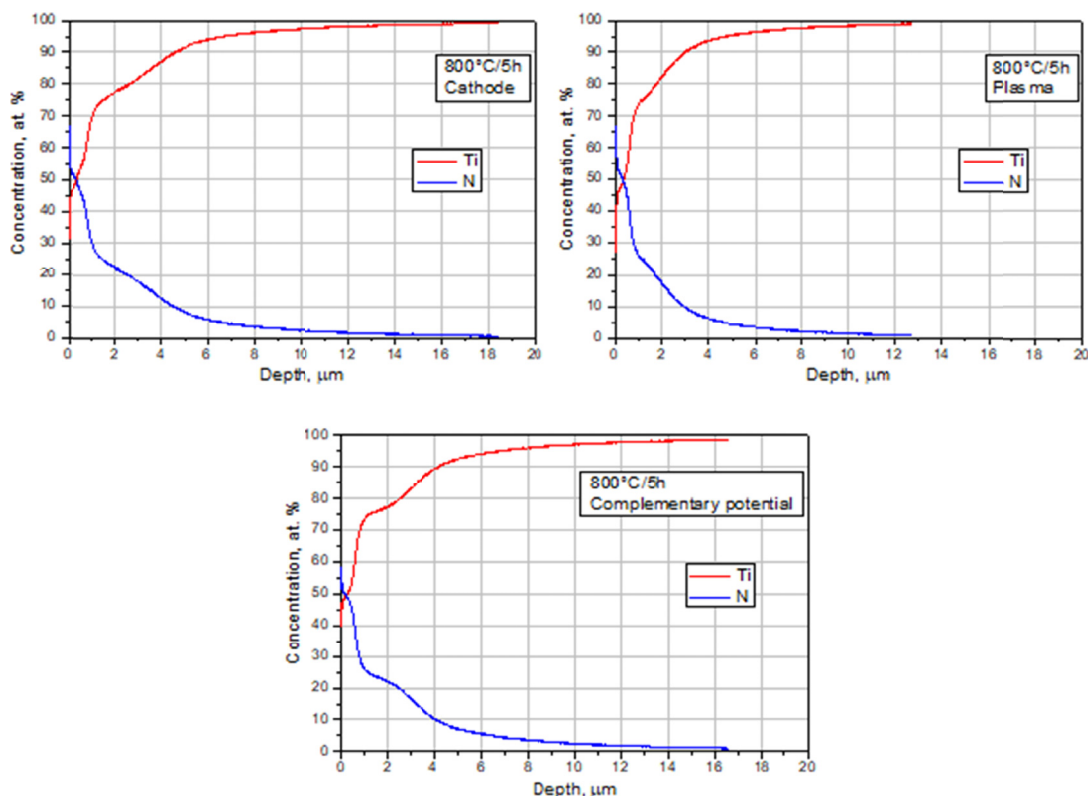
Fig. 2. Macrophotography of nitrided samples – time 5h

Fig. 3. Nitrogen and titanium concentration distribution profiles (Glow Discharge Optical Emission Spektroskopy) for nitrided samples
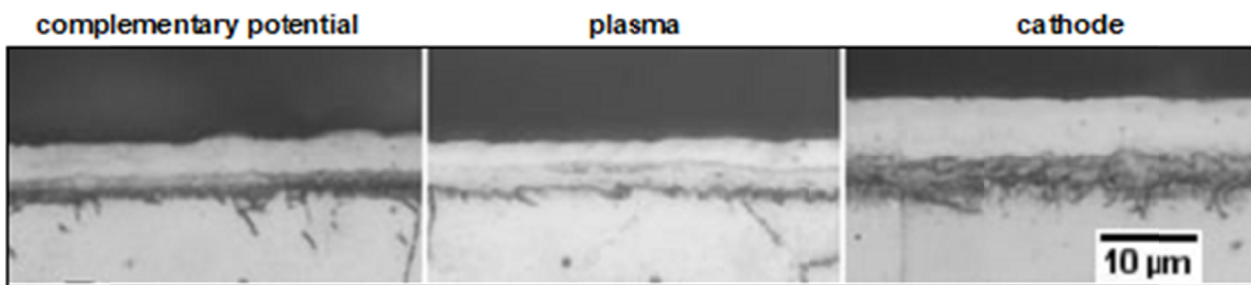
Fig. 4. Microstructure of the surface layer after plasma nitriding; LM (Light Microscopy)

titanium substrate – Fig. 4. Ossowski and others [18] showed that the use of the active screen method allows for the formation of diffusion layers of a uniform thickness and of a pre-determined surface topography.

Based on the GDOES (Glow Discharge Optical Emission Spektroskopy) results, the depth of nitrogen diffusion for the samples after the individual nitriding processes was determined (Fig. 5).
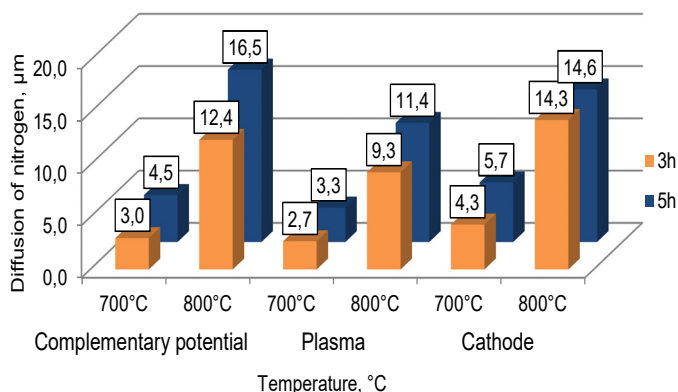

Fig. 5. Depth of nitrogen diffusion in nitrided layers depending on the parameters used and process variant; GDOES method

Applying the complementary potential at 800°C for 5 h resulted in a diffusion layer 45% thicker compared to the layer formed at plasma potential. An analogous increase in thickness was obtained for 3h processes where the increase in the diffusion depth of nitrogen was 33%. For the processes carried out at 700°C, the use of complementary potential increased the diffusion depth by 36% compared to plasma nitriding (for 5 h) and 11% for 3 h.

Analysis of the results showed that the main parameter determining the depth of diffusion and concentration of nitrogen in the surface layer is the process temperature. The samples nitrided at 800°C had a 3÷4 times greater depth of nitrogen diffusion in the surface area compared to the samples nitrided at 700°C.

Microscopic analysis of the obtained surface layers showed an increase in the thickness of nitrided layers in nitriding processes at complementary potential compared to processes at plasma potential. However, it should be emphasized that the highest thicknesses were obtained in the cathode nitriding processes. These layers were close to 2÷3 times thicker than those obtained at complementary potential and at plasma potential.

Nitrogen diffusion depth studies and analysis of its concentration in the surface layer conducted by GDOES confirm the microscopic observations – Figs. 3,5.

According to the author of [19], the factor determining the depth increase of the nitrided layer and the change in kinetics of the nitriding process is the ion energy value acting on the nitrided substrate. In the case of cathode nitriding, the surface of the substrate is bombarded with high energy ions whose value depends on the polarization voltage of the cathode and to a lesser extent, the pressure. On the other hand, in the case of the nitriding process at plasma potential, the ions have much lower energy resulting from the smaller size of the floating potential. The use of complementary potential increases the polarity of the workpiece relative to nitriding at plasma potential. This results in intensification of phenomena occurring on the surface of the workpiece, and an increase in the concentration of nitrogen in the surface layer.

Phase analysis carried out on the samples nitrided at 700°C (Fig. 6) showed an increase in reflectance intensity from the Ti_2N phase on the nitrided samples at complementary potential compared to the nitrided samples at plasma and cathode potential, while the most intense reflectance from the TiN phase was observed on the nitrided sample at the plasma potential.

Analysis of the X-ray diffractogram of the samples nitrided at 800°C (Fig. 7) showed similar reflex intensities from the Ti(α) phase. For the nitrided samples at complementary potential, stronger reflections from the Ti_2N phase were observed. The nitrided sample at plasma potential was characterized by stronger TiN phase reflexes. The occurrence of the strongest reflections from the Ti_2N phase may indicate a higher thickness of this zone in the composition of the surface layer.

The use of an active screen with complementary potential caused a qualitative and quantitative change in the physical phenomena occurring in glow discharge conditions. This resulted in an increase in the depth of the nitrided layer and a change in the kinetics of the nitriding process. The basic role in the observed phenomena is played by high energy ions – the influence of the active screen shows the effect of their interaction with the nitrided part. The substrate surface, under cathode nitriding conditions, is bombarded with ions of high energy values depending on the cathode drop value (approx. 100 eV). On the other hand, for the other nitriding process conditions (plasma potential) – the ionic effects have a negative polarity with respect to the plasma of about 20 eV and do not cause cathode sputtering. Introducing the
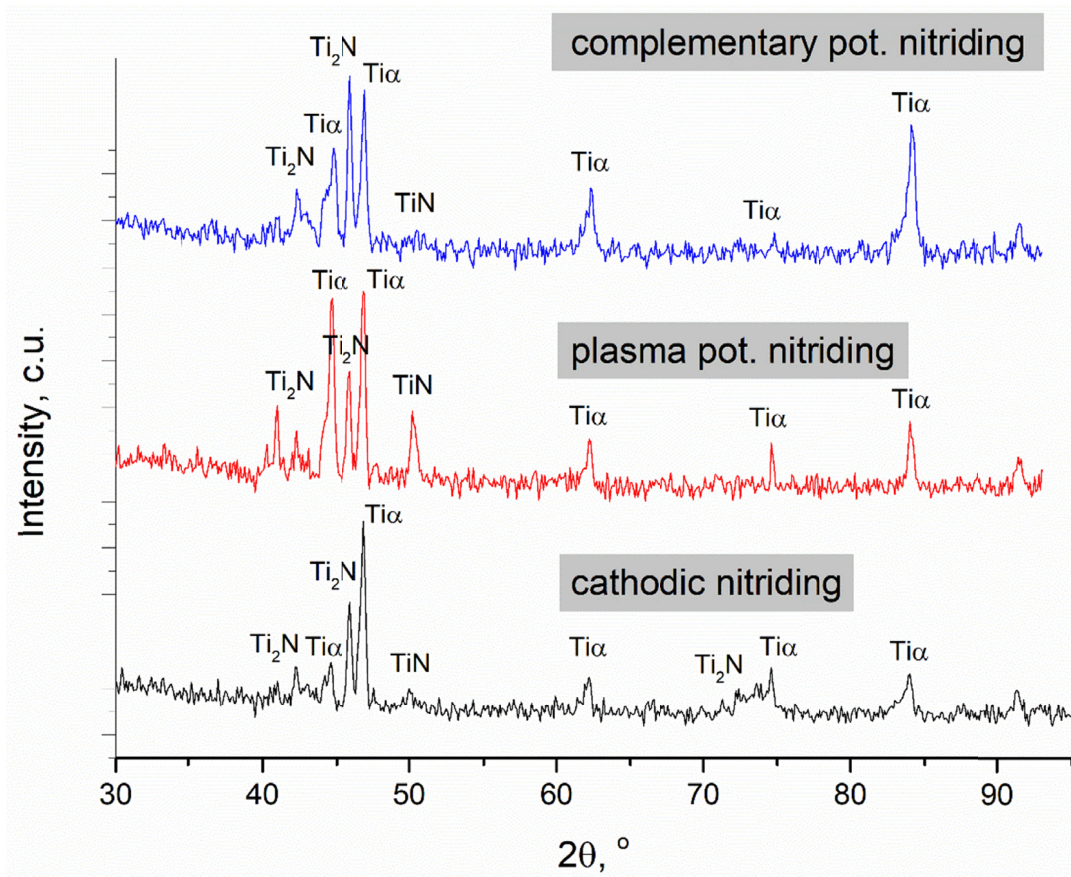
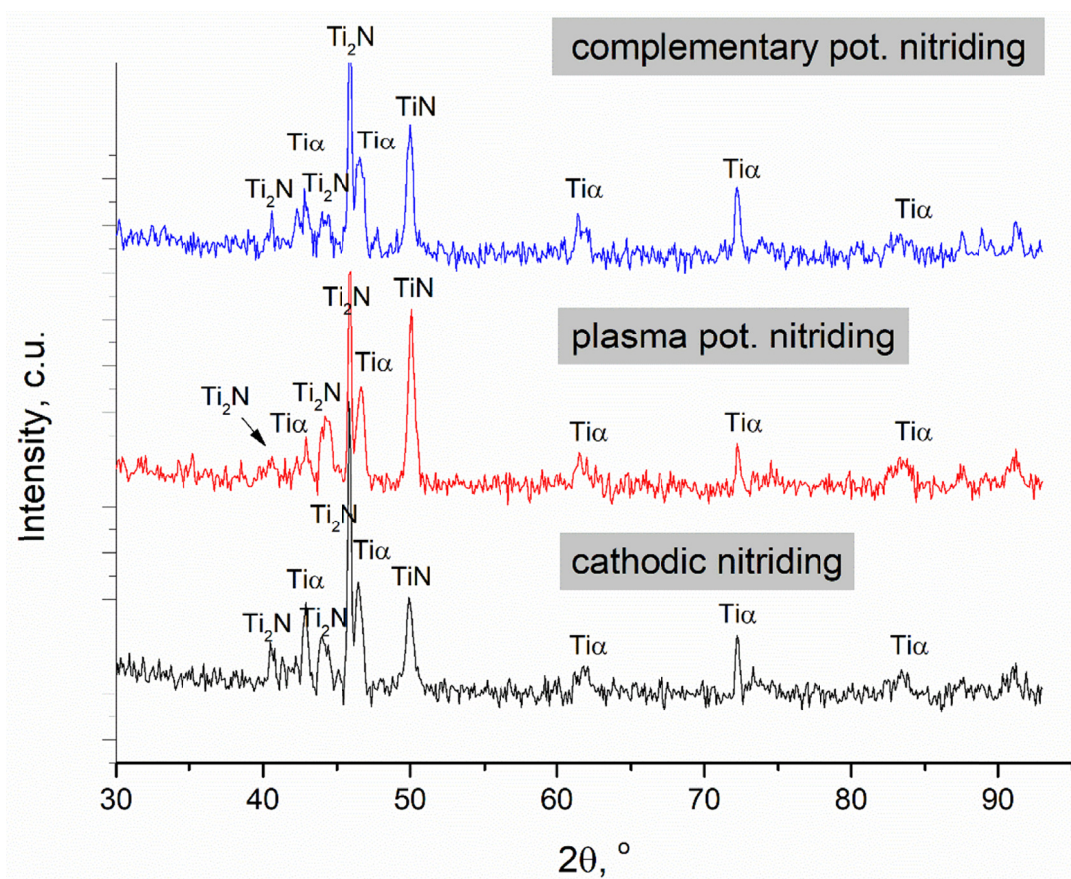Fig. 6. Diffraction patterns of layer nitride using active screen at 700°C for 5 h obtained by XRD method

Fig. 7. Diffraction patterns of layer nitrided using active screen at 800°C for 5 h obtained by XRD method

active screen causes additional strong voltage pulses to appear in the cathode drop zone, interacting with the nitrogen ions present in this area. The duration of the voltage pulses is conducive to the ions attaining high velocity values corresponding to the kinetic energy of about 300 eV. Nitrogen ions are implanted in the substrate material forming in the surface layer a non-equilibrium zone supersaturated with nitrogen. The resulting high concentration gradient favors the diffusion of nitrogen into the substrate material. That is why in the initial stage diffusion takes place right across the grains and then along the grain boundaries. The occurence of different diffusion routes results in the formation of a nitrided layer with high homogeneity of phase composition of the microstructure.

5. Conclusions

It was found that the samples nitrided at plasma potential and at complementary potential were uniform in color, without a visible edge effect (Fig. 2). The visible edge effect was always present for the cathode nitride variant. It should be noted that the applying the complementary potential in the glow nitriding process with the active screen allows to reduce the adverse phenomena occurring in the nitrided sample zone.

It should be noted that the kinetic of the titanium glow nitriding process using the active screen and the complementary potential is influenced by the energy of the nitrogen ions interacting with the nitrided titanium substrate. The use of complementary potential increases the polarity of the workpiece, relative to nitriding at the plasma potential. The result is an intensification of phenomena occurring on the surface of the workpiece, and an increase in the concentration of nitrogen in the surface layer.

Based on the research results presented in this paper, it can be concluded that the complementary potential has a significant impact on the morphology, structure and properties of nitrided layers produced on titanium. The beneficial effect of the complementary potential favors the formation of nitrided layers of greater thickness than in the case of nitriding at the plasma potential. In addition, limiting the occurrence of edge effect occurring in the case of nitriding processes at the cathode.

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