Surface Morphology and Mechanical Strength of AISI M2 Tool Steel Treated in Abnormal Glow Region of Plasma

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Plasma ion nitriding is a flexible and multi-functional casehardening technique used in the given study for surface modifications of AISI M2 tool steel (0.9% C, 4.2% Cr, 5.0% Mo, 6.0% W, and 2.0% V). By varying the plasma treatment time from 1 to 4 hour and the filling gas pressure from 1to 4 mbar, the surface nitriding was carried out in the abnormal glow region of a pulsed DC discharge. Pre-plasma treatment heating of the samples was performed by a heating unit; the substrate temperature was raised to 500°C, with the ramping rate of 15°C. The resultant microscopic changes in the surface properties of the plasma treated tool steel were studied with different surface characterization techniques such as X-ray Diffraction, Scanning Electron Microscopy and Vickers's micro-hardness testing. These investigations confirmed the formation of a compound layer on the plasma exposed surface. It was observed that the layer thickness initially increases and then decreases with nitriding time. Similar results were obtained for increasing filling gas pressure. The X-ray Diffraction results showed a down-shift in the original diffraction peaks, which confirms the nitrogen diffusion into the exposed surface and a compound layer formation. A significant improvement in the surface hardness was also vivid, which might be due to the nitrogen diffusion and the formation of a compound layer on the target surface.

Keywords: DC glow discharges, ion implantation, abnormal glow region, tool steel, surface hardness.

УДК 621.039

INTRODUCTION

Nitriding is the surface hardening process that introduces nitrogen into the surface of a metal at high temperatures (400°C to 600°C). It is actually a thermo-chemical method of diffusing nitrogen into the surface of the material to be treated. This diffusion process is based upon the solubility of nitrogen into a metal matrix. In this process the material to be nitrided is heated to a sufficiently high temperature, which makes the diffusion of nitrogen from few tens to hundreds of nm deep from the surface. Among all of the plasma-assisted surface engineering technologies that are well proven scientifically and technically for designing the surface/subsurface of various engineering components, the plasma nitriding ranks among the first few to be accepted and used extensively in industry [1]. Plasma ion nitriding is especially suitable in applications where treatment temperatures should be well below the tempering temperature. In such cases, the impinging plasma particles can destroy the passive layer of highly alloyed steel. This results in unchanged core properties after the treatment. During nitriding the molecular nitrogen is converted into the nascent nitrogen and impinged onto the surface of the material under process. A vacuum is generated within the plasma chamber and an intensive electric field is applied to generate the plasma and active species that are accelerated by the electric field, this is how these active species penetrate into the work piece. The surface becomes harder and cleaner by plasma ion nitriding [2].

The tribo-mechanical characteristics of a plasma treated material strongly correlate to the nature and size of the precipitates formed during nitriding as well as to their evolution when they are exposed to stresses and/or heating. The top surface compound layer of a nitrided tool steel consists mainly of ε-carbonitrides and γ´-Fe_4N nitride. Below this compound layer, there is a so-called diffusion zone 'α´' where the steel matrix is supersaturated by the in-diffusion nitrogen. As a whole, the thicknesses of the compound plus the diffusion zone correlate very well with the cross-sectional micro-hardness profile [3]. So, when the stress is applied to the nitride material surface, the atoms are not displaced from their positions. It results in an increased surface hardness, corrosion resistance and wear resistance of the treated material [4].

In this study, the plasma ion nitriding of AISI M2 tool steel was carried out between two conductive electrodes enclosed by a vacuum tight chamber. The DC discharge plasma was energized in an abnormal

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glow region using a high voltage power source. When the source voltage reaches a certain breakdown value, a glow discharge is established. Initially at a low input power, the discharge covers only the area near the rim of the cathode. As the power is raised, the current increases and the discharge starts covering the whole surface of the cathode. When the current of the discharge passes the point of the complete cathode coverage, the voltage begins to rise once again. The corresponding region of the I–V characteristic curve is called the abnormal glow discharge region as identified in Fig. 1. The abnormal glow region is considered as most suitable region for materials processing applications. A further increase in the power beyond the abnormal glow will cause the heating of the cathode rather than an increase in current, which should be avoided. At a certain stage, such heating causes thermionic emissions, which results in a voltage decrease, and the discharge can enter into the arc region [4, 5].

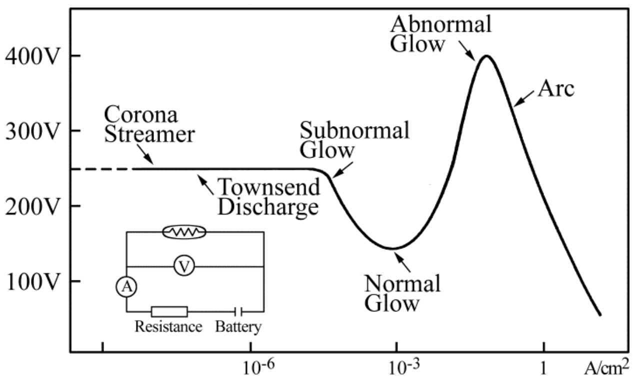


Fig. 1. General behavior of I–V characteristics of DC glow discharge.

MATERIAL AND METHODS

In this study, the plasma ion nitriding of tool steel was carried out in a vacuum tight chamber furnished with two electrodes and an active screen cage surrounding the cathode. The screen cage was used to provide uniform nitride layers and avoid extra heating of the substrate. The plasma chamber was also equipped with four multi-role quartz windows of 9.8 cm diameter each. The pulse DC discharge was operated at higher input powers commonly used in plasma technological applications. The schematic of a similar experimental setup used in the given research is shown in Fig. 2. The tool steel slices with the surface area of 5×5 mm^2 were generated and polished with different grit sized silicon carbide papers followed by the Metkon GRIPO 2V polishing machine. The finalized samples were also mirror-polished with 100 and 10 μm Al_2O_3 powder and cleaned with menthol in an ultrasonic bath for 15 minutes before being placed inside the processing chamber. A pulse DC voltage with the pulse width of 7 ms was obtained from a 50 Hz AC voltage source through a conventional step-up transformer and diode chain. That voltage was applied between the anode and the cathode of the discharge system through a 1500 Ω inductive load [6]. The cathode of the system was grounded; it also served as a substrate holder. For substrate heating purposes, a heater was placed outside the processing chamber and thermally coupled with the cathode. The chilled water was also circulated across the plasma chamber through an auxiliary copper pipe so as to avoid insulation damages. The samples were placed on a substrate holder inside the processing chamber and their pre-plasma treatment cleaning was performed in an argon-rich environment. This helped in reducing the oxide formation during the nitriding process. After the pre-treatment cleaning of the samples, the nitrogen and hydrogen gases were introduced into the processing chamber at the 50:50 mixture ratio via mass flow meters. The gas mixture pressure inside the chamber varied from 1 to 4 mbar and was monitored by a capsule type pressure gauge. Finally, the samples were treated for different but fixed time periods, chamber pressures, input powers, but constant temperature. The resultant microscopic changes in the surface properties of the plasma treated AISI M2 tool steel were studies with different surface characterization techniques including the X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Vickers's micro-hardness testing [7].

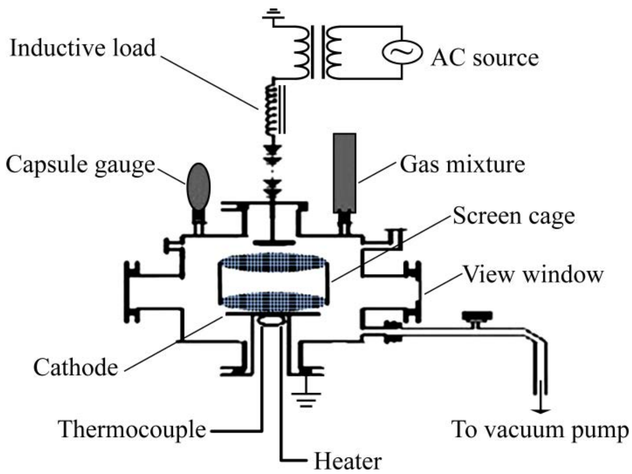


Fig. 2. Schematic of DC discharge plasma setup.

RESULTS AND DISCUSSION

The improvements in nitriding process are possible by controlling different parameters like temperature, pressure, gas composition, and current; therefore, efforts are underway for achieving better nitriding process conditions. In these studies, the nitriding of the AISI M2 steel was performed by using a new technique called active screen plasma nitriding (ASPN) or cage (TC) plasma nitriding. The samples were placed on a ceramic plate fitted over a cathode.

This ceramic was enclosed by a metal screen or cage. As the ceramic is an insulator, so the samples inside the ceramic were kept at a floating potential while the cage screen was at the cathode potential due to a direct contact with the cathode. Therefore, the term ‘active screen’ was employed. The active screen establishes an environment for efficient nitriding without surface damages. The treated samples were analyzed by the XRD, which gives information about the microstructures formed during nitriding process, about elemental composition of the treated samples and the changes produced in the crystallographic structure of nitrided samples. Surface morphology was determined by SEM. The Vickers micro hardness tester was used to evaluate the surface hardness as a function of the indentation depth (μm).

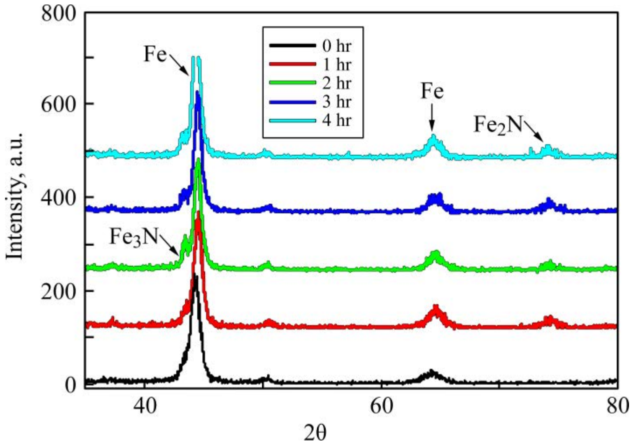


Fig. 3. XRD patterns of untreated and treated AISI M2 tool steel samples at 500°C.

In plasma processing, the average electron energy drives the kinetic processes involved in population and depopulation of the excited states of plasma species. At near atmospheric pressures, the highly energetic electrons are the main source of excitation and ionization of the corresponding nitrogen and hydrogen [8–10]. The dissociation of nitrogen gas molecules results in production of nitrogen ions and radicals. In the plasma ion nitriding, these ions are accelerated under intense electric fields, and finally bombarded onto the sample surface placed on a high temperature substrate. In this study, the tool steel samples were nitrided at the substrate temperature of 500°C. The XRD patterns of the treated and untreated tool steel samples, as a function of the treatment time, are shown in Fig. 3. The Philips X’ Pert PRO MRD machine with CuK-α (λ = 1.54 A°) radiation was operated at the voltage of 40 kV and the current of 40 mA; the respective microscopic changes produced in the crystallographic structures were analyzed. The results clearly showed the presence of Fe (110) in the untreated tool steel. In addition, after treatment with the N_2–H_2 DC discharge plasma, results confirmed also the presence of nitrogen traces in the form of different nitrides [8–10].

Plasma ion nitriding depends upon the ionization rates of the working gases, the pressure inside the chamber, and the electric field strength, but shows less dependence on the substrate temperature. Therefore, several temperature ranges are possible for plasma ion nitriding starting from 250–600°C. For example, it was noticed that at normal temperatures (like 420°C), the stainless steel can be nitrided free from chromium nitride precipitates, which results in improved corrosion resistance properties [8]. Novak and co-authors treated tool steel through nitriding and observed wear and corrosion resistance with a niobium alloy coating [9]. Their purpose was to analyze the wear and corrosion resistance of the tool steel. Best results for wear resistance were observed at the temperature of 500°C and treatment time of 3 hours. They demonstrated that nitriding led to an increase in the free corrosion potential. In the same year, Bacci and co-authors described the glow discharge nitriding of AISI 316 austenitic stainless steel and studied the influence of the treatment pressure [10]. They investigated the influence of the process parameters for the low temperature DC glow discharge. On AISI 316 austenitic stainless steel, the glow discharge nitriding treatment was performed at 703K for 5 hours, at the working pressure ranging from 1.5 to 20 Pa. The morphology and microstructure of both untreated and treated samples were studied by microscopy techniques, energy dispersive X-ray spectroscopy (EDX), XRD, using also micro hardness measurements and corrosion resistance tests. Those researchers observed a hard layer, so-called ‘S’ phase, with an improved corrosion resistance. Sharma et al. [11] presented pulsed nitriding of austenitic stainless steel in N_2 and N_2–H_2 mixture powered by a high frequency DC pulsed discharge. They noticed that hardness increases 3–4-fold in the presence of the N_2–H_2 mixture. In their studies, the uniformity in the surface hardness was obtained at the sample temperature of 830°C. Basu et al. [12] described the corrosion resistance improvement of a high carbon low alloy steel by plasma nitriding. They carried out experiments under specific conditions, using a DC glow discharge and considering the voltage in the range of 540–710 V, current in the range of 3–6 A, temperature in the range of 450–550°C, and the treatment time in the range of 1–5 hours. The treated samples were analyzed by different analytical methods, and it was proved that the corrosion resistance improves significantly by confirming the formation of a nitride layer.

In the present case, for untreated samples, the most concentrated diffraction peak was observed at 2θ = 44.475° and d = 2.03 A°, according to (110) preferred orientation of the iron α phase. From the processed samples, the most intense peak of iron nitride was obtained at 2θ = 43.429 and *d* = 2.08201 A°, corresponding to (111) plane. Another peak for Fe_2N was observed at 2θ = 74.272 and *d* = 1.27550 A°, corresponding to (141) plane. Before plasma treatment, only iron, chromium, and carbon elements were present in the samples. The data demonstrates the penetration of nitrogen into the treated samples, when nitrides with iron are formed as well as their corresponding phases α (Fe_2N, Fe_3N). It is evident that the ion nitriding is a very effective technique in forming a compact and dense plasma layer on the sample surface without any distortion materials [13, 14].

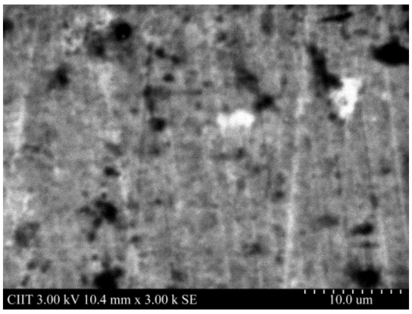
The enlarge images of the treated and untreated samples were also obtained using the SEM technique as shown in Fig. 4, where highly energetic electrons were bombarded over the sample surface. The energy of the electrons accelerated through a high potential was kept constant at 40 keV. These electrons strike the sample surface and push off after taking the information on the surface. These scattered electrons were detected by a sensor, and the surface images were taken as a function of electronic currents which are afterwards amplified and projected over a computer monitor. After careful inspection of the SEM images, a clear difference was revealed between the treated and untreated surfaces [15]. The untreated tool steel surface looked light gray, whilst smooth and bright surfaces with black gray color were evident in case of treated samples. It was also seen that there is an oxide layer on the surface of untreated sample, which had been removed from the surface through argon gas sputtering. The sputtering is another important process in the glow discharge, which occurs at sufficiently high voltages. When the ions and fast atoms from the plasma are bombarded on the substrate surface, they release not only the secondary electrons, but also atoms of the exposed surface. The images of treated samples for different treatment times (1–4 hours) depicted the existence of nitrogen on the surface, and it was also noticed that the nitrided layer grows better with increasing the treatment time up to 2 hours, thereafter, the surface is becoming brittle.

Hardness is the property of a material which gives us information about the resistance of the material against deformation. To measure the hardness of the sample surface, an indent was made on the sample surface with the help of a diamond tip using different load values. The dimensions of the indent were measured using a microscope that gives the hardness value of the surface. At least, five measurements were made for each load to get the average of micro hardness values. Wilson Wolpert 401 MVA Vickers micro-hardness tester equipped with a 136° diamond indenter was used to measure the surface hardness of both untreated and treated samples as a function of an externally applied load in the range of 10–300 g. The hardness test data were recorded in HV units and later on converted into GPa for better handling of the results, as shown in Fig. 5.

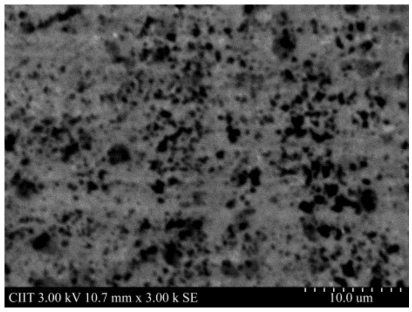
Judging by the results of the micro hardness test, the surface hardness of the treated samples increased approximately by 30%. The maximum hardness of the samples was achieved for the 2 hour treatment time. After 2 hour treatment at 550°C, the brittleness of samples began to increase, which predicts a decrease in hardness at higher treatment times. The hardness profiles also predicted highest values near the surface depth of < 200 nm for the substrate temperature of 500°C. The overall hardness varied from 8.13 GPa to 10.36 GPa, with respect to the treatment time, and from 5.33 GPa to 10.36 GPa, with respect to the applied load. The hardness was decreasing with the load and acquired the value near that of the untreated substrate. The rapid decrease in hardness with the indentation depth showed a rapid decrease in nitrogen concentration as we move from the surface to the core. These results indicate a shallow modified diffusion layer. An increase in the hardness at higher temperatures and low load treatment confirms the presence of iron-nitrides and readjustment of the lattice structures. The presence of iron-nitrides was also verified in the XRD pattern given in Fig. 3.

At a high substrate temperature, the reduction in hardness with time might be due to the coarsening of carbides, growth of ferrite grains and recovery of dislocation structure [10]. In fact, the precipitates having certain size and number are most important and effective in hindering the movement of dislocations and in inducing the maximum strength and hardness. At higher nitriding temperatures, precipitates result, having large particle sizes and being more prone to coarsening. It leads to a lower precipitate density and consequently a lower hardness. Softening of the substrate at a higher nitriding temperature might be attributed to coarsening of carbides, dislocation structure recovery and growth of ferrite grains [16, 17].

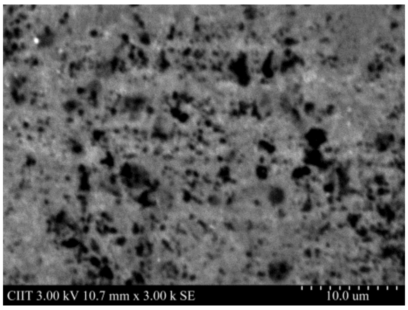
In addition, the effect of the filling gas pressure on the nitriding process was also considered in those studies. A substantial increase in hardness was noticed with an increase in the filling gas pressure up to 3 mbar. The nitrogen content was found increasing with an initial increase in pressure, thereafter, a decreasing trend was evident. After passing 3 mbar limit, the penetration of nitrogen into the treated samples was insignificant. At low pressure of < 2 mbar, the glow became too much foggy and nitriding was ineffective. Similar results were obtained for 4 mbar pressure. It is found that the degree of ionization in the process also strongly



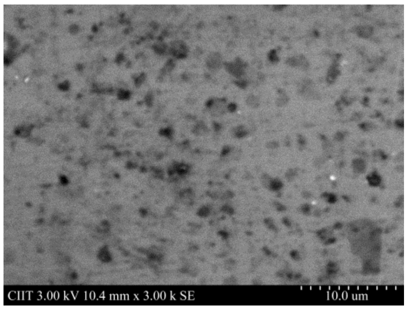
Untreated



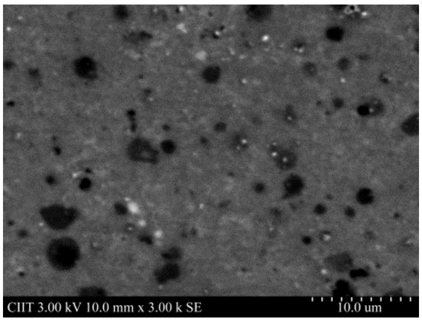
After 1 hour



After 2 hours



After 3 hours



After 4 hours

Fig. 4. SEM images of untreated and treated samples for different exposure times.

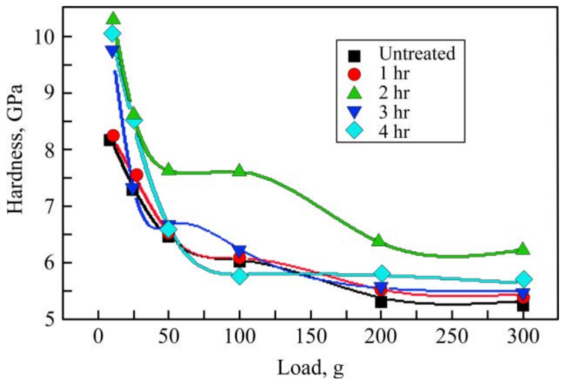


Fig. 5a. Comparison of hardness of untreated and treated tool steel at fixed substrate temperature of 500°C.

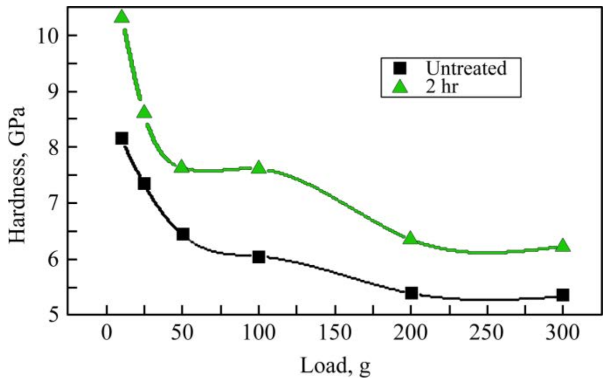


Fig. 5b. Comparison of hardness of untreated and 2-hour treated samples at fixed substrate temperature of 500°C.

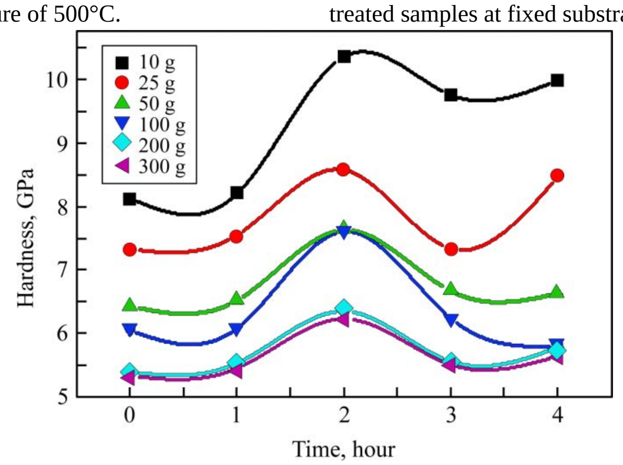


Fig. 5c. Vickers hardness profiles as a function of treatment time at fixed substrate temperature of 500°C.

depends on the filling gas pressure. Therefore, for self-sustained and chemically reactive plasma, the formation of electron-ion pairs must be sufficient to compensate the loss of charged particles due to pressure variations. The ionization process becomes ineffective at low pressures because the electron-neutral collisions are too small; whereas at high pressures the electrons are not able to reach the energies which are high enough for ionization. Hence, pressure is one of the principal areas of control. By keeping a suitable pressure and controlling voltage, the required nitriding results can be achieved [5].

CONCLUSIONS

- In this study, plasma ion nitriding of AISI M2 tool steel was performed in pulsing DC discharge plasma at the fixed substrate temperature of 500°C, the treatment time of 0–4 hours, and the filling gas pressure of 1–4 mbar.
- The XRD patterns of the treated samples confirmed the formation of iron nitrides. The amplitude of the iron nitride peak was found to be maximum for the two-hour treatment period, which gives the optimum hardness. The nitrogen content was found to increase with an initial increase of the treatment time, thereafter, a decreasing trend was evident. After 2 hour treatment, the brittleness starts developing in the samples. The SEM analysis also confirmed the existence of nitrogen over the surface of the substrate in the form of a compact and dense plasma layer.
- The effect of the filling gas pressure on nitriding was also studied. The nitrogen content in the treated samples was found to increase with an initial increase of pressure, thereafter, a decreasing trend was evident. After passing the 3 mbar limit, the penetration of nitrogen into the treated samples was insignificant.
- Finally, it can be concluded that nitriding becomes more efficient and uniform in the presence of a screen cage that preserves the surface from damages caused by sputtering.

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Реферат

Азотирование ионами плазмы, которое является гибким и многофункциональным методом поверхностного упрочнения, использовалось в данном исследовании для поверхностной модификации инструментальной стали AISI M2(0.9% C, 4.2% Cr, 5.0% Mo, 6.0% W, 2.0% V). Поверхностное азотирование было выполнено в режиме аномального свечения с использованием импульсных разрядов постоянного тока, причем изменялось время плазменной обработки от 1 до 4 часов и давление газовой среды от 1 до 4 миллибар. Предварительный нагрев образцов для плазменной обработки был выполнен с помощью нагревателя, причем температура поднималось до 500°C, через каждые 15°C. Поверхностные характеристики плазменно обработанной инструментальной стали изучались с применением различных методов характеризации поверхности, такими как: рентгеновская диффрактометрия, сканирующая электронная микроскопия, измерение микротвердости по Викерсу. Исследование свойств показало образование на плазменно обработанной поверхности слоя сложного строения. Наблюдалось первоначальное увеличение толщины слоя, а затем уменьшение с увеличением времени азотирования. Аналогичные результаты были получены при увеличении давления газовой среды. Результаты рентгеновской диффрактометрии показали наличие смещения вниз оригинальных дифракционных пиков, что подтверждает диффузию азота в обработанную поверхность и образование обогащенного слоя. Также было подтверждено значительное повышение поверхностной твердости, которая может быть следствием диффузии азота.

Ключевые слова: тлеющий разряд, ионная имплантация, область аномального свечения, инструментальная сталь, поверхностная твердость.