Accelerated ion-plasma nitriding of austenitic steels in a low-frequency ferromagnetic enhanced induction discharge

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Abstract. In the present work, a possibility of the accelerated ion-plasma nitriding of austenitic stainless steels at elevated temperatures is discussed. Experimental data on the plasma-assisted nitriding process of AISI 304 stainless steel are presented in the temperature range of 400−500 °C, with the use of ferromagnetic enhanced induction discharge with a low-frequency and low-pressure as an external source of nitrogen ions and radicals.

1. Introduction
The high corrosion resistance of austenitic stainless steels determines their demand in industry and energy. However, relatively low surface hardness of about 2 GPa and poor wear resistance significantly limit the area of their possible application. The ion-plasma nitriding process results in a several-fold increase of the stainless steel surface layer hardness, due to the formation of a supersaturated solid solution of metastable nitrogen (expanded austenite, or S phase). Usually, the process of ion-plasma nitriding is carried out at a steel temperature below 450 °C, since the higher process temperature causes the S phase decomposition with the chromium nitride precipitation leading to a decrease in the steel corrosion resistance [1,2]. With reduction of the process temperature, the diffusion rate of nitrogen in the metal decreases significantly. As a result, the process of the low-temperature (<450 °C) ion-plasma nitriding takes a rather long period of time of several hours.

Studying the dynamics of the formation and decomposition of the S phase at elevated temperatures (>450 °C) creates new possibilities for the technology of ion-plasma nitriding. It was shown by Manova et al. [3] that at the process temperature of 550 °C the formation of S phase occurs during the initial (20−30 min) phase of AISI 316Ti stainless steel nitriding, followed by a gradual decomposition over the next hour. Thus, with a correctly chosen nitriding time, it is possible to obtain the S phase even at temperatures above 450 °C. For example, nitrided layers consisted mainly of the S phase were obtained by Li et al. [4] at the process temperature of >520 °C and nitriding time of 15−60 min, and at the same time the nitried AISI 316L samples demonstrated a high corrosion resistance. An increase in the diffusion rate of nitrogen in the metal lattice with temperature rise allows the creation of a nitried layer for lesser time.

In addition to temperature, atomic nitrogen and nitrogen ions’ densities have a significant effect on the rate of ion-plasma nitriding. The advantages of high-density plasma sources with a high concentration of ions and nitrogen radicals for plasma-assisted nitriding, in comparison with the “classical” DC glow discharges (used in [4]), were discussed by Czerwiec et al. [5]. In the present work, the process of a high-temperature (>450 °C) ion-plasma nitriding of AISI 304 stainless steel was studied...
using a low-frequency ferromagnetic enhanced induction discharge [6] as an alternative source of high-density nitrogen plasma.

2. Experimental setup
A principal scheme of experimental setup is shown in figure 1. O-shaped gas discharge chamber 1 was made of quartz tubes with internal diameter of 5.5 cm and the total length of 120 cm. To maintain the discharge, six ferrite cores 2 with the total cross-section of about 100 cm² were installed on the gas discharge chamber. Each ferrite core had a three-turn primary winding 3, all windings were connected in parallel to an AC power supply 4 through a matching network 5. The matching network consisted of a variable LC circuit, and was used for the discharge “ignition” and the discharge current stabilization. Thus, the plasma source operated as a step-up electric transformer with a voltage of induction discharge being two times higher than the voltage of the primary winding 3. Such a connection of the primary windings is necessary for the breakdown and maintenance of the discharge in molecular gases having an increased voltage (compared with gas discharges in inert gases). The cores 2 enhance magnetic coupling between the toroidal induction discharge 1 and induction coils 3, which allows reducing the discharge driving frequency and increasing the power transfer efficiency [6]. As a result, power supplies for induction heating with the current frequency of ~10–100 kHz can be used for inductive discharge generation, instead of specialized radio frequency (13.56 MHz) power supplies. Inductive discharge current I was measured with a current transformer (Rogowski coil) 6. Discharge voltage U was measured with a voltage loop 7 encircling the ferrite cores and collecting the alternating magnetic flux \( \Phi(t) \) that drives the inductive current \( U = -d\Phi/dt \). Plasma forming gas pressure was measured with a vacuum meter 8. A constant flow of plasma forming gas (nitrogen) was organized to remove impurities from the discharge chamber. Gas was pumped out with a fore pump 9.

A stainless steel sample (AISI 304) 10 was introduced into the chamber through a vacuum tight side entry. The sample temperature was measured with a thermocouple 11. A negative bias was applied to the sample using a DC power supply 12, with respect to a reference electrode 13 introduced into the plasma. During the nitriding process, the sample current \( I_s \) actually being an ion current at a large negative bias was measured. Thereby, a plasma-assisted nitriding process [5] was realized in the setup, with the ferromagnetic enhanced inductive discharge serving as a source of nitrogen ions and atoms for the process. The electrodeless principle of discharge generation allows obtaining a high plasma density and significantly increases the life time of the setup, while the decreased frequency of discharge generation reduces the AC power supply requirements and cost. Thereby, the low-frequency ferromagnetic enhanced induction discharge has several advantages that allows using it as an external plasma source for the plasma-assisted nitriding process.
3. Results and discussion

Plasma-assisted nitriding process of AISI 304 samples is performed within one hour at the samples temperature of 400−500 °C, plasma forming gas pressure of 50 mTorr and negative bias of -300 V. The low plasma-forming gas pressure ensures a collisionless movement of ions in the electric sheath near the surface of the biased sample. In this case, nitrogen ions accelerated by the electric field do not exhibit collisions with neutrals and gain the maximum of kinetic energy \( e = -qU_s \), where \( q \) is the ion charge and \( U_s \) is the bias potential of the sample. High-energy nitrogen ions sputter an oxide film on the sample surface limiting the diffusion of nitrogen into the sample, which improves the nitriding process [5]. To adjust the sample temperature, FMICP current density varies in the range of 65−145 mA/cm\(^2\). With an increase in the discharge current density, plasma density increases proportionally, which in turn leads to an increase in the sample ion current density from 1.2 to 2.6 mA/cm\(^2\). A comparable sample current density of 3.2 mA/cm\(^2\) is achieved in a low-pressure arc plasma-assisted nitriding process [7].

After the plasma-assisted nitriding process, surface microhardness tests are performed using 200 g load with a PMT-3 microhardness tester. At the given load, the indenter penetration depth is about 4 μm. In figure 2, a dependence of the sample surface microhardness on the nitriding temperature is shown.

![Figure 2. Surface microhardness vs. the sample temperature (nitriding time of 1 h).](image)

It is seen that in the studied temperature range the surface microhardness grows with the surface temperature almost linearly. Since the sample temperature increases due to an increase in the induction discharge current, the observed growth in the surface microhardness is caused not only by the elevated temperature but also by the increased fluxes of the atomic and ionized nitrogen on the sample surface. It is impossible to separate the influences of these factors on the surface microhardness in our work. However, as was shown by Li et al. [4], an increase in the sample temperature by 40 °C leads to a several times increase in the thickness of the nitried layer, i.e. temperature has a significant effect on the process of ion-plasma nitriding. Thereby, the elevated temperature is the key for the accelerated ion-plasma nitriding. A further increase in the temperature of the sample would result in a further increase of the surface microhardness. It is shown in [4] that even a standard DC glow discharge nitriding allows reaching the surface microhardness of about 10 GPa at the process temperature of 540 °C and the process time of 1 hour. However, according to Manova et al. [3], a process of the S phase thermal decomposition may start at this temperature level and the nitriding time. Thus, corrosion resistance of the samples should be controlled at high nitriding temperatures.
Conclusions
Combination of high atomic nitrogen and nitrogen ions concentrations in plasma, low gas pressure and elevated surface temperature is of interest for the realization of the accelerated plasma-assisted nitriding of stainless steels. At the same time the life time, efficiency and cost of the plasma source are of key importance for the practical application of the plasma-assisted nitriding technology. Ferromagnetic enhanced induction discharge provides an effective generation of dense low-pressure electrodeless plasma at low driving frequencies with the use of simple and mass-produced power supplies. The process of AISI 304 stainless steel ion-plasma nitriding has been investigated at the elevated temperatures of 400–500 °C and reduced process time of 1 hour, with the use of the low-frequency (100 kHz) low-pressure (50 mTorr) ferromagnetic enhanced induction discharge as the source of nitrogen active particles. A linear increase in surface microhardness versus surface temperature is shown for the studied temperature range. A higher temperature range of 500–550 °C seems to be more preferable for the nitriding acceleration. However, higher temperatures pose a higher risk of the corrosion resistance decline, which complicates the task of searching the most optimal process temperature and process time for the high temperature nitriding.

Acknowledgments
This work was carried out under state contract with IT SB RAS.

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