Low temperature plasma-assisted nitriding of austenitic steel in a ferromagnetic enhanced inductive discharge

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Abstract. Plasma-assisted nitriding of austenitic stainless steel AISI 321 has been performed with the use of a ferromagnetic enhanced inductive discharge as the source of nitrogen ions and radicals, in the temperature range of 300–400°C, gas pressure of 50 mTorr and ion densities of about (2.5–7.7) \times 10^{10} \text{ cm}^{-3}. A significant increase in the nitriding rate was achieved, in comparison with a low temperature glow-discharge nitriding process. A possible mechanism of the nitriding rate increase is a high atomic nitrogen density achieved in the ferromagnetic enhanced inductively coupled plasma.

1. Introduction
Austenitic stainless steels have high corrosion resistance and are widely used in various fields of industry. The main disadvantages of stainless steels are low surface hardness (\sim 2 \text{ GPa}) and poor wear resistance leading to short life-time under the intensive wear. Low temperature (< 450 °C) ion-plasma nitriding can significantly increase the hardness and wear resistance of a thin (of order of 10 \text{ µm}) surface layer of stainless steels without the loss of corrosion resistance, due to formation of a metastable nitrogen supersaturated solid solution (expanded austenite) [1]. However, for the most widely used process of glow-discharge nitriding, a decrease in the surface temperature leads to a significant decrease in the rate of nitriding process and an increase in processing time. To enhance the nitriding rate, modern methods of plasma-assisted nitriding (PAN) can be applied, with the use of high-density (10^{10}–10^{12} \text{ cm}^{-3}) low-pressure (< 0.1 \text{ Torr}) plasma sources [2]. Ferromagnetic enhanced inductively coupled plasma sources (FMICP) are the promising ways of plasma production for PAN technology, as they implement an effective generation of high-density low pressure electrodeless plasma in a low frequency radio range [3]. The electrodeless (inductive) principle of discharge generation eliminates the sputtering of electrodes at high discharge current densities and low gas pressures, and significantly enhances the service life of a plasma source. Adding of a ferromagnetic core to an induction coil enhances the magnetic coupling between the coil and plasma, improves the power transfer efficiency, and reduces the frequency of inductive discharge generation from \sim 10 \text{ MHz} down to \sim 100 \text{ kHz}. In this case, mass produced power supplies for induction heating can be used instead of specialized radio-frequency generators. Thereby, FMICP can be used as a source of nitrogen ions and radicals for PAN technology [4]. The aim of this work is to reveal the rate of the low-temperature plasma-assisted nitriding of austenitic stainless steel in the nitrogen FMICP.
2. Experimental setup

A principal scheme of experimental setup is shown in figure 1. Gas discharge chamber 1 is made of quartz tubes with the inner diameter of 55 mm and the total length of 120 cm. Six ferrite cores 2 with the total cross-section of 106 cm² are used to enhance magnetic coupling between the toroidal inductive discharge and the ICP coil. Each ferrite core has a three-turn primary winding 3, all windings are connected in parallel to an AC power supply 4 through a matching network 5. As the power supply, a transistor generator for induction heating INTERTM TGI 12/100–6 is used, with the output voltage of 225 V, maximal output current of 60 A and frequency range of 50–100 kHz. As the matching network, a variable LC circuit is used with capacitors connected in parallel with the primary winding and a variable inductance connected in series with the power supply. The matching network is used for the discharge ignition and for discharge current stabilization and regulation. A sample 6 made of 12 mm stainless steel bar was placed on the axis of the discharge chamber and connected to a DC power supply 7. A negative bias potential was applied to the sample, relatively to a grounded reference electrode 8. The sample temperature was measured with a thermocouple of type K 9. The inductive discharge current was measured with a current transformer (Rogowski coil) 10. Surface microhardness tests were performed with a PMT-3 microhardness tester.

3. Results and discussion

Low temperature plasma-assisted nitriding of AISI 321 samples was performed in the temperature range of 300–400°C, at the nitrogen pressure of 50 mTorr. FMICP current strength was varied in the range of 1.5–4.7 A, which corresponded to the discharge power range of 300–800 W. A negative bias of -300 V was applied to the samples, for sputtering of a thin oxide surface layer limiting the speed of nitrogen diffusion [5]. The ion current density on the sample surface was varied in the range of 1–3 mA/cm², increasing with the FMICP current strength and the FMICP ion density, respectively. To estimate the FMICP nitrogen ion density \( n_i \), equation (1) was used:

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j = e n_e v_d (E/N), \tag{1}\]

where \( j \) is the FMICP discharge current density, \( e \) is the electron charge, \( n_e \) is the electron density (due to the plasma quasineutrality \( n_i \approx n_e \)), \( v_d \) is the electron drift velocity depending on the ratio of discharge electric field strength \( E \) to the neutral gas density \( N \). For the investigated low pressure nitrogen FMICP under the above mentioned conditions, typical \( E/N \) ratio is about 160 Td. Estimations of the nitrogen ion density by equation (1) give characteristic values of about \((2.5–7.7) \times 10^{10} \) cm⁻³. Therefore, the conditions typical of PAN processes are realised in the low pressure nitrogen FMICP (high ion densities of about \(10^{10}–10^{11} \) cm⁻³ at low gas pressures of <100 mTorr [2]).
The samples were treated in the low pressure nitrogen FMICP during 2 h and 1 h. Surface microhardness tests were performed using 200 g load. At the same time, the indenter penetration depth was varied in the range of 2.5–5 μm. Since a low temperature PAN process creates a ~10 μm nitried layer even at 1 h treatment [1], the relatively small indenter penetration depth ensures the measurement of the nitried layer hardness. In figure 2, a dependence of the sample surface microhardness on the nitriding temperature is shown for the case of 2 h treatment.

Figure 2 shows that with the rise of nitriding temperature the surface microhardness increases due to the increase in the nitrogen diffusion rate. With the sample temperature rise from 300°C up to 400°C, the surface microhardness increases from 4.7 GPa up to 12.5 GPa. For comparison, conventional glow-discharge nitriding of various stainless steels during 5 h at the sample temperature of 400°C, gas pressure of 7.5 Torr (80% N₂, 20% H₂) and the current density of 2.5 mA/cm² leads to an increase in the surface microhardness up to 9–10 GPa [6]. In contrast to the low pressure PAN technologies, in the glow-discharge nitriding process hydrogen is used to prevent the formation of the surface oxide film, while in the low pressure PAN processes the oxide layer is sputtered by high-energy (a few hundred eV) nitrogen ions. The low gas pressure (<0.1 Torr) is the key condition for ions to gain the necessary kinetic energy due to collisionless movement in the electric field of the sample.

In the case of plasma-assisted nitriding, active particles are created by an “external” high-density plasma source, which realizes significantly higher nitrogen ion and atom densities than a glow discharge due to a higher value of discharge current density. For example, discharge current density of the investigated nitrogen FMICP is 25–80 times higher than discharge current density of the glow discharge [6]. Since the diffusion of atomic nitrogen into a bulk lattice probably plays the key role in the nitriding process [7, 8], the enhancement of the atomic nitrogen concentration leads to the increase of its flux onto the sample surface and the consequent increase in the nitriding rate.

For comparison, a low pressure (4.5 mTorr) arc discharge PAN of AISI 316L austenitic stainless steel at 400 °C during 1 h with the bias voltage of -700 V enhances the surface microhardness up to 9.5 GPa [1]. The low pressure nitriding in the nitrogen FMICP at the same sample temperature and processing time increases the surface microhardness up to 7.8 GPa. Unfortunately, the authors of [1] report only the arc discharge current strength (55–95 A), but do not provide the size of the arc plasma nitriding device, so it is not possible to estimate the arc discharge current density and to compare it with the current densities obtained in the investigated low pressure nitrogen FMICP. It is necessary to underline that low pressure arc plasma generators face the problem of cathode sputtering due to the ion bombardment, while the elecrodeless FMICP has no limitations on the discharge current strength,
therefore high atomic nitrogen concentrations and high nitriding rates can be achieved with the use of nitrogen FMICP.

**Conclusion**

Electrodeless principle of the FMICP operation allows the achievement of high discharge current densities and implementation of the conditions needed for an effective plasma-assisted nitriding process: high nitrogen ion and atom densities at low (<0.1 Torr) nitrogen pressures. In contrast to the well-known high-density radio-frequency (13.56 MHz) inductively coupled plasma sources, the FMICP can be effectively generated in a low-frequency radio range (~10–100 kHz) using cheap mass-produced power supplies for induction heating. Experimental investigation of low temperature (300–400 °C) plasma-assisted nitriding of AISI 321 stainless steel has been performed in low pressure (50 mTorr) nitrogen FMICP, a significant enhancement of the stainless steel nitriding rate was observed, in comparison with a conventional glow-discharge nitriding process using N₂/H₂ mixture. The enhancement of the nitriding rate can be explained by an increase in atomic nitrogen concentration achieved in the high-density FMICP in comparison with the glow discharge with the current densities an order of magnitude lower. Based on the FMICP principle, new low pressure plasma sources of nitrogen ions and atoms can be developed for plasma-assisted nitriding technology, with high efficiency and long life-time of the plasma source.

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