Experimental diagnostic and choice of technological parameters of ion nitriding process

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Abstract. Modern hardening coatings, known as duplex coatings, are a combination of two types of surface treatment: preliminary ion nitriding of the substrate and subsequent deposition of a thin hardening film based on ceramic coatings. Nitriding is a process of diffusion saturation of the metal surface with a doping element (nitrogen from the gas phase). The key process parameters are the operating pressure and the temperature of the substrate, which determine the intensity of diffusion fluxes and the efficiency of processing. In this paper, we present a research of the influence of the pressure range ($p_1 = 1000 \, \text{Pa}$, $p_2 = 400 \, \text{Pa}$, and $p_3 = 200 \, \text{Pa}$) in the nitriding process of high-speed steel substrates and the development of a temperature measurement system with ceramic insert made of aluminum nitride that enabled us to control the temperature during the process in the range $470 \, ^\circ\text{C} − 570 \, ^\circ\text{C}$. The results show that pressure should not exceed $200 \, \text{Pa}$.

1. Introduction

All types of gas nitriding processes (gaseous or glow discharge plasma) involve heating the product to high temperatures to increase the diffusion coefficients. Typical nitriding temperature is in the range of $470 \, ^\circ\text{C} − 570 \, ^\circ\text{C}$. Operation at higher temperatures is inadmissible, as the recrystallization temperature for most steels is in the range of $600 \, ^\circ\text{C} − 700 \, ^\circ\text{C}$. In terms of pressure, there is a technological optimum that provides sufficient surface hardening and corresponds to the volt-ampere characteristic of the glow discharge used for ion nitriding [1–4].

Nitrogen surface content depends strongly on the nitriding time. Hannula, et al. measured up to 42% nitrogen content on the ion nitrided surface of 304 stainless steel treated during 24 hours, with a significant reduction a few microns in depth from the surface. Moreover, when the processing time is just 15 minutes, the nitrogen content on the surface is reduced to about 21% and the resulting layer is much thinner ($< 1 \, \mu\text{m}$) [5]. Jindal demonstrated that the layer thickness satisfies a parabolic dependence law on time, and the nitriding rate is faster in plasma than the neutral gas atmosphere [6].

Experimental data show that microstructure, residual stresses and the surface state before the processing also affect the surface nitrogen concentration and the layer thickness when a nitriding process is applied [7,8]. In particular, the before nitriding treatments as sand-blasting, polishing, annealing and tempering, strongly influence the resulting nitrided layer properties [9,10]. In
addition, Berg, et al. found that higher mean energy of ions bombarding the surface leads to thicker layers and higher nitrogen content [11].

The Joint Universal Plasma and Ion Technologies Experimental Reactor (JUPITER) has been previously used to study surface modification [12–15] and now it was upgraded to investigate the technological possibilities for duplex coatings manufacturing.

2. The experimental setup
The scheme of the experimental setup is based on the JUPITER reactor configuration shown in Figure 1.

![Diagram of the experimental setup for plasma nitriding.](image)

In the Figure 1, the turbomolecular and mechanical pumping system is used to obtain residual pressure of less than 20 $mPa$ in the vacuum camera; inside the chamber, a sample holder is supplied with high voltage from a SCIENS DC500E power supply operating in direct current (DC) mode with current stabilization. The temperature is measured by a specially designed thermocouple sensor, whose data are processed by the TMCON FT3403 controller. The two-channel piezoelectric system SNA2 provides a sequential or mixed flow of working gas into the chamber, the working pressure of which is monitored by the PIRANI THYRACONT VSP63D sensor.

At the initial stage, the vacuum chamber is evacuated with the turbomolecular pump, then the vacuum gate is closed and the operating pressure is provided by the rotary vane pump and the gas flow from the piezo system. This pumping sequence provides high purity of working atmosphere and a wide range of operating pressures up to 5 $kPa$. The sample holder is designed to work with samples with dimensions not exceeding 30 $mm$ and weighing up to 50 $g$. Since there may be an overheating problem with the risk of thermal tempering of the substrate during the nitriding process, accurate control of the process temperature is necessary. Due to the low thermal reactivity, it is necessary to use a temperature sensor with low thermal inertia while providing galvanic isolation to the measuring circuits up to 800 $V$. To solve this problem, a
A thermocouple sensor was developed with a ceramic insert on the measuring surface made of aluminum nitride (AlN). This material has high electrical resistance (16 kV/mm) and, at the same time, it has high thermal conductivity ($\lambda = 180$ W/mK), ten times higher than the alundum ceramic ($\text{Al}_2\text{O}_3$) of the sensor box.

In view of the fact that $\nabla T = q/\lambda$, the use of AlN ceramics provides accurate temperature measurement of the small sample even across the ceramic barrier. In addition, a K-type thermocouple made of a thin wire ($\varnothing 0.127$ mm) was used to reduce the specific heat fluxes $q$. The schematic of the thermocouple measuring system with a galvanic barrier is shown in Figure 2.

![Figure 2. Scheme of the thermocouple temperature measurement with a galvanic barrier made of AlN ceramic.](image)

In the Figure 2, the contact of the thermocouple with the sample is made through the AlN ceramic disc ($\varnothing 8$ mm) with a thickness of 2 mm. The contact pad protrudes slightly above the sensor’s surface, which ensures contact with the object of measurement only along the plane of the thermoconductive ceramic. These two designed elements are housed in a composite housing of alundum ceramic, the heat fluxes going into the oxide ceramic are minimal and do not distort the thermocouple data. The ceramic parts of the sensor are bonded with high-temperature ceramic glue, which maintains performance up to 800 °C.

The signal from the thermocouple is fed to the thermocouple controller through a sealed connector, which ensures that the sensor works in a vacuum chamber under low-pressure conditions. At the controller’s input, protection against high voltage is used, which can appear in consequence of the breakdown of the ceramic insert along the bonding line. The protection diodes have a cutoff voltage of 300 mV and do not affect the thermocouple because, at 500 °C, its signal does not exceed 30 mV.
3. Results

The samples used were high-speed steel (HSS) discs with a diameter of $\varnothing 8 \times 5 \, mm$ subjected to standard heat treatment forming coarse carbides and martensitic-austenitic matrix; the samples were etched with a metallographic solution (5% of nitric acid in ethanol), see Figure 3(a), and then polished with diamond paste with a dispersion of 3 $\mu m$ (see Figure 3(b)) before the nitriding.

![Figure 3](image1.png)

**Figure 3.** The surface of the HSS sample before the nitriding process: (a) etched, and (b) polished.

To determine the range of the working pressure, the experimental processing of HSS steel samples was carried out in a nitrogen atmosphere for 150 minutes at a pressure $p_1 = 1000 \, Pa$, $p_2 = 400 \, Pa$, $p_3 = 200 \, Pa$ under temperature 500 $^\circ C$. The sample placed on the conductive holder is the cathode of the glow discharge and therefore, its surface is sputtered intensively. The sputtered atoms experience numerous collisions with the working gas molecules, the mean free path is short and the sputtered atoms return to the cathode, forming a film on its surface. The surface of three samples treated at three operating pressures is shown in Figure 4.

![Figure 4](image2.png)

**Figure 4.** Samples of HSS processed at various working pressures of (a) $p_1 = 1000 \, Pa$, (b) $p_2 = 400 \, Pa$, and (c) $p_3 = 200 \, Pa$. 
It can be seen that at pressures above 200 Pa a rather loose film of the cathode material is formed on the surface, which will not allow further deposition of a hardening coating with good adhesion. Based on the analysis, we experimentally selected technological modes of processing HSS steel samples. The cyclograms are shown in Figure 5. The treatment is carried out in two stages: in the first stage, the sample is cleaned in argon for 30 minutes, and then, the gas is replaced by nitrogen and the nitriding process is carried out for 150 minutes. The temperature of the substrate (see Figure 5(a)), the working pressure inside the chamber (see Figure 5(b)), and the electric power with its corresponding current and voltage (see Figure 5(c)), remain constant during the whole nitriding process. To heat the sample up to 490 °C, an electric power of 35 W is enough.

4. Conclusions
Experimental equipment for implementing nitriding processes as part of the combined coating process of the duplex type has been created. In addition, the experimental results have shown that the working pressure during nitriding should not exceed 200 Pa due to the reduction in the mean free path of the atoms expelled from the surface, leading to the formation of loose films. Finally, based on the analysis were developed cyclograms of processing high-speed steel samples.

Acknowledgment
This work was carried out with the support of the Departamento Administrativo de Ciencia, Tecnología e Innovación, Colombia, and Ministerio de Ciencia Tecnología e Innovación, Colombia, through the announcement No 582-2019 (1102-852-69674) and the Universidad Industrial de Santander (UIS), Colombia, (Project ID: 9483-2666).
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