INFLUENCE OF THE SPECIAL PAINTS FOR THE LOCAL PROTECTION AGAINST PLASMA NITRIDING ON FUNDAMENTAL PROCESSES IN THE IONISED GAS

Cristian Deac\textsuperscript{a}
Valentin Petrescu\textsuperscript{a}
Toderita Nemes\textsuperscript{a}

\textsuperscript{a} “Lucian Blaga” University of Sibiu, Emil Cioran str. 4, 550025 Sibiu, Romania, cristian.deac@ulbsibiu.ro

Abstract
The researches presented in this paper concern the elaboration of local protection technologies against plasma nitriding. When plasma nitriding is applied to metallic parts that need local isolation with special elaborated paints, the elementary fundamental physical-chemical processes that take place in the discharge gas volume are divided into three separate categories: processes attenuated by the protective paints, processes completely cancelled and processes that develop normally without being influenced by the insulating layer. The experiments carried out allowed an analysis of the way in which the basis cathode and gas volume processes are influence or not by the paint layers.

1. INTRODUCTION

When plasma nitriding is applied to metallic parts which require a local protection with isolating paints that are specially elaborated for this purpose, the elementary physical-chemical processes that occur in the discharge volume (in the recipient of the plasma nitriding installation) can be grouped in three different categories:

\begin{itemize}
    \item processes that are slowed down due to the protection layer;
    \item processes that are completely annulled due to the applied protection layer;
    \item processes that unfold as normal, without being influenced by the protective layer;
\end{itemize}

Following the researches regarding the elaboration of more advanced and more efficient technologies for the local protection of metallic parts with isolating layers against the effects of plasma nitriding, there were realised two original types of paints that can be used for this purpose. They are mixtures based on sub-microscopic lamellar copper powder (with particle dimensions of $5...50 \text{ m}$) combined with magnesium oxide. The two components are dispersed either in a polystyrene lacquer (polystyrene dissolved in carbon tetrachloride) or in carbon tetrachloride alone [1], [2],[4].

For the case in which plasma nitriding is applied to parts which need, for technological reasons, a local protection against the treatment in certain areas, the main objectives of this protection are:

\begin{itemize}
    \item to avoid the hardening of the protected metallic surfaces (i.e. to stop the adsorption, absorption and diffusion of nitrogen at the surface and in the interior of the superficial layers of the parts);
    \item to keep the mechanical properties and the physical-chemical characteristics of the protected areas at their levels prior to the applying of plasma nitriding [6].
\end{itemize}

It was examined, in first place, if the elaborated paints, through their chemical compositions, modify or not the gaseous environment during plasma nitriding and if this can still achieve its goals. The efficiency of the gaseous environment was determined by means of hardness tests carried out on the protected surfaces.
The researches presented here were carried out as a complement to the analyses done until now with regard to the influence of protective layers on the fundamental processes at the cathode and on the properties of protected metallic surfaces that existed before the plasma nitriding (chemical composition, metallographic structure, internal stress state etc.) [1]. During the plasma nitriding process, the particles from within the plasma (electrons, positive or negative ions, neutral atoms or molecules in fundamental or excited state, photons) contribute and lead to the starting and unfolding of physical-chemical phenomena in the gases that fill the heating chamber of a plasma nitriding installation. These processes are very complex, being determined by the special conditions under which the plasma nitriding is carried out [5], [7].

The composition and pressure of the plasma nitriding atmosphere are two important parameters, which influence primarily the structure and composition of the combination layer, acting on the duration and speed of cathodic pulverisation [8], [9].

The cathodic pulverisation dislocates particles from the protective layer, particles that get into the working environment composed of nitrogen and hydrogen [1].

In a first research stage we determined the chemical composition of the active atmosphere during the plasma nitriding of parts protected on selected areas by protective paint layers.

2. THE EXPERIMENTAL RESEARCHES

The experimental researches were carried out on disc-shaped test samples made of a special nitriding steel - 39MoAlCr15. The chemical composition of this steel is: 0.35...0.42% C; 0.35...0.60% Mn; 1.35...1.65% Cr; 0.15...0.25% Mo; 0.20...0.45% Si; 0.70...1.10% Al; max. 0.035% S; max. 0.035% P.

The discs, with the diameter of 60 mm and the thickness of 10 mm, were tempered to 28...30 HRC, fine ground Ra=0.025 mm and degreased.

These discs were assembled in two distinct assemblies (M1 and M2), each one consisting of a column with 9 discs (fig. 1):

? M1 – with unprotected discs: P1 m1 ... P9 m1;

? M2 – with protected discs: P1 p1 ... P9 p1.

The protective paint has been applied with a paintbrush in two layers, on a thickness of 0.45 mm, with a drying period of 10 minutes between the layers.

The heating phase was carried out at a temperature T = 500°C and a pressure p = 1 torr, while the plasma nitriding phase took place at the temperature T = 550°C over a period of t = 7 h, at a pressure p = 3 torr, the composition of the active gas mixture being 25% N2 and 75% H2.

The test samples were fastened by screwing on two rods that were placed in the loading device of the recipient of a plasma nitriding installation INI – 70 (figure 2).
The samples and rods were placed so that an optimal distance was kept between them, in order to avoid the double cathode effect. One disc from each column had a notch in which were introduced the ceramic sheaths and the thermocouples needed for the temperature control during the process.

In order to check the composition of the gases from the recipient of the plasma nitriding installation INI – 70, the authors have used the gas analyser HAL 200, (fig. 3), which uses a gas sampling system with a capillary tube (a capillary tube with a length of 3 m, mechanically supported by a stainless steel pipe ? 8 x 1 mm). In its lower part, the pipe is curved, so that by rotating and moving it on axial direction, the gas composition can be determined in various points of the installation's gas vessel. Because the pressure difference which ensures the flow of the gas through the capillary tube is relatively small (a few torr) and the flowing speed is low, the time period after which the composition in the spectrometric chamber is stabilised and similar to the one in the nitriding area, is relatively long (20…30 minutes).

The study of gas distribution was therefore a very difficult operation, that required a long time to obtain correct and concrete data that could be used for the drawing of conclusions concerning the influence of the paint layers on the processing atmosphere's chemical composition.

The columns with test samples were heated successively to the temperature of 500°C. First, the assembly M₁ (with unprotected samples) was processed. During its heating, the modification of the treatment atmosphere's composition was monitored on the display of the gas analyser. When the partial pressures have stabilised, their values were recorded, after which the analyser was abruptly separated from the capillary, so that the base values existing in the spectrometric chamber could also be determined and recorded.

After this, the M₁ assembly was disconnected and the M₂ column (with paint-protected discs) was connected instead, going through the same stages as in the previous case.

The comparison of the two data sets obtained for the M₁ samples and for the M₂ samples, respectively, is presented in the following paragraph.
3. RESULTS

The parameters of the process for the column M₁ were: \( t = 0 \ldots 1.15 \) h; \( p = 1 \ldots 0.90 \) torr; \( T = 0 \ldots 580^°C \); \( U_d = 360 \ldots 600 \) V; \( I_d = 0.20 \ldots 0.51 \) A; \( P_d = 72 \ldots 296 \) W (with degassing at \( 200^°C \) and process stabilisation at \( 500^°C \)).

The values of the partial pressures for \( H_2, H_2O, N_2, O_2 \) and \( CO_2 \), in the case M₁ were: \( p_{H_2} \times 10^{-6} = 2.50 \ldots 1.85 \) torr; \( p_{H_2O} \times 10^{-7} = 8.74 \ldots 7.40 \) torr; \( p_{N_2} \times 10^{-7} = 2.20 \ldots 1.82 \) torr; \( p_{O_2} \times 10^{-5} = 5.85 \ldots 5.14 \) torr; \( p_{CO_2} \times 10^{-8} = 1.02 \ldots 1.16 \) torr; \( p_{O_2} \times 10^{-7} = 9.42 \ldots 6.82 \) torr.

The parameters of the process for M₂ were: \( t = 0 \ldots 1.16 \) h; \( p = 0.8 \ldots 0.90 \) torr; \( T = 0 \ldots 500^°C \); \( U_d = 450 \ldots 590 \) V; \( I_d = 0.18 \ldots 0.60 \) A; \( P_d = 81 \ldots 354 \) W (with degassing at \( 200^°C \) and process stabilisation at \( 500^°C \)).

The values of the partial pressures for \( H_2, H_2O, N_2, O_2 \) and \( CO_2 \), in the case M₂ were: \( p_{H_2} \times 10^{-6} = 1.74 \ldots 1.89 \) torr; \( p_{H_2O} \times 10^{-7} = 6.24 \ldots 4.04 \) torr; \( p_{N_2} \times 10^{-7} = 2.35 \ldots 2.11 \) torr; \( p_{O_2} \times 10^{-5} = 5.56 \ldots 4.89 \) torr; \( p_{CO_2} \times 10^{-8} = 0.98 \ldots 0.72 \) torr; \( p_{O_2} \times 10^{-7} = 6.59 \ldots 4.88 \) torr.

The composition of the work atmosphere from the plasma nitriding installation, for the case of the unprotected parts (M₁) is: 79.07\%\( H_2 \); 20.83\%\( N_2 \) and 0.10\%\( O_2 \).

For the case of test samples protected by the special protection paint (M₂), the work atmosphere composition is as follows: 79.25\%\( H_2 \); 20.64\%\( N_2 \) and 0.11\%\( O_2 \).

During the heating of the batch with test samples protected against the effects of plasma nitriding, the mass spectrum was monitored closely, in order to detect the possible presence in the atmosphere of substances resulted from the heating of the protected layer. However, no substance beneath those already existing (\( H_2, N_2, O_2 \)) has been detected.

The presence of oxygen can be explained if we take into account the gases desorbed from the vessel's walls.

The components of the paint used for the local protection have obviously no influence on the work atmosphere's composition. The copper powder and the magnesium oxide diffuse in the surface of the part and form there the protective layer, withstanding even relatively high temperatures. As for the polystyrene lacquer, when the temperature surpasses the value corresponding to its thermal stability, the organic compounds are destroyed, but being in a relatively small quantity, they do not affect the atmosphere.

4. CONCLUSIONS

Based on the previously described experiments, following conclusions can be drawn with regard to the influence of the paints on the processes taking place in the work atmosphere:
- the protective layers placed on the parts do not influence the chemical composition of the gas mixture from within the plasma nitriding installation.
- there are no changes in the chemical composition, metallographic structure and internal stress state of the metallic surfaces that are protected by the special paints, because there is virtually no interaction between the atmosphere and the paint layer.
- no changes were noticed or expected with regard to the effect of the plasma nitriding process on unprotected areas of the parts.
- there is no need to take preventive action against the chemical combinations which the copper, magnesium oxide, polystyrene or carbon tetrachloride particles could form with the active elements contained in the work environment.

The protection paints offer several advantages:
- the time needed for the unfolding of the degassing-preheating and heating phases is reduced significantly;
- the number of transitions of the luminescent discharges in electric arcs is considerably lower;
- the energy consumption during the degassing-preheating and heating phases is also reduced;

Based on all analyses carried out: study of the gas mixture's chemical composition, microhardness measurements, spectrometric and X-ray diffraction analyses of the elements' concentration, analyse of the technological (pressure, discharge voltage, temperature, duration) and electrical (current density, secondary electron emission coefficients, voltage, current intensities, absorbed energy) parameters etc.[1], both on protected and on unprotected surfaces subjected to a plasma nitriding process, have proven, on the one hand, the efficiency of the process for the unprotected surfaces, but also the efficiency of the protective measures in the areas covered with the special paint.

BIBLIOGRAPHY