

GLOW DISCHARGE OPTICAL EMISSION SPECTROSCOPY OF CARBONITRIDED LAYERS

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ABSTRACT: The aim of the present work is to investigate the possibility of applying glow discharge optical emission spectroscopy while building the profile of nitrogen and carbon distribution in carbonitrided layers. 25CrMnSiNiMo steel and Armco-iron have been carbonitrided in low-temperature plasma in ammonia and argon medium. The results show that increased amount of carbon is observed both in the combined zone and in the diffusion zone of the carbonitrided layer. It has been established that after carbonitriding of 25CrMnSiNiMo steel and Armco-iron at $t=550\text{ }^{\circ}\text{C}$, $P_{\text{NH}_3} = 280\text{ Pa}$, $P_{\text{Ar} + 18\% \text{ CO}_2} = 120\text{ Pa}$, $\tau = 4\text{ h}$, the most gradual change of the distribution of nitrogen and carbon is achieved in the carbonitrided zone of the layer.

KEYWORDS: carbonitrided layers, low-temperature plasma, GDOES analysis

INTRODUCTION

Since the beginning of the 1970s glow discharge sources have been used predominantly in the field of investigating alloys. The scientific literature suggests a great number of applications based on glow discharge spectrometers, not supposed so far, including polymeric mass-spectrometry, sensitive assessment of nano-materials, as well as analysis of very thin ($<0,1\text{ }\mu\text{m}$) layers [1, 2, 3, 4]. The glow discharge optical emission spectroscopy (GDOES) is an atomic emission process for carrying out deep profile analysis. It combines pulverization and atomic emissions in order to enable an extremely fast and sensitive analysis. The plasma is generated in the chamber by applying voltage between the anode and the cathode with the availability of argon under low pressure. The ionized argon atoms cause pulverization in the area of the sample. The deposited atoms are excited in the plasma and radiate photons with characteristic wave lengths.

The glow discharge is initiated by the application of high enough voltage between two electrodes in contact with inert gas (typically Ar). The potential difference (250-2000V) leads to inert gas decomposition which results in forming positively charged ions and free electrons. The relative potential of the cathode (-) and the anode (+) leads to originating an electrical field and the positively charged ions are accelerated until they reach the cathode surface. The products of the pulverizing process are atoms and small particles from the cathode material, as well as ions and secondary electrons. The positive Ar^+ ions, derived from the glow discharge plasma, are focused onto the sample. The energy of the ions and the intensity of the irradiation can be different. As a result from the ion irradiation the surface of the sample erodes due to the ion

pulverization and the pulverized atoms cross into the gas phase.

The atoms, freed from the sample, are excited by the plasma, chiefly due to the electron collisions and become a source of characteristic radiation detected by the spectrometer. If the surface erosion percentage is known, the time, depending on the intensity of the characteristic elementary radiation line, measured experimentally, can be converted into quantitatively distributive profile of the element in the volume of the sample [2].

The GDOES investigations are carried out by means of a glow discharge source and an optical spectrometer. They enable performing a deep profile of the chemical composition of a solid material layer. For the purposes of the analysis of the solid material layers argon ions are forced into the glow discharge plasma on the cathode combined sample surface. As a consequence of an impulse exchange of argon ions, mostly atomic particles are detached from the surface of the sample. The positive argon ions are derived from the glow discharged plasma, and then they are focused and directed towards the sample. The atoms, freed from the sample, are excited in the plasma, mostly due to the electron collisions and they become a source of characteristic radiation, detected and analyzed by the spectrometer.

The GDOES is usually used for defining surface coatings, hidden connections, and deep profiles. The technique suggests quick, reliable and economically effective decisions. It suggests additional information for the rest of the surface analysis methods [3].

The aim of the present work is to investigate the possibility for defining the nitrogen and carbon distribution in depth of a layer, formed in low-temperature plasma in a medium of ammonia and argon.

METHODOLOGY OF INVESTIGATION HEAT TREATMENT

The following materials have been chosen for the investigation: Armco-iron and construction steel alloy - 25CrMnSiNiMo. The chemical composition of the above materials has been tested by means of equipment for automatic analysis “Spectrotest” and given in Table 1.

Table 1. Chemical composition of the investigated materials

Materials	Chemical elements, weight percentages				
	C	Si	Mn	Cr	Ni
Armco-iron	0.02	0.01	0.07	0.02	0.03
25CrMnSiNiMo	0.24	1.45	1.28	0.87	1.36
Materials	Chemical elements, weight percentages				
	S	P	Mo	V	
Armco-iron	0.002	0.002	0.02	-	
25CrMnSiNiMo	0.002	0.002	0.12	-	

Samples, sizing 15 x 15 x 10 mm, have been made from the materials; 25CrMnSiNiMo steel has been thermally treated to hardness 35HRC, and the hardness of the Armco-iron is 75HB. Treated this way, the samples have been then grinded to surface roughness $R_a = 0.63 \mu\text{m}$. Afterwards they have been ion nitrided and carbonitrided in an installation for nitriding “Ion-20” under the modes, given in Table 2. Ammonia (NH_3) and corgon (82 % Ar u 18% CO_2) in different percentages have been used as saturating gases. The temperature of treatment for both processes – nitriding and carbonitriding – is 550°C.

Table 2. Modes and results from the ion carbonitriding and the nitriding of the samples from 25CrMnSiNiMo–steel and Armco-iron

№ mode	τ [h]	P_1 NH_3 [Pa]	P_2 corgon [Pa]	P total [Pa]	25CrMnSiNiMo		
					$HV_{0,1}$	δ_{tot} [μm]	$\delta_{c,z}$ [μm]
1	2	360	40	400	940	160	5
2	6	360	40	400	860	290	8
3	6	200	200	400	920	240	8
4	2	200	200	400	890	150	5
5	4	280	120	400	930	210	9
6	4	400	-	400	1072	250	10

№ mode	τ [h]	P_1 NH_3 [Pa]	P_2 corgon [Pa]	P total [Pa]	Armco-iron			
					$HV_{0,1}$	δ_{tot} [μm]	$\delta_{c,z}$ [μm]	U [V]
1	2	360	40	400	430	260	6	470
2	6	360	40	400	420	340	7.5	470
3	6	200	200	400	440	330	7	415
4	2	200	200	400	370	210	6	415
5	4	280	120	400	480	280	7	435
6	4	400	-	400	415	290	6	530

GLOW DISCHARGE OPTICAL EMISSION SPECTROSCOPY

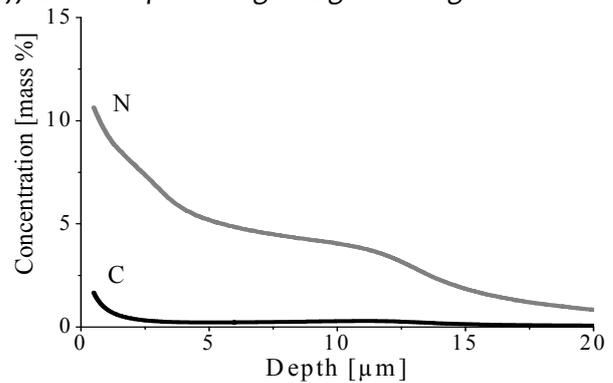
The process of defining the distribution of nitrogen and carbon in the nitrided and carbonitrided samples has been realised by means of the GDOES device GDA – 750, vom Spectruma-Analytik GmbH. The parameters of the glow discharge plasma are as follows: current - 20 mA, voltage - 800 V, plasma density - 10^{10} - 10^{11} cm^{-3} , electron temperature 0.1 - 0.5 eV and plasma volume 15 cm^3 . The turbomolecular pump (56 l s^{-1}) works constantly. The basic pressure is 10^{-6} Pa . The surfaces are polished beforehand in order to achieve

congestion in the plasma sector of the GDOES device. The standardizing of the device has been carried out with a sample containing 7 weight per cents of nitrogen and 1 weight per cent of carbon.

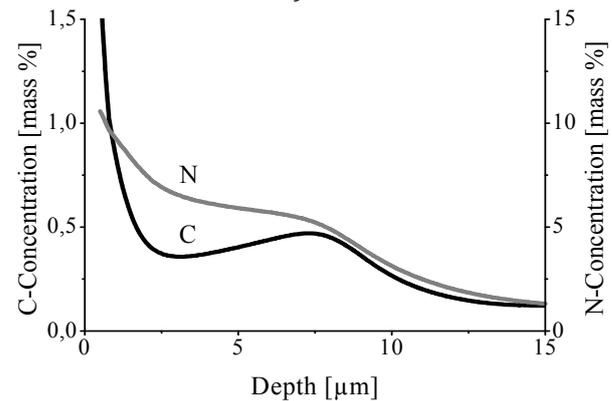
RESULTS FROM THE ANALYSIS AND THE INVESTIGATIONS

25CrMnSiNiMo STEEL

After nitriding under the mode 6 (Table 2) a layer is formed in 25CrMnSiNiMo steel with micro-hardness of 1072 $HV_{0,1}$, total thickness of 250 μm and combined zone thickness of 10 μm . The distribution of the diffused in depth nitrogen is given in Figure 1.



a) after nitriding of 25CrMnSiNiMo steel at: $t = 550 \text{ }^\circ\text{C}$, $P_{\text{NH}_3} = 400 \text{ Pa}$, $\tau = 4 \text{ h}$



b) after carbonitriding of 25CrMnSiNiMo steel at: $t = 550 \text{ }^\circ\text{C}$, $P_{\text{NH}_3} = 360 \text{ Pa}$, $P_{82\% \text{ Ar} + 18\% \text{ CO}_2} = 40 \text{ Pa}$, $\tau = 6 \text{ h}$

Figure 1. Carbon (C) and nitrogen (N) concentration in depth

From Figure 1a it can be noted that the concentration of the nitrogen in the nitrided layer has not changed (0,25%) at the border of the basic material and the combined zone (8.7 μm). This can be explained by the fact that during the process of nitriding carbon has diffused from the core material out to the surface. The pulverization on the surface and the obtained concentration gradient of the carbon are prerequisites for diffusion of carbon into the surface at the initial phase of the process of nitriding. The nitrogen concentration on the surface of the combined zone reaches 11,1%. After the process of ion nitriding the curve of nitrogen and carbon distribution in the nitride zone of the layer changes gradually.

When, except for ammonia, 10% corgon is introduced into the chamber in addition, (Table 2, mode 2), a

carbonitrided layer with lower total thickness (290 μm) and combined zone thickness (8 μm) than they are in the nitrided layer is obtained.

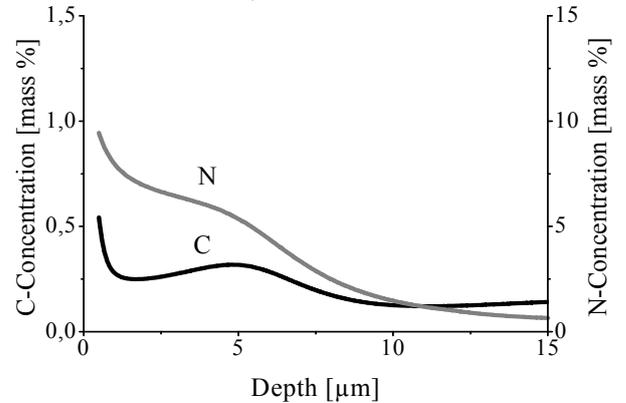
It can be noted that after carbonitriding in the media of 90% NH_3 + 8.2% Ar + 1.8% CO_2 at 400Pa pressure, a layer with lower micro-hardness, total thickness and combined zone thickness, than after the process of nitriding, is obtained. This is probably due to the availability of argon in the saturating medium, which, owing to its bigger atomic mass, has strong pulverizing action. With the high coefficient of pulverization the length of the free run of the pulverized atoms is bigger and the possibility for backward diffusion of the nitrogen and carbon is lower. Lower concentration of nitrogen (10%) and higher content of carbon by nearly 50% is obtained in the combined zone of the carbonitrided layer, compared to the nitrided one – Figure 1b.

It can be seen from Figure 1b that the concentration of carbon (0,48%) has increased at the border between the basic material and the combined zone, while under the carbonitride zone gradual change of the carbon content has been observed. This can be explained by the simultaneous saturation of the surface both with nitrogen and carbon, where part of the nitrogen atoms is replaced by the carbon ones.

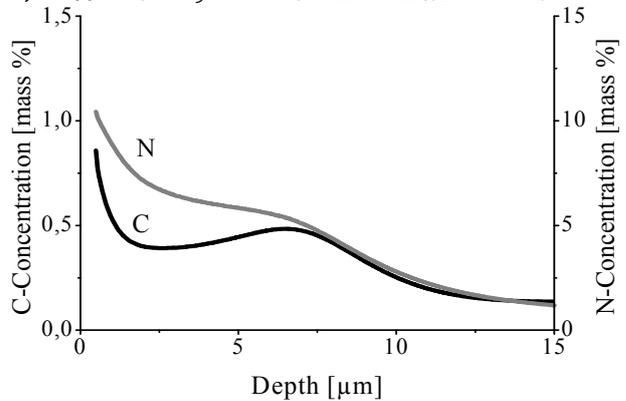
With the increase in the argon pressure ($P_{82\% \text{ Ar} + 18\% \text{ CO}_2} = 200 \text{ Pa}$, Table 2, modes 3 and 4) in the gas medium, after carbonitriding of 25CrMnSiNiMo steel, carbonitrided layers are formed, having lower micro-hardness (890 – 920 $\text{HV}_{0,1}$), total thickness (150 – 240 μm) and combined zone thickness than under the rest of the modes of treatment. This is due to the increased activity of pulverization, as the amount of argon in the gas medium is higher – 41%. The higher degree of pulverization leads to decreasing the probability for collisions between the atoms and ions, as a result of which lower amount of nitrogen and carbon is delivered to the surface. Lower concentration of nitrogen (20%) and increased content of carbon with nearly 20% is obtained in the combined zone of the carbonitrided layer in comparison with the nitrided one – Figure 2.

It can be seen from Figure 2a that at the end of the combined zone of the layer, at 5 μm depth, slight increase of the carbon up to 0,3 % is observed, while at the beginning of the combined zone the carbon is over 0,5 %. The concentration of the nitrogen in the carbonitrided zone decreases sharply, reaching at the end of the combined zone the level of 4.9 %, while the nitrogen on the surface is 9.1%. With prolongation of the time of carbonitriding from 2 to 6h (Table 2, mode 3) the micro-hardness and the combined zone thickness increase. Significant increase in the concentration of carbon in the combined zone can be

seen from Figure 3, where it achieves the level of 0,81% on the surface and slightly decreases at the end of the zone – down to about 0,5%. The distribution of the nitrogen in the carbonitrided zone decreases gradually. At the border between the diffusion zone and the combined zone the nitrogen concentration is 5.8 %, while on the surface it is 10.5%.



a) $t = 550 \text{ }^\circ\text{C}$, $P_{\text{NH}_3} = 200 \text{ Pa}$, $P_{82\% \text{ Ar} + 18\% \text{ CO}_2} = 200 \text{ Pa}$, $\tau = 2 \text{ h}$



b) $t = 550 \text{ }^\circ\text{C}$: $P_{\text{NH}_3} = 200 \text{ Pa}$, $P_{82\% \text{ Ar} + 18\% \text{ CO}_2} = 200 \text{ Pa}$, $\tau = 6 \text{ h}$
Figure 2. Distribution of carbon (C) and nitrogen (N) in depth after carbonitriding of 25CrMnSiNiMo steel

After carbonitriding of 25CrMnSiNiMo steel under the 5th mode of treatment from Table 2 in the gas medium of 70% NH_3 + 24,6 % Ar + 5,4 % CO_2 at 400 Pa pressure, a layer is obtained with total thickness 210 μm , maximum micro-hardness 930 $\text{HV}_{0,1}$ and combined zone thickness 9 μm . The distribution of the nitrogen and carbon in depth of the carbonitrided zone changes gradually, staying almost the same up to 7,5 μm – Figure 3.

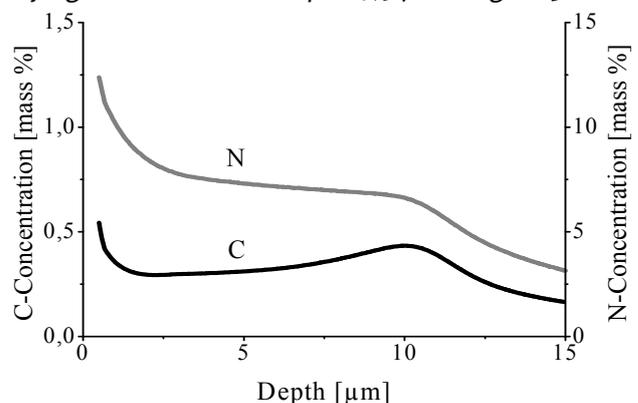


Figure 3. Distribution of carbon (C) and nitrogen (N) in depth after carbonitriding of 25CrMnSiNiMo steel at: $t = 550 \text{ }^\circ\text{C}$, $P_{\text{NH}_3} = 280 \text{ Pa}$, $P_{82\% \text{ Ar} + 18\% \text{ CO}_2} = 120 \text{ Pa}$, $\tau = 4 \text{ h}$

Significant increase in the concentration of carbon at the beginning of the combined zone can be seen from Figure 3, where it reaches the level of 0,52% and slightly decreases at the end of the carbonitrided zone, going to about 0,48 %. The distribution of the nitrogen in the carbonitrided zone changes gradually and its concentration at the end of the combined zone reaches the level of 7%, while at the beginning of the combined zone it is about 12,2 %. Under this mode of treatment the highest level of nitrogen concentration 12.2 % is achieved in the combined zone and the most gradual change of the content of nitrogen and carbon in the formed layer occur in comparison to all the other modes of ion carbonitriding of 25CrMnSiNiMo steel.

ARMCO-IRON

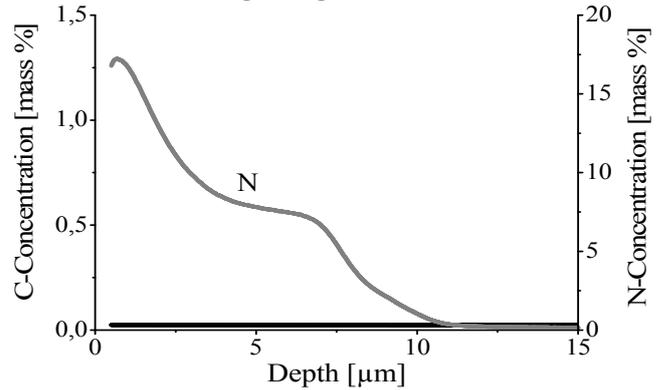
After nitriding of Armco-iron under the 6th mode of treatment from Table 2 a layer with micro-hardness of 415HV_{0,1}, total thickness of 290 μm and combined zone thickness of 6 μm is obtained. It can be noted from Figure 4a that the concentration of carbon in the nitrided layer has not changed at the border between the basic material and the combined zone. No increase of the carbon concentration on the surface of the layer is observed. The nitrogen concentration on the surface of the combined zone reaches 17,1%. After the process of ion nitriding the curve of the nitrogen distribution in the nitride zone does not change gradually.

Under the modes of nitriding 25CrMnSiNiMo steel is with higher micro-hardness but lower total thickness of the layer and thicker combined zone than Armco-iron. This is explained by the content of alloying constituents in the steel, which take part in forming the nitrides and hardening the surface layer. They inhibit the diffusion of nitrogen in depth, as a result of which thinner layers with thicker combined zones are obtained.

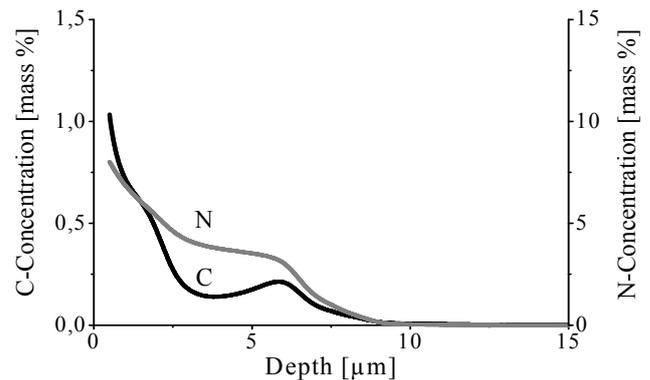
In Armco-iron carbonitriding under the 4th mode of treatment (50%HN₃ + 41% Ar + 9 %CO₂) from Table 2 a layer with surface micro-hardness of 370HV_{0,1}, total thickness of 210 μm and combined zone thickness of 6 μm is obtained and the distribution of nitrogen and carbon in depth of the carbonitrided zone is given in Figure 4b.

From Figure 4b it can be seen that at the end of the combined zone at 6 μm depth slight increase of the carbon content to 0,24 % is observed, while at the beginning of the combined zone the carbon content reaches 1 %. The figure shows that the distribution of carbon in depth of the combined zone is sharp to 3 μm depth with concentration of 0,20 %. At the end of the carbonitrided zone the carbon concentration increases to 0,24 %. The nitrogen distribution change in the carbonitrided layer goes gradually. At the end of

the combined zone (6 μm) its concentration reaches 3.4 %, while at its beginning the concentration is 8.3%.

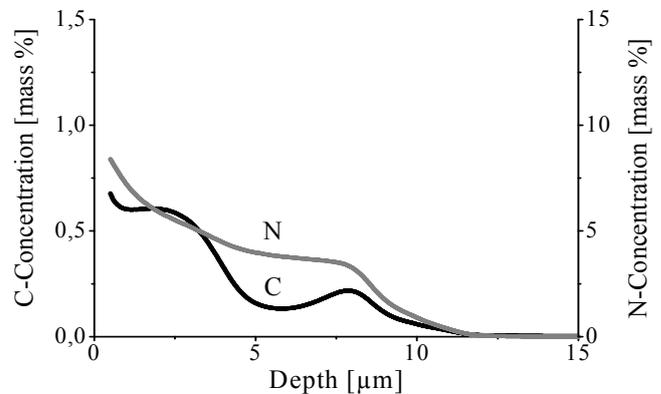


a) after nitriding $t = 550^{\circ}\text{C}$, $P_{\text{NH}_3} = 400 \text{ Pa}$, $\tau = 4 \text{ h}$

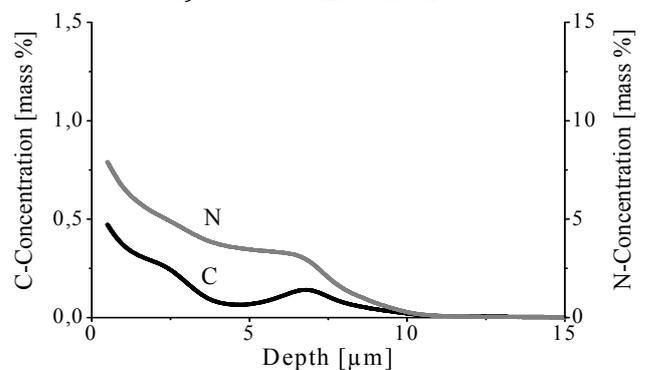


b) after carbonitriding $t = 550^{\circ}\text{C}$, $P_{\text{NH}_3} = 200 \text{ Pa}$, $P_{82\% \text{ Ar} + 18\% \text{ CO}_2} = 200 \text{ Pa}$, $\tau = 2$

Figure 4. Distribution of carbon (C) and nitrogen (N) in Armco-iron



a) after carbonitriding at: $t = 550^{\circ}\text{C}$, $P_{\text{NH}_3} = 280 \text{ Pa}$, $P_{82\% \text{ Ar} + 18\% \text{ CO}_2} = 120 \text{ Pa}$, $\tau = 4 \text{ h}$



b) after carbonitriding at: $t = 550^{\circ}\text{C}$, $P_{\text{NH}_3} = 360 \text{ Pa}$, $P_{82\% \text{ Ar} + 18\% \text{ CO}_2} = 40 \text{ Pa}$, $\tau = 2 \text{ h}$
 Figure 5. Distribution of carbon (C) and nitrogen (N) in Armco-iron

After ion carbonitriding of Armco-iron under the 5th mode (70%HN₃ + 24,6% Ar + 5,4 %CO₂) from Table 2, a layer with the highest surface micro-hardness 480HV_{0,1} is obtained, in comparison to all the other modes of treatment, which can be explained by the distribution of carbon and nitrogen in the carbonitrided zone - Figure 5a.

The figure illustrates that in depth of the combined zone increased carbon concentration of up to 0,68 % on the surface is observed, while it stays almost constant (0,65 %) at 3 μm depth. After that, at 6 μm, sharp decrease of the carbon content is observed, together with its increase (0,25%) at the end of the carbonitride zone of the layer.

The distribution of nitrogen in the carbonitride zone goes up gradually reaching 8,5 % on the surface, while at 3 μm depth it is 5.1%. It can be noted that under this mode of carbonitriding the nitrogen and carbon concentration changes more gradually and this concentration is higher in depth of the carbonitrided zone of the layer.

Figure 5b illustrates the distribution of carbon and nitrogen in Armco-iron after carbonitriding at: t = 550 °C, P_{NH₃} = 360 Pa, τ = 2 h, P_{82% Ar + 18% CO₂} = 40 Pa, mode 1, Table 2.

Under this mode of treatment a layer with surface micro-hardness of 430HV_{0,1}, total thickness of 260 μm and combined zone thickness of 6 μm is obtained. The concentration of carbon in depth of the layer is relatively low and reaches 0,48 % on the surface, while at 4,3 μm from the surface it has the lowest value (0,16%). At the end of the combined zone the concentration slightly increases (0,21%).

The distribution of nitrogen in the carbonitrided zone goes up gradually, reaching on the surface the level of 8.1 % and decreasing to 3.9 % at 4,3 μm from the surface. Under this mode of carbonitriding the carbon and nitrogen concentration changes gradually; however, their concentration is lower in depth of the combined zone than it is under the 5th mode of treatment from Table 2.

It can be noted that when in the process of carbonitriding the saturating medium contains bigger amount of CO₂ (9%), on the surface of Armco-iron combined zone with highest carbon concentration 1% is formed (mode 4, Table 2), while at (1.8 %) content of CO₂ the concentration is the lowest - 0.48%.

From the modes of carbonitriding of Armco-iron under consideration the most uniform distribution of nitrogen and carbon in depth of the layer is observed under the 5th mode from Table 2. The active role of argon for delivering carbon and nitrogen on the surface of the treated material is worth mentioning. As a result of its bigger atomic mass, argon has strong

pulverizing action. With the high coefficient of pulverization the length of the free run of the pulverized atoms is bigger and the possibility for backward diffusion of carbon and nitrogen is lower. By changes in the pressure, as well as in the content of argon in the saturating medium, the backward diffusion of nitrogen and carbon can be regulated, thus making it possible to obtain layers with different features and properties.

On the basis of the conducted glow discharge optical emission spectral analysis of samples from Armco-iron and 25CrMnSiNiMo steel it is necessary to note that under all modes of ion carbonitriding carried out in ammonia and corgon medium layers are formed with concentration of carbon in the combined zone, which, for the 25CrMnSiNiMo steel is within 0.6 % - 1.4 %, while for Armco-iron it is between 0.45% and 1%.

CONCLUSIONS

1. It has been established that the glow discharge optical emission spectroscopy can be used for investigating carbonitrided layers formed in low-temperature plasma in ammonia and corgon medium.
2. It has been proved that after carbonitriding of the investigated materials at t=550 °C, P_{NH₃} = 280 Pa, P_{82% Ar + 18% CO₂} = 120 Pa, τ = 4 h the most gradual change of the carbon and nitrogen content in the carbonitrided zone of the layer occurs.
3. Increased amount of carbon has been found both in the combined and in the diffusion zone of the carbonitrided layer.

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