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# Carbonitriding of Materials in Low Temperature Plasma

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Additional information is available at the end of the chapter

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## 1. Introduction

Nitriding and carbonitriding are used as basic processes for details and tools surface strengthening, during which a layer is formed on their surface, containing nitrogen or a combination of nitrogen and carbon.

When these two methods are used in conventional gas furnaces or in salt baths, the thickness of the layer or the composition of the resultant layers could not be reliably regulated, which necessitates varying with the potentials of nitrogen and carbon in the gas mixture or the liquid medium. The percentage of nitrogen and active carbon is defined by a few parameters, namely, temperature and composition of the gas mixture, and the possibilities for variation are limited.

During the process of carbonitriding and nitriding in glow discharge plasma these difficulties are resolved, which is an essential advantage of this method. The usage of glow electric discharge is a perspective method for nitriding and carbonitriding of materials in modern machine building.

The works [1,2,3,4,5] consider mainly the mechanism of building, the structure and the properties of the nitrided layers, obtained in low-temperature plasma, and present the peculiarities of carbonitriding in glow electric discharge. There is lack of data concerning carbonitriding in glow discharge plasma in an actuating medium, consisting of ammonia and gas corgon (82% Ar and 18% CO<sub>2</sub>), and there also lacks sufficient information of any comparative investigations between the two processes – nitriding and carbonitriding.

It is established in the works [3,5] that, when in the process of carbonitriding propane-butane is used as a carbon-carrier, the phase composition of the combined zone in the carbonitrided layer could not be precisely regulated. Better results could be obtained when

using a mixture of methane and argon [15]. In metal welding the role of the protective gas is often taken by carbon, which contains both argon and carbon dioxide in a particular ratio.

One of the aims of the present paper is to investigate the possibility to use gas corgon not only in welding but also as an indirect carbon-carrier in the process of simultaneous saturation of a metal surface with nitrogen and carbon (carbonitriding) at low temperatures. The small percentage (18%) of carbon dioxide in the gas corgon makes it possible to regulate the amount of carbon, introduced into the vacuum camera.

Despite the numerous investigations, conducted with the use of ammonia, nitrogen or a mixture of nitrogen and hydrogen as saturating media, there is no an integrated model yet, representing the mechanism of nitriding and carbonitriding in glow discharge. There are two principle methods concerning the question of forming diffusion capable nitrogen and carbon atoms on the surface of the treated articles.

According to the first method, iron nitrides are formed initially, which then dissociate into lower substances and release nitrogen, in its turn diffusing into the treated material. According to the model, developed by Kölbl, it is assumed that, as a result from the pulverization of iron in the glow discharge, iron nitrides rich of nitrogen are formed and they deposit on the surface of the treated articles. The deposited nitrides decompose and release nitrogen, which diffuses into the interior of the material. The availability of ions could increase the number of the centers of chemisorption. In nitrogen and hydrogen containing atmospheres the process goes with the participation of NH-radicals, which, after taking hydrogen, turn into the very active radical  $\text{NH}_2$ . In result from the interaction between the iron and the neutral nitrogen atoms or radicals on the surface of the substrate iron nitrides are formed, which release diffusion capable nitrogen.

According to the second method, diffusion capable nitrogen is directly formed on the surface of the treated articles, i.e., without the preliminary forming of iron nitrides. Materials, having cathode, anode or floating potential, have been treated by the comparatively new method of nitriding in two-step vacuum-arc discharge under low pressure. The fact, that the samples with a positive potential can be nitrided renounces the idea of forming iron nitrides in the gas medium, as a surface, subject to electron impact does not pulverize [15]. The high activity of the saturating medium in this case is due to the neutral nitrogen atoms. The process depends only on the concentration of atomic nitrogen and the temperature of the article, while the electron/ion impact plays the role of a convenient tool for ensuring the temperature needed for the process. By investigating the area of the dark cathode space of a direct current glow discharge in the presence of hydrogen the work for electron detachment from the iron is reduced and thus the absorption of the nitrogen atoms is facilitated. Ultimately, during the process of glow discharge nitriding, atomic nitrogen is formed on the surface of the articles, which, depending on their temperature, diffuses into their interior.

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 spectroscopes, not supposed so far, including

polymeric mass-spectroscopy, sensitive assessment of nano-materials, as well as analysis of very thin ( $<0.1 \mu\text{m}$ ) layers [ 6, 7, 8, 9]. 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 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.

Ensuring high quality of manufactured products is directly related to increasing their reliability and durability, which, in turn, are determined to a large extent by the internal stresses in the details.

One of the basic methods of increasing the wear resistance of details is the purposeful improvement of their surface layer properties by means of mechanical, thermal, chemical-thermal and other types of hardening treatment.

Since the values of the internal stresses are often below the limit of flow of the corresponding material, their measuring is highly demanding to the measuring equipment. There are plenty of methods for defining the internal stresses and they can be divided into the following two groups: destructive methods – the methods of disassembling, of hanging down (the slack method), of drilling, boring and trimming; non-destructive methods – the Roentgen method, the magnetic method, the ultrasound method and the neutron rays method.

The Roentgenographic method allows registering submicroscopic changes in the distances between the atoms corresponding to the measured planes in the crystal lattice of the grains for a mono-crystal material. It is a completely non-destructive method. Because of the limited depth of penetration of the X-rays, which, for steel is  $l \leq 20 \mu\text{m}$ , only the tense state of the closest to the surface layer is registered. The calculation principle used here allows determining of only two-axial internal stresses, parallel to the surface.

The distance between the atoms in the crystal lattice is normally about several nanometers. The wave length  $\lambda$  of the X-rays is also several dozens of nanometers, i.e., these quantities are of the same order. Therefore the Roentgen rays are considered to be among the most reliable for investigating the crystal structure.

The aim of the present work is to investigate the influence of the carbonitriding in a low-temperature plasma in an actuating medium consisting of ammonia and argon (82% Ar and 18%  $\text{CO}_2$ ) over the surface hardness, the total thickness of the carbonitrided layer, as well as its influence on the type and size of the formed compressive residual stresses on the surface and also to study the distribution of the nitrogen and carbon in depth of the formed layer of Armco-Fe and 25CrMnSiNiMo steel.

## 2. Methodology of investigation

### 2.1. Investigated materials and modes of thermal treatment

The investigated materials (Armco-Fe, 25CrMnSiNiMo steel) differ significantly by the availability and amount of alloying elements in them. The chemical composition of the materials mentioned above is checked by the equipment for automatic analysis “Spectrotest” [Table 1]. The low percentage of sulphur  $< 0.015\%$  in them guarantees a high level of hardness and toughness of the investigated materials.

Material	Chemical elements, weight percentage							
	C	Cr	Mo	Ni	P	Si	Mn	S
Armco-Fe	0.02	0.02	0.02	0.03	0.002	0.01	0.07	0.002
25CrMnSiNiMo	0.24	0.87	0.12	1.36	0.002	1.45	1.28	0.002

**Table 1.** Chemical composition of the materials

The requirement for a preliminary thermal treatment is imposed mainly by the following consideration: for achieving the desired mechanical parameters and structure, enabling a favorable process of nitrogen diffusion in depth. The investigated steel is thermally treated in a chamber furnace under modes [Table 2].

Material	$t_{\text{hard}}$ ( $^{\circ}\text{C}$ )	Cooling medium	$t_{\text{temp.}}$ (K)	$t_{\text{temp.}}$ ( $^{\circ}\text{C}$ )	Cooling medium
25CrMnSiNiMo	900	Oil	873	600	Air

**Table 2.** Modes of preliminary thermal treatment

Treated this way, the samples are then subjected to ion carbonitriding in the installation “Ion – 20”, according to the modes [Table 3]. Ammonia ( $\text{NH}_3$ ) and corgon (82 % Ar и 18%  $\text{CO}_2$ ) in different percentages are used as saturating gases. The temperature of treatment for the process of carbonitriding is 823K ( $550^{\circ}\text{C}$ ).

№ of the mode	Treatment	$\tau$ h	$P_1$ $\text{NH}_3$ Pa	$P_2$ corgon Pa	P total Pa	U V
1	nitriding	2	400	-	400	530
2	carbonitriding	2	360	40	400	470
3	carbonitriding	6	360	40	400	470
4	nitriding	6	400	-	400	530
5.	carbonitriding	6	200	200	400	415
6	carbonitriding	2	200	200	400	415
7	carbonitriding	4	280	120	400	435
8	nitriding	4	400	-	400	530
9	carbonitriding	2	350	350	700	380
10	carbonitriding	6	350	350	700	380

**Table 3.** Modes of nitriding and carbonitriding

## 2.2. Metallographic investigations

In order to clear out the morphological peculiarities of the nitrated and carbonitrided layers, metallographic analysis has been done.

When defining the structure and the thickness of the obtained layers metallographic pictures taken by means of a microscope – Axioscop – have been used.

The thickness of the nitrated and carbonitrided layer has been defined by the depth, to which hardness, equal to the core, has been achieved. Measuring the micro hardness has been done by means of a micro hardness-meter "Shimadzu" at a load of 0.98 N (100 g), following the Vickers' method.

## 2.3. Glow discharge optical emission spectroscopy

The process of defining the distribution of nitrogen and carbon in the nitrated 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<sup>-3</sup>, electron temperature 0.1 - 0.5 eV and plasma volume 15 cm<sup>3</sup>. The turbomolecular pump (56 l·s<sup>-1</sup>) works constantly. The basic pressure is 10<sup>-6</sup> 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.

## 2.4. Internal stresses

The investigation of the internal stresses in the carbonitrided samples is performed by means of a Roentgen diffraction-meter SET-X ENSAM, following the „sin<sup>2</sup>Ψ” method.

The direction of measuring is characterized by the angles Ψ: 0°, 14.96°, 21.42°, 26.57°, 31.09°, 35.26°, 37.23°, -10.52°, -18.43°, -24.09°, -28.88°, -33.21°, -37.27° and two angles φ=0 and φ=90 [Fig 1].

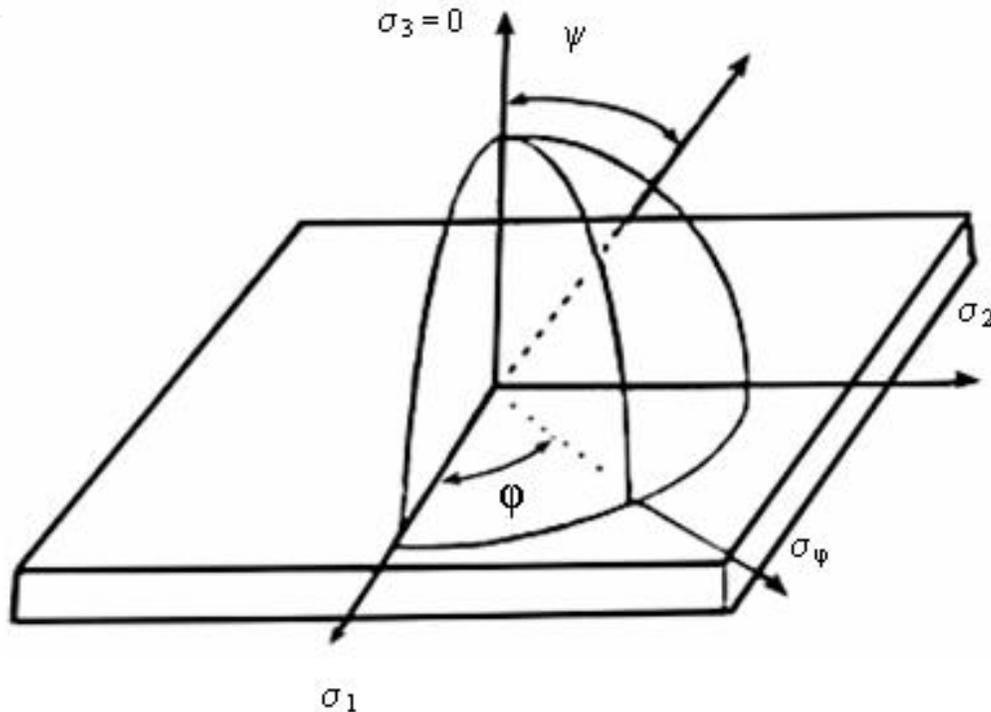
A powdered sample is used for standardizing the Roentgen diffraction-meter. Since the powdered sample is free of residual stresses, it allows checking and easily adjusting the device. In this particular case chromium Roentgen radiation Cr – Kα with a wave-length of λ=2.29Å was used. Information about the formed stresses is obtained at a distance of 7μm from the surface of the sample in a plane α - Fe {2 1 1}, i.e. the stresses are measured in α - Fe<sub>n</sub> - phase just under compound zone.

By means of the Roentgen diffraction-meter the diffraction angles in the carbonitrided layers are measured. The data are introduced into the program „MATHLAB-2008”. Through graphical representation of a straight line, built in the coordinates „2θ - sin<sup>2</sup> Ψ”, the value of the diffraction angle 2θ at sin<sup>2</sup> 90° is defined.

The residual stresses are defined by the following dependence:

$$\sigma_{\phi} = \frac{E}{2(1+\mu)} \cdot \cot \theta (2\theta_{\psi=0} - 2\theta_{\psi=90}) \frac{\pi}{180}$$

The values of the elasticity constants in the given formula are chosen for non - carbonitrided steel: Poisson's ratio  $\mu = 0.29$ , elasticity modulus  $E = 210$  GPA. The master diffraction angle is  $2\theta = 156^{\circ}30'$  and  $\theta = 78^{\circ}15'$ . The miscunt at defining stresses depends on the relative mistake  $\Delta\theta/\theta$  at defining the angle  $\theta$ . It is within 2 - 3%.



**Figure 1.** Characteristics of the direction of measuring by the angles  $\Psi$  and  $\phi$

### 3. Experimental results and analysis

#### 3.1. Metallurgical analysis of carbonitriding fixtures

By measuring the micro hardness of thermally treated and ion-nitrided samples in depth, the maximum surface hardness -  $HV_{0.1}$  - and the total thickness of the nitrided layer -  $\delta_{tot}$  - have been defined; by means of a metallographic microscope the thickness of the combined zone -  $\delta_{cz}$  - has been determined. The results are given in [Table 4].

It can be seen [Table 4] that after nitriding 25GrMnSiNiMo steel and Armco-Fe, under the modes [1, 8 and 4], a nitrided layer with different surface micro hardness, total thickness and combined zone thickness is obtained. Under these three modes of nitriding 25GrMnSiNiMo steel has a higher micro hardness but a lower total thickness of the layer and a thicker combined zone than Armco-Fe. This fact could be explained by the presence of alloying constituents in the steel, which actively participate in forming nitrides and

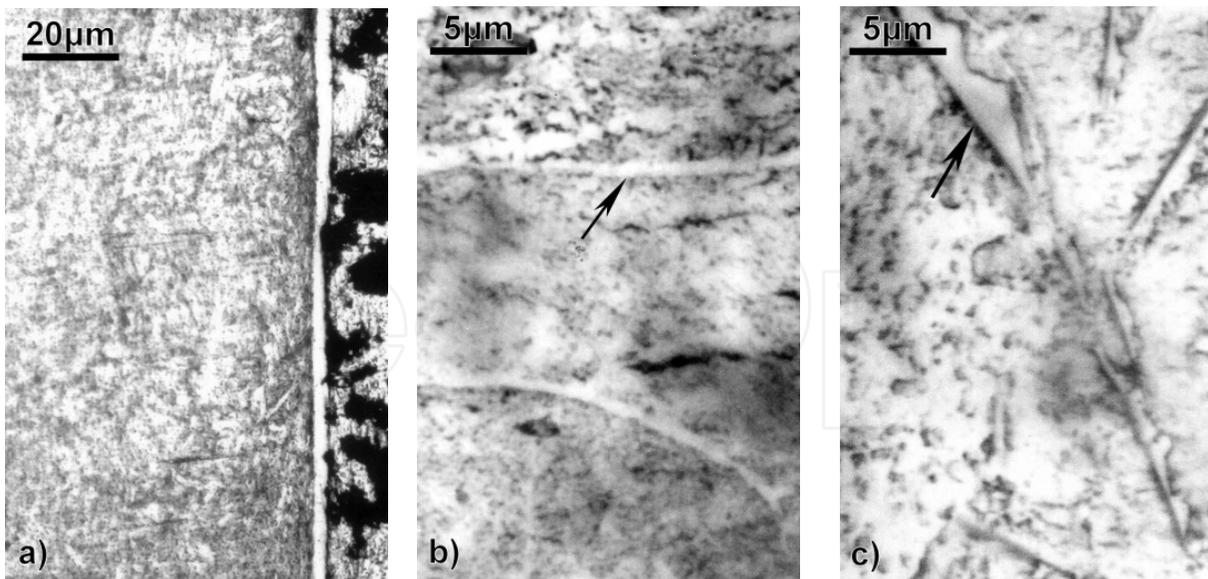
strengthening the surface layer. They impede the diffusion of the nitrogen in depth, and in consequence, thinner layers with a thicker combined zone are obtained.

№ of the mode	25GrMnSiNiMo			Armco-Fe			
	HV <sub>0.1</sub> MPa	$\delta_{tot}$ $\mu\text{m}$	$\delta_{cz}$ $\mu\text{m}$	HV <sub>0.1</sub> MPa	$\delta_{tot}$ $\mu\text{m}$	$\delta_{cz}$ $\mu\text{m}$	U V
1	8500	170	6	3800	220	5	530
2	9400	160	5	4300	260	6	470
3	8600	290	8	4200	340	7	470
4	9800	300	11	4200	350	10	530
5	9200	240	8	4400	330	7	415
6	8900	150	5	3700	210	6	415
7	9300	210	6	4800	280	6	435
8	9500	230	7	4150	290	6	530
9	7400	140	4	5400	210	4	380
10	7500	230	5	5600	320	8	380

**Table 4.** Results from carbonitriding and nitriding of 25GrMnSiNiMo steel and Armco-Fe samples

During the process of carbonitriding of 25GrMnSiNiMo steel in a medium, consisting of 90% NH<sub>3</sub> + 8.2% Ar + 1.8 % CO<sub>2</sub> at the pressure of 400Pa, a layer with a lower micro hardness (HV<sub>0.1</sub>= 9400 - 8600MPa), total thickness (160 - 290  $\mu\text{m}$ ) and combined zone thickness (5 - 8 $\mu\text{m}$ ) is obtained, than after the process of nitriding without addition of a carbon-containing gas. This is most likely due to the small percentage of argon (8.2%) in the gas medium, since argon, because of its bigger atomic mass, has a strong pulverizing action. At the high coefficient of pulverizing the length of the free run of the pulverized atoms is bigger and the possibility for a backward diffusion of carbon and nitrogen is lower. A carbonitrided layer with a lower concentration of nitrogen and carbon is obtained. The more active pulverization does not allow the combined zone to grow and, as a result, a more deficient in nitrogen and carbon combined zone is obtained. In the diffusion zone of the carbonitrided layer of the steel detectable nitrided (carbonitrided) precipitations are not observed – [Fig.2.a].

After Armco-Fe carbonitriding under the same mode there are no similar dependences established during the process of forming the layer as the ones, described for 25GrMnSiNiMo steel. The obtained carbonitrided layer has a higher surface micro hardness (HV<sub>0.1</sub>= 4200 – 4300 MPa), total thickness (260-340  $\mu\text{m}$ ) and combined zone thickness (6-7  $\mu\text{m}$ ). In the diffusion zone of a carbonitrided layer considerable amounts of nitrided (carbonitrided) precipitations are observed, mainly in the area of the grains. The precipitations originate at the boundary of the grains and propagate inward the volume. A bigger amount of precipitations is observed under the longer mode (6h) of carbonitriding – [Fig.2.c].



**Figure 2.** Microstructure of 25GrMnSiNiMo steel [a] and Armco-Fe [b, c] after carbonitriding at:  $t = 550^{\circ}\text{C}$ ,  $P_{\text{NH}_3} = 360\text{Pa}$ ,  $P_{82\% \text{Ar} + 18\% \text{CO}_2} = 40\text{Pa}$ ; a, c -  $\tau = 6\text{h}$ , b -  $\tau = 2\text{h}$

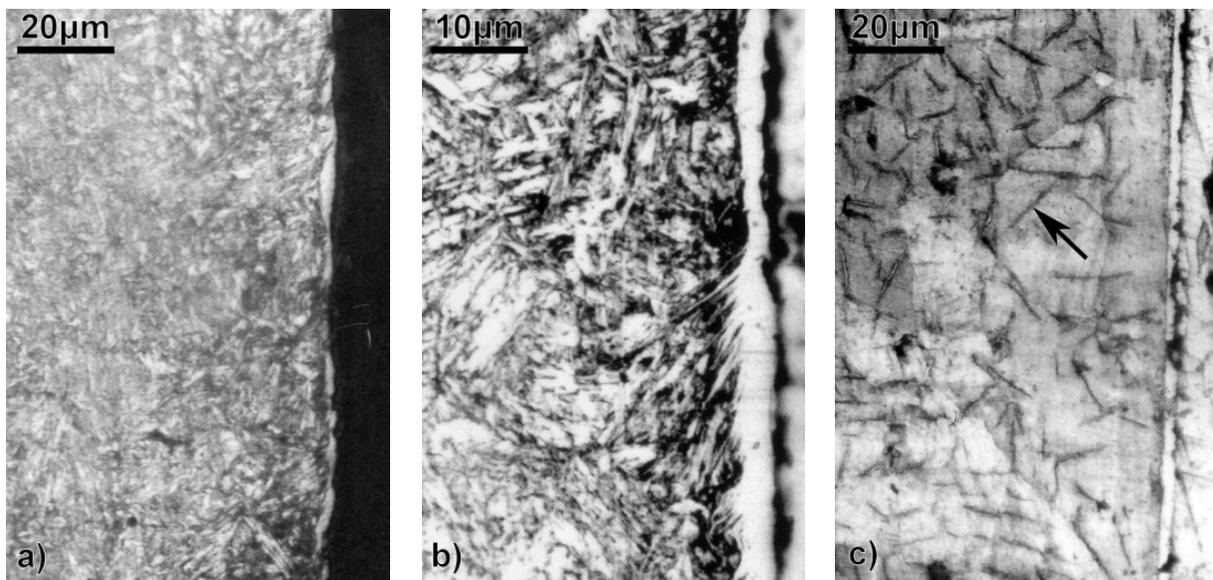
Together with the increase in the pressure of carbon ( $P_{82\% \text{Ar} + 18\% \text{CO}_2} = 200\text{Pa}$ , [Table 4]) in a gas medium, in case of 25GrMnSiNiMo steel treatment carbonitrided layers are formed, having lower micro hardness ( $\text{HV}_{0.1} = 8900\text{--}9200\text{ MPa}$ ), total thickness ( $150\text{--}240\ \mu\text{m}$ ) and combined zone thickness ( $5\text{--}8\ \mu\text{m}$ ), than under the modes of treatment, considered so far. It is due to the increased activity of pulverizing, since the amount of argon in the gas medium is bigger - 41%. The higher rate of pulverizing leads to decreasing the probability for collisions between the atoms and ions, in consequence of which smaller amount of nitrogen and carbon is delivered to the surface. The microstructure analysis of the layer does not show detectable differences in the precipitations in the diffusion zone – [Fig.3 a-b].

The process of Armco-Fe carbonitriding under the same conditions ( $P_{82\% \text{Ar} + 18\% \text{CO}_2} = 200\text{Pa}$ , [Table 4], [modes 5-6]) leads to obtaining a layer with higher micro hardness ( $\text{HV}_{0.1} = 4400\text{ MPa}$ ) than in the process of nitriding -  $\text{HV}_{0.1} = 4200\text{ MPa}$ . It can be seen from [Fig.2.2c] that in the obtained carbonitrided layer there are carbonitrided (nitrided) precipitations with smaller sizes but in greater amount than in the layer, obtained after treatment with a bigger amount of ammonia ( $90\% \text{NH}_3 + 8.2\% \text{Ar} + 1.8\% \text{CO}_2$ ).

After 25GrMnSiNiMo steel carbonitriding under the mode 7 [Table 4] in a gas medium of  $70\% \text{NH}_3 + 24.6\% \text{Ar} + 5.4\% \text{CO}_2$  at the pressure of  $400\text{Pa}$ , a  $210\ \mu\text{m}$  layer with maximum micro hardness  $\text{HV}_{0.1} = 9300\text{ MPa}$  and combined zone thickness of  $6\ \mu\text{m}$  is obtained.

During the process of Armco-Fe carbonitriding under the same mode [mode 7], [Table 1] a layer with highest surface micro hardness of  $\text{HV}_{0.1} = 4800\text{ MPa}$  is obtained, in comparison to all the modes of treatment, considered so far. In the diffusion zone of the formed carbonitrided layer carbonitrided (nitrided) precipitations are observed [Fig. 2.3], which are of smaller sizes and in greater amount than the ones, obtained at using  $90\% \text{NH}_3$  and  $10\% \text{Ar}$  [Table 4, modes 2- 3, Fig.2.]; and bigger in size but in a smaller amount at

carbonitriding with 50% NH<sub>3</sub> and 50 % carbon [Table 1, modes 5-6, Fig.3]. This is probably due to the diffusion of carbon in the diffusion zone of the carbonitrided layer as well. Together with the increase of the pressure of the gas medium to 700Pa (NH<sub>3</sub> - 350 Pa and argon -350 Pa – [modes 9-10, Table 1] in the process of carbonitriding of the two materials under investigation, layers with essential differences are formed. After 25GrMnSiNiMo steel carbonitriding layers with a lowest surface micro hardness ( $HV_{0.1} = 7400 - 7500$  MPa) and total thickness (140 -230  $\mu\text{m}$ ) in comparison to all the other modes of nitriding and carbonitriding are obtained. The white zone is non-uniform and broken – [Fig.4]. This is probably due to the increased amount of argon in the gas medium and the high density of the current at the higher pressure of the gas medium, as well as to the low voltage of the discharge [380V, Table 4.].



**Figure 3.** Microstructure of 25GrMnSiNiMo steel [a, b] and Armco-Fe[c] after carbonitriding at:  $t = 550^{\circ}\text{C}$ ,  $P_{\text{NH}_3} = 200\text{Pa}$ ,  $P_{82\% \text{ Ar} + 18\% \text{ CO}_2} = 200\text{Pa}$ ; a, c -  $\tau = 2\text{h}$ , b -  $\tau = 6\text{h}$

After Armco-Fe carbonitriding under the same modes of treatment a layer with highest micro hardness ( $HV_{0.1} = 5400-5600$  MPa) and lowest combined zone thickness (4  $\mu\text{m}$ ) in comparison to all the other modes of nitriding and carbonitriding is obtained. In the diffusion zone of the carbonitrided layer the smallest amount of precipitations with the smallest sizes in comparison to all the other modes of carbonitriding is observed.

Under the same mode of treatment, 25GrMnSiNiMo steel possesses higher micro hardness and smaller total thickness of the nitrided and carbonitrided layer, than Armco-Fe. After certain treatment of 25GrMnSiNiMo steel with an additionally introduced carbon-containing gas (carbon) in the ammonia medium at different percentage ratios layers with lower depth, surface hardness and combined zone thickness than in the process of nitriding are obtained.

After conducting the process of carbonitriding of the investigated materials with carbon (82 % Ar + 18 % CO<sub>2</sub>) and ammonia, layers of small combined zone thickness are obtained. For

Armco-Fe the thickness is within 4 to 8  $\mu\text{m}$ . During the process of nitriding of technical iron, a nitrided layer is formed, having the biggest combined zone [10  $\mu\text{m}$ , mode 4, Table 4], which is not valid for the other modes of nitriding. The increase in the duration of the process and the decrease in carbon pressure lead to combined zone growth. During the process of 25GrMnSiNiMo steel carbonitriding this dependence remains the same. After 25GrMnSiNiMo steel nitriding a layer with a bigger combined zone is observed, than during the process of carbonitriding (6-11  $\mu\text{m}$  against 4-8  $\mu\text{m}$ ). This is explained by the stronger pulverizing action of plasma as a consequence of the increase in current density and decrease in voltage after introducing carbon into the ammonia medium.

It could be noted that the use of carbon together with ammonia in the process of carbonitriding leads to decrease in the pressure of plasma discharge, which depends on the ratio between the two gases. When introducing carbon into the camera, the pressure of the discharge falls down. In order to reach the required temperature of carbonitriding in this case it is necessary to increase the current of the discharge. Thus the power of plasma remains the same. The increase of the current density leads to an increase in the pulverizing action of plasma, despite of the low voltage level. This is explained by the bigger amount of ions, bombing the surface of the detail. The bigger current density does not lead to an increase in the kinetic energy of the ions. The decrease in the pressure of the gases in the camera causes an increase in the discharge voltage and the kinetic energy of the ions increases at the same time as a result, though their amount remains unchanged. The coefficient of pulverizing could also be increased this way, which would lead to a decrease in the combined zone thickness.

### 3.2. Roentgenographic determination of internal stresses

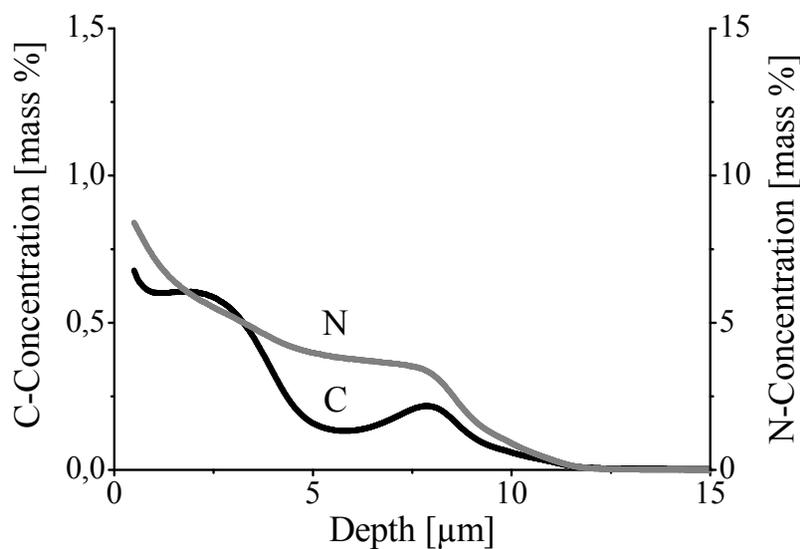
By means of the Roentgen diffraction-meter the diffraction angles at different angles of rotation of the sample -  $\Psi$  и  $\phi$  - are measured in the carbonitrided layers. The data are introduced into the program „MATHLAB-2008“, by means of which graphs are built and the values of the angle  $2\theta$  for  $\sin^2\Psi$ , at  $\Psi=90^\circ$  are calculated.

After defining the angle  $2\theta^s$  at  $\Psi=90^\circ$  for all carbonitrided samples, residual compressive stresses in the carbonitrided layers have been calculated. The results are given in Table 5. Three ways of defining the diffraction angles have been used: the maximum intensity method -  $\sigma^{\phi s}$ , the chord method -  $\sigma^{\phi c}$ , and the body centre method -  $\sigma^{\phi b}$ .

Material	$\tau$ [h]	$P_1$ NH <sub>3</sub> [Pa]	$P_2$ corgon [Pa]	HV <sub>0.1</sub>	$\delta_{\text{tot}}$ [ $\mu\text{m}$ ]	$\delta_{\text{cz}}$ [ $\mu\text{m}$ ]	$\sigma^{\phi s}$ [MPa]	$\sigma^{\phi c}$ [MPa]	$\sigma^{\phi b}$ [MPa]
Armco-Fe	4	280	120	480	280	6.5	-54	-28	-14
25CrMnSiNiMo	4	280	120	930	210	6.3	-584	-621	-521
25CrMnSiNiMo	2	200	200	890	150	4.5	-829	-713	-655
25CrMnSiNiMo	2	350	350	740	140	4.1	-90	-63	-41

**Table 5.** Results from the obtained residual stresses

It can be seen [Table 5] that after ion carbonitriding of Armco-iron at  $t_{\text{nit.}} = 823\text{K}$  ( $550^\circ\text{C}$ ),  $P_{\text{NH}_3} = 280\text{Pa}$ ,  $\tau = 4\text{h}$ , a carbonitrided layer with total thickness  $\delta_{\text{tot}}=280\mu\text{m}$ , compound zone thickness  $\delta_{\text{cz}} = 6,5 \mu\text{m}$  and maximum micro-hardness of  $480\text{HV}0.1$  is obtained. In the so formed layer compressive residual stresses occur. From the three methods of defining the diffraction angles the method of maximum intensity is the one from which the highest value of residual stresses ( $\sigma^{\text{ps}} = -54\text{MPa}$ ) results. The compressive stresses, resulting after the ion carbonitriding in the surface layer of Armco-Fe are much lower than those of 25CrMnSiNiMo. During the process of Armco-Fe carbonitriding, a diffusion layer with bigger specific volume is formed, than it occurs with alloyed steel. This can be explained by the bigger total amount of nitrogen and carbon in depth the carbonitrided layer for 25CrMnSiNiMo steel [Fig.4].



**Figure 4.** Nitrogen and carbon profile analysis according to GDOES in depth of a layer, carbonitrided at:  $t = 823\text{K}$  ( $550^\circ\text{C}$ ),  $P_{\text{ammonia}}=280\text{Pa}$ ,  $P_{\text{carbon}}=120\text{Pa}$ ,  $\tau = 4\text{h}$ , 25CrMnSiNiMo

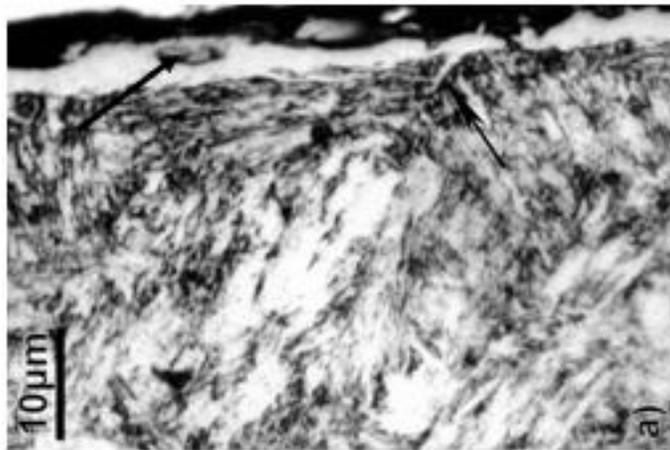
Because of the lack of alloying elements in the Armco-Fe, no special carbonitrides are formed in it, and the difference in the specific volumes of the carbonitrided layer and the core material is therefore smaller. This leads to reducing the value of the residual stresses formed in the carbonitrided layer in Armco-Fe.

After ion carbonitriding of 25CrMnSiNiMo steel at  $t_{\text{nit.}} = 823\text{K}$  ( $550^\circ\text{C}$ ),  $P_{\text{NH}_3} = 200\text{Pa}$ ,  $P_{\text{carbon}} = 200\text{Pa}$ ,  $\tau = 2\text{h}$ , a carbonitrided layer with total thickness  $\delta_{\text{tot}} = 150\mu\text{m}$ , compound zone thickness  $\delta_{\text{cz}} = 4.5\mu\text{m}$  and maximum micro-hardness of  $890\text{HV}0.1$  is obtained. In thus obtained carbonitrided layer residual compressive stresses with the highest value of  $\sigma^{\text{ps}} = -829\text{MPa}$  are formed.

With prolongation of the time of 25CrMnSiNiMo-steel carbonitriding from 2 to 4 hours and reducing the carbon pressure from 200 to 120 Pa while increasing ammonia pressure from 200 to 280 Pa, a carbonitrided layer with higher total thickness  $\delta_{\text{tot}} = 210\mu\text{m}$ , compound zone thickness  $\delta_{\text{cz}} = 6.3 \mu\text{m}$ , and higher maximum micro-hardness -  $930\text{HV}0.1$  - is formed. The resultant compressive stresses on the carbonitrided surface are lowered to  $\sigma^{\text{ps}} = 584$

MPa. The explanation can be found in the phase composition and the thickness of the compound zone ( $\delta_{cz}=6.3 \mu\text{m}$ ).

Together with increasing ammonia and carbon pressure from 200 to 350 Pa for 2 hours' time of treatment a carbonitrided layer with total thickness  $\delta_{tot} = 140 \mu\text{m}$ , compound zone thickness  $\delta_{cz} = 4.1 \mu\text{m}$  and maximum micro-hardness 740HV0.1 is obtained. In the carbonitrided layer, obtained this way, the smallest residual compressive stresses of  $\sigma^{\phi s} = -90 \text{MPa}$  are formed. The high pressure of the two saturating gases  $P_{tot} = 700 \text{ Pa}$  does not activate the process of pulverizing and therefore a bigger amount of nitrogen and carbon is delivered to the surface. This probably leads to forming a bigger amount of micro-pores in the white zone [Fig.5], as a consequence of which the specific volume of the carbonitrided surface formed is bigger than the one in the core material.



**Figure 5.** Microstructure of 25CrMnSiNiMo -steel after carbonitriding at:  $t = 823 \text{K}$  ( $550^\circ \text{C}$ ),  $P_{\text{NH}_3} = 350 \text{Pa}$ ,  $P_{82\% \text{ Ar} + 18\% \text{ CO}_2} = 350 \text{Pa}$ ,  $\tau = 2 \text{h}$

In the process of 25CrMnSiNiMo-steel ion carbonitriding the increase of ammonia pressure ( $P_{\text{NH}_3} = 200\text{-}350 \text{ Pa}$ ) in the saturating medium forms a carbonitrided layer with approximately the same total thickness ( $\delta_{tot} = 140\text{-}150 \mu\text{m}$ ) and compound zone thickness ( $\delta_{cz} = 4.1 - 4.5 \mu\text{m}$ ), but with lower micro-hardness (890 – 740 HV0,1). This leads to a considerable decrease of the residual compressive stresses on the carbonitrided surface ( $\sigma^{\phi s} = 829 - 90 \text{MPa}$ ).

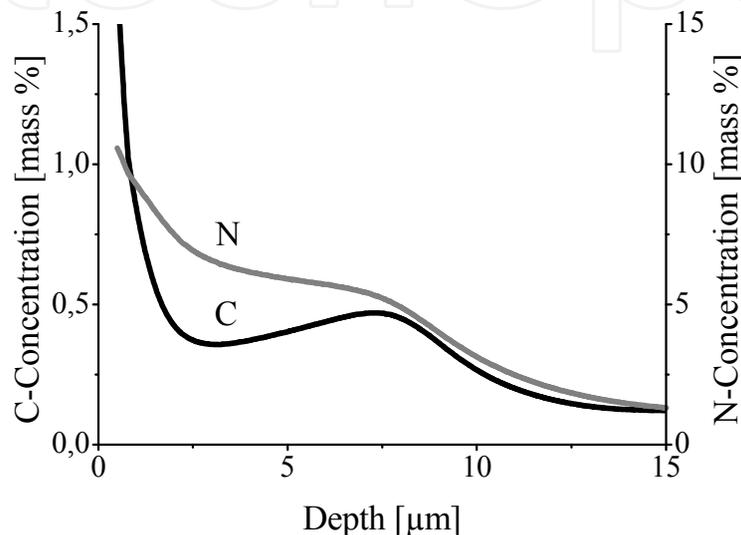
It can be noted that under the same modes of ion carbonitriding [modes 1 and 2, Table 5] the two materials under investigation form different residual compressive stresses on their surfaces ( $\sigma^{\phi s} = 54\text{-}584 \text{ MPa}$ ). This significant difference is explained by the availability of alloying elements in the 25CrMnSiNiMo-steel, which, after the process of carbonitriding, form disperse carbonitrides. This leads to certain increase in the micro-hardness and in the specific volume of the carbonitrided layer and thence, to increase in the residual compressive stresses on the surface as well.

It can be noted from the conducted investigations that the chosen modes of ion carbonitriding form on the surface of the materials carbonitride layers with a bigger specific volume than on the core.

Depending on the concentration of nitrogen and carbon in the carbonitrided layer, as well as on the alloying elements contained in the materials, the specific volume of the surface changes; this, in turn, leads to forming residual compressive stresses of different values.

### 3.3. Results from the analysis and the investigations of 25CrMnSiNiMo steel

After nitriding under the mode 6 [Table 2] a layer is formed in 25CrMnSiNiMo steel with micro-hardness of 1072HV<sub>0,1</sub>, total thickness of 250  $\mu\text{m}$  and combined zone thickness of 10  $\mu\text{m}$ . The distribution of the diffused in depth nitrogen is given in [Fig. 6].



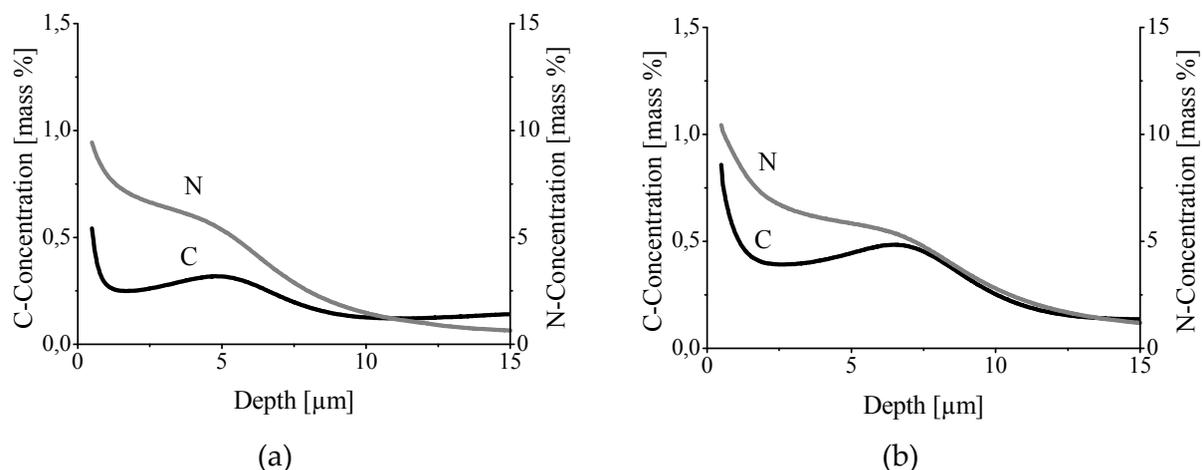
**Figure 6.** Carbon (C) and nitrogen (N) concentration in depth after carbonitriding of 25CrMnSiNiMo steel at:  $t = 550\text{ }^{\circ}\text{C}$ ,  $P_{\text{NH}_3} = 360\text{ Pa}$ ,  $P_{82\% \text{ Ar} + 18\% \text{ CO}_2} = 40\text{ Pa}$ ,  $\tau = 6\text{ h}$

When, except for ammonia, 10% carbon is introduced into the chamber in addition, a carbonitrided layer with lower total thickness (290  $\mu\text{m}$ ) and combined zone thickness (8  $\mu\text{m}$ ) than they are in the nitrided layer is obtained.

It can be noted that after carbonitriding in the media of 90%  $\text{NH}_3$  + 8.2%  $\text{Ar}$  + 1.8%  $\text{CO}_2$  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 carbon 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 – [Fig.6].

It can be seen from [Fig.6] 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 carbon 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  $\mu\text{m}$ ) 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 – [Fig.7].



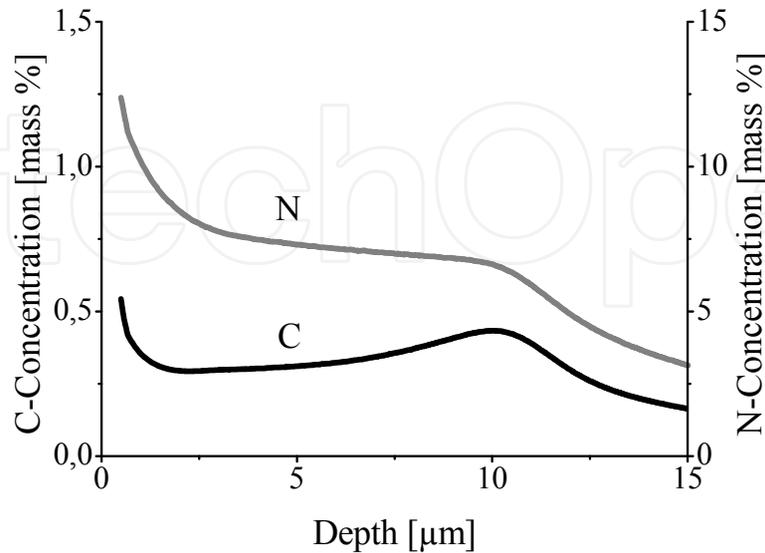
**Figure 7.** Distribution of carbon (C) and nitrogen (N) in depth after carbonitriding of 25CrMnSiNiMo steel at: a)  $t = 550 \text{ }^\circ\text{C}$ ,  $P_{\text{NH}_3} = 200 \text{ Pa}$ ,  $P_{82\% \text{ Ar} + 18\% \text{ CO}_2} = 200 \text{ Pa}$ ,  $\tau = 2 \text{ h}$ , b)  $t = 550 \text{ }^\circ\text{C}$ :  $P_{\text{NH}_3} = 200 \text{ Pa}$ ,  $P_{82\% \text{ Ar} + 18\% \text{ CO}_2} = 200 \text{ Pa}$ ,  $\tau = 6 \text{ h}$

It can be seen from [Fig.7.a].that at the end of the combined zone of the layer, at 5  $\mu\text{m}$  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 the micro-hardness and the combined zone thickness increase. Significant increase in the concentration of carbon in the combined zone can be seen from [Fig.8], 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%.

After carbonitriding of 25CrMnSiNiMo steel under the 5<sup>th</sup> mode of treatment [Table 2] in the gas medium of 70%  $\text{NH}_3 + 24.6 \text{ } \%$  Ar + 5.4 %  $\text{CO}_2$  at 400 Pa pressure, a layer is obtained with total thickness 210  $\mu\text{m}$ , maximum micro-hardness 930 $\text{HV}_{0,1}$  and combined zone thickness 9

$\mu\text{m}$ . The distribution of the nitrogen and carbon in depth of the carbonitrided zone changes gradually, staying almost the same up to  $7.5 \mu\text{m}$  – [Fig.8].



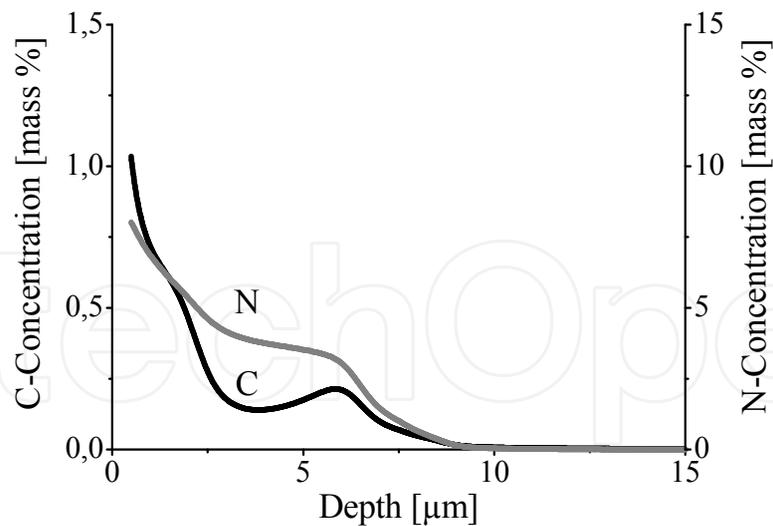
**Figure 8.** Distribution of carbon (C) and nitrogen (N) in depth after carbonitriding of 25CrMnSiNiMo steel at:  $t = 550 \text{ }^\circ\text{C}$ ,  $P_{\text{NH}_3} = 280 \text{ Pa}$ ,  $P_{82\% \text{ Ar} + 18\% \text{ CO}_2} = 120 \text{ Pa}$ ,  $\tau = 4 \text{ h}$

Significant increase in the concentration of carbon at the beginning of the combined zone can be seen from [Fig. 8], 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 occurs in comparison to all the other modes of ion carbonitriding of 25CrMnSiNiMo steel.

### 3.4. Armco-iron

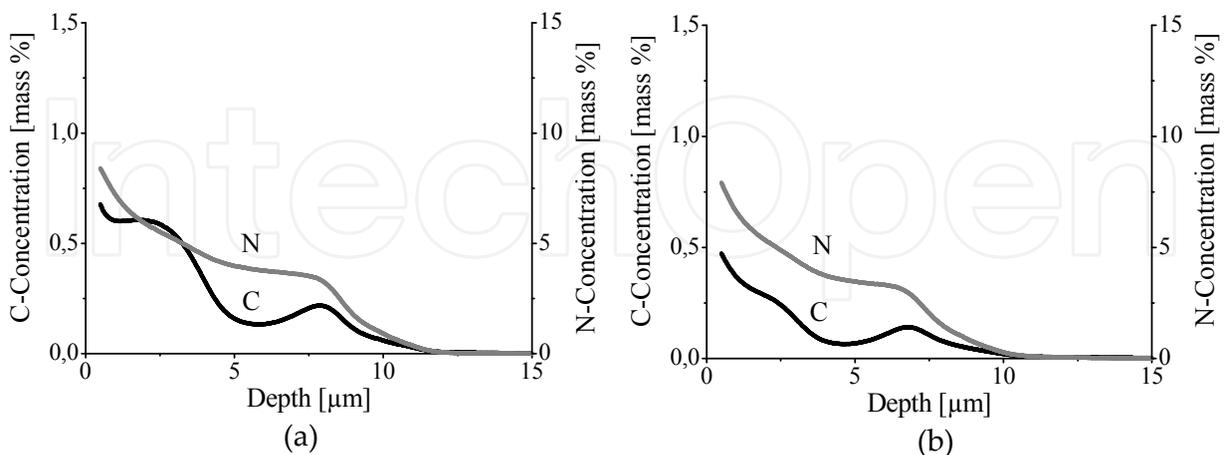
In Armco-iron carbonitriding under the 4<sup>th</sup> mode of treatment (50% $\text{HN}_3$  + 41% Ar + 9% $\text{CO}_2$ ) from Table 2 a layer with surface micro-hardness of 370HV<sub>0.1</sub>, total thickness of 210  $\mu\text{m}$  and combined zone thickness of 6  $\mu\text{m}$  is obtained and the distribution of nitrogen and carbon in depth of the carbonitrided zone is given in [Fig. 9].

From [Fig.9] it can be seen that at the end of the combined zone at 6  $\mu\text{m}$  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  $\mu\text{m}$  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  $\mu\text{m}$ ) its concentration reaches 3.4%, while at its beginning the concentration is 8.3%.



**Figure 9.** Distribution of carbon (C) and nitrogen (N) in Armco-iron after carbonitriding  $t = 550\text{ }^{\circ}\text{C}$ ,  $P_{\text{NH}_3} = 200\text{ Pa}$ ,  $P_{82\% \text{ Ar} + 18\% \text{ CO}_2} = 200\text{ Pa}$ ,  $\tau = 2$

After ion carbonitriding of Armco-iron under the 5<sup>th</sup> mode (70% $\text{HN}_3$  + 24.6% Ar + 5.4 % $\text{CO}_2$ ), a layer with the highest surface micro-hardness 480HV<sub>0.1</sub> 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 – [Fig. 10a]. 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  $\mu\text{m}$  depth. After that, at 6  $\mu\text{m}$ , 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  $\mu\text{m}$  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 10.** Distribution of carbon (C) and nitrogen (N) in Armco-iron, after carbonitriding at: a)  $t = 550\text{ }^{\circ}\text{C}$ ,  $P_{\text{NH}_3} = 280\text{ Pa}$ ,  $P_{82\% \text{ Ar} + 18\% \text{ CO}_2} = 120\text{ Pa}$ ,  $\tau = 4\text{ h}$ , b)  $t = 550\text{ }^{\circ}\text{C}$ ,  $P_{\text{NH}_3} = 360\text{ Pa}$ ,  $P_{82\% \text{ Ar} + 18\% \text{ CO}_2} = 40\text{ Pa}$ ,  $\tau = 2\text{ h}$

[Fig.10.b] illustrates the distribution of carbon and nitrogen in Armco-iron after carbonitriding at:  $t = 550\text{ }^{\circ}\text{C}$ ,  $P_{\text{NH}_3} = 360\text{ Pa}$ ,  $\tau = 2\text{ h}$ ,  $P_{82\% \text{ Ar} + 18\% \text{ CO}_2} = 40\text{ Pa}$ .

Under this mode of treatment a layer with surface micro-hardness of 430HV<sub>0.1</sub>, total thickness of 260 μm and combined zone thickness of 6μm 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 4.3μm 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 5<sup>th</sup> mode of treatment [Table 2].

It can be noted that when in the process of carbonitriding the saturating medium contains bigger amount of CO<sub>2</sub> (9%), on the surface of Armco-iron combined zone with highest carbon concentration 1% is formed, while at (1.8 %) content of CO<sub>2</sub> 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 5<sup>th</sup> mode [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 carbon 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 %.

### 3.5. Dissociation and ionization of carbon dioxide and ammonia

It is necessary to note that two areas could be distinguished in the structure of the glow discharge: the zone of the discharge, where the processes of dissociation of the employed gases (CO<sub>2</sub>, NH<sub>3</sub>, Ar) occur, and the zone of the discharge, where reactions of recombination proceed.

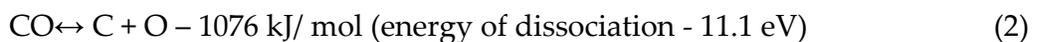
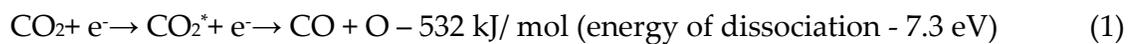
Carbon dioxide dissociation has been investigated by a great number of authors both theoretically and experimentally by using various sources of plasma such as a microwave discharge, a plasma reactive burner or radio frequency arc discharge. Despite the numerous works the kinetic mechanism of CO<sub>2</sub> dissociation has not been studied very well yet [2.5]. Actually the mechanism of CO<sub>2</sub> dissociation is determined mainly by the parameters of the glow discharge (average energy of the electrons in the plasma) and the properties of the plasma gas (pressure, velocity of flow, energy) [10.11].

In the cathode space of the glow discharge [Fig.11] the ordered motion of electrons and the position of the positively charged ions is the predominant event, while in the anode section the chaotic motion of the electrically charged particles prevails. Electrons are detached from

the cathode and they are accelerated in the direction towards the anode, acquiring energy, sufficient for dissociation and ionization of the atoms and molecules. The obtained positive ions are directed toward the cathode (C) and, colliding with its surface, they cause an emission of new electrons, while the secondary electrons, formed during the ionization, are accelerated by the field toward the anode (A). The cathode dark space in the structure of the glow discharge [Fig.11] includes the whole area of the cathode up to the next section of the negative glowing. This area is related to a big part of the voltage, called cathode fall of the potential. In this area the gas glowing is weak, as the energy of the electrons is higher than the maximum for excitation. This energy is sufficient for causing dissociation and ionization of the employed gases. The electrons, originated from the ionization of the atoms, are accelerated by the field and move toward the area of the negative glowing.

The gases in this area are in ionized state (plasma). The plasma results from the accelerated electrons, coming from the cathode dark space. At the moment the accelerated electrons impact the CO<sub>2</sub> molecule, it decomposes in result from the bond breakage, which leads to forming CO, C and O, expressed by the following reactions [12, 13]:

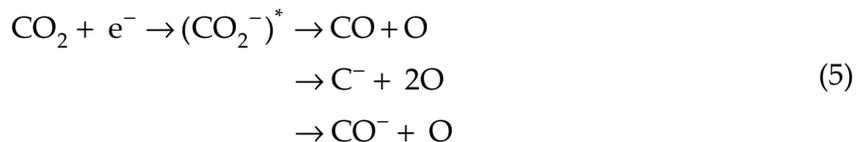
a. Dissociation at direct electron impact:



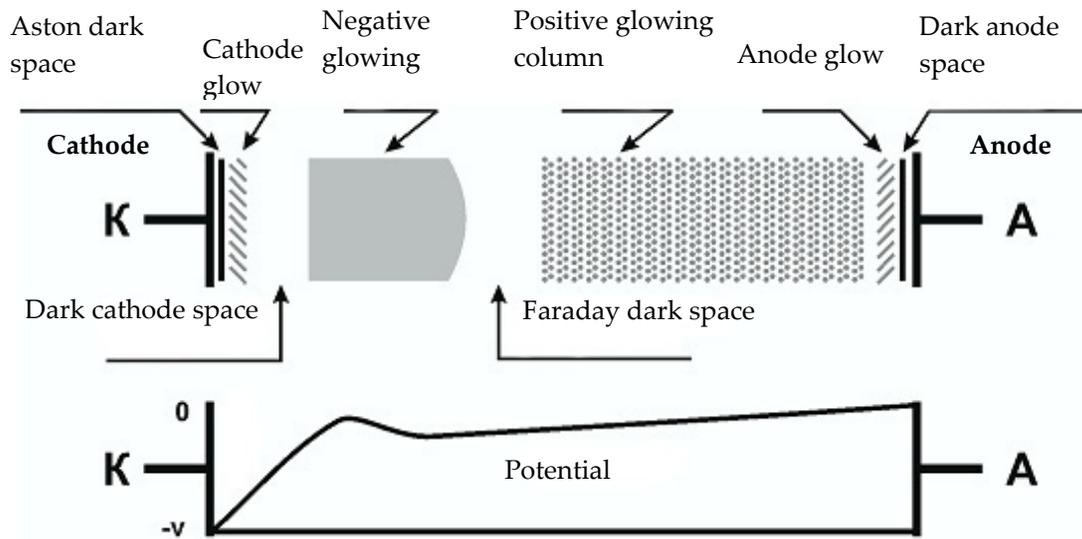
The symbol \* corresponds to the state of high excitation. The addition of inert gases (He, Ar) into the CO<sub>2</sub> medium leads to increasing the average energy of the electron in the discharge. At sufficient concentration of CO<sub>2</sub>, considerable reduction in the energy used for dissociation of one molecule is achieved.

It can be noted that with the increase in the vibration temperature the energy consumption for forming an atom reduces significantly since in these cases the decomposition of molecules is facilitated. However, the energy consumption for forming a carbon atom many times exceeds the energy for molecular dissociation. This is the case with CO. It can be explained first of all by the higher energy of dissociation of CO so that it considerably exceeds the average energy of the electron and the process of dissociation becomes a multiple-stage one.

b. dissociation bonding

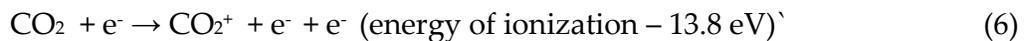


During the reaction the negative ions from CO<sub>2</sub> are minority [12]. The last reaction could lead to forming vibration excited CO<sub>2</sub> molecules by recombination of CO<sup>-</sup> and O, causing dissociation in CO + O after that.

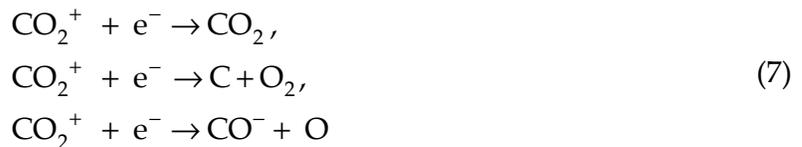


**Figure 11.** Glow discharge structure

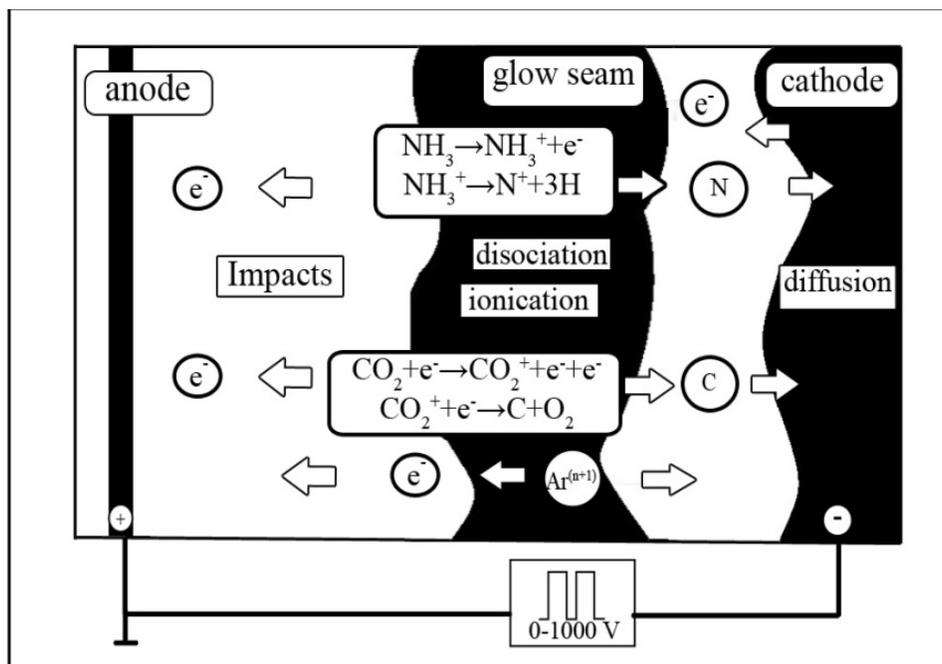
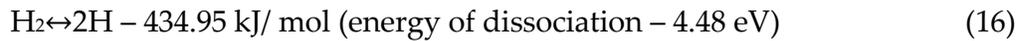
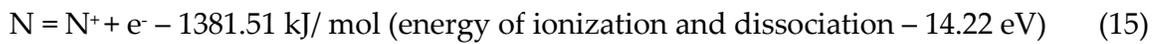
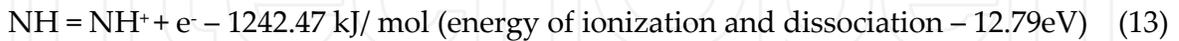
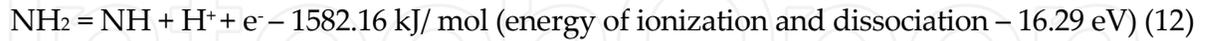
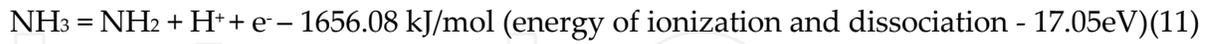
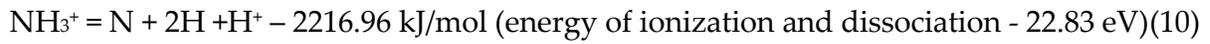
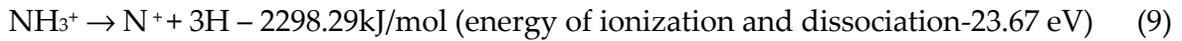
c. ionization at electron collision



For the initial process of ionization many different types of positive ions are obtained ( $\text{CO}^+$ ,  $\text{O}^+$ ,  $\text{O}_2^+$ ), but the most important is  $\text{CO}_2^+$ , the others are usually neglected [11,12]. Recently the following reactions have been identified [1,5]:



It can be noted that  $\text{CO}_2^+$  molecules can be formed in two excited states and forming a stable  $\text{CO}_2^+$  dominates.  $\text{CO}_2$  dissociation is mainly due to vibration excitation caused by electron collisions. It is clear in this case that by heating the employed gases in imbalanced conditions higher efficiency of dissociation can be achieved, since then the introduced energy is not used in all degrees of freedom. As the molecular dissociation goes due to vibration excitation, the effective dissociation could occur at imbalanced conditions, in which the increase in the vibration excited states is higher than it is at balanced conditions. Therefore it is assumed that molecular dissociation occurs in imbalanced plasma with high vibration temperature. With the imbalanced gas the efficiency of the dissociation increases for two reasons. The first reason is the comparatively smaller energy, used for excitation of translational and rotational degrees of freedom. The second reason is the inharmoniousness of the molecules, leading to an increase of the relative number of vibration excited molecules. Due to it the same extent of dissociation of the molecules is obtained at lower temperature of vibration, than the temperature at the lack of inharmoniousness. It can be noted that in the zone of the negative glowing of the glow discharge both processes of dissociation and ammonia ionization occur, leading to obtaining nitrogen and hydrogen by the following probable reactions:



**Figure 12.** Reactions, going in close proximity of the cathode space in a medium of ammonia, carbon dioxide and argon

On the basis of the above exposed data the following probable mechanism of carbonitriding in a saturating medium of ammonia and argon could be suggested:

As the energy of dissociation and ionization of ammonia and carbon dioxide is higher, in the area of the cathode fall of the glow discharge probably atomic carbon should form initially by the reaction  $\text{CO}_2^+ + \text{e}^- \rightarrow \text{C} + \text{O}_2$  and atomic nitrogen by the reaction  $\text{NH}_3^+ = \text{N} + 3\text{H}$ . The dissociation of the ammonia molecule and the breakage of the carbon-oxygen bonds go close to the cathode in the zone of the negative glowing. Consequently, processes of ionization of

the carbon (reaction  $\text{CO}_2 + e^- \rightarrow \text{CO}_2^+ \rightarrow \text{C}^+ + 2\text{O}$ ) and nitrogen (reaction  $\text{NH}_3^+ = \text{N}^+ + 3\text{H}$ ) atoms occur; these atoms impact the surface and diffuse at a certain distance into the material – [Fig.12]. The process of saturation of the metal surface depends only on the concentration of the atomic carbon and nitrogen in the plasma, as well as on the temperature of the article, while the electron or ion impact plays role for ensuring the necessary temperature of the details.

The availability of argon in the saturating medium in combination with  $\text{CO}_2$ , leads to increasing the average energy in the discharge, which, at sufficient concentration of  $\text{CO}_2$ , results in considerable reduction of the energy spent on the dissociation of a molecule.

In the process of carbonitriding part of the nitrogen atoms are replaced by the bigger carbon atoms, which causes forming the  $\epsilon$ -phase in the carbonitrided layer. It is possible for two reasons: approximately the same ion radius of the nitrogen [ $r_{\text{ion}} = 13(5+1)$  pm,  $r_{\text{ion}} = 16(3+1)$  pm] and the carbon [ $r_{\text{ion}} = 16(4+1)$  pm]; the possibility for the carbon atoms to take up the vacant junctions.

#### 4. Conclusion

1. It is established that, after ion carbonitriding of 25GrMnSiNiMo steel at the same temperature of treatment and time of saturation but different composition of the two gases in the vacuum camera (ammonia – 50, 70, 90, 100% and corgon - 50, 30 , 10%), the layers obtained have smaller thickness and micro hardness than after ion nitriding.
2. It is established that, the gases corgon and ammonia can be used in different percentage ratio in the role of saturating medium during the process of carbonitriding in glow discharge plasma.
3. 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.
4. It has been proved that after carbonitriding of the investigated materials at  $t=550$  °C,  $P_{\text{NH}_3} = 280$  Pa,  $P_{82\% \text{ Ar} + 18\% \text{ CO}_2} = 120$  Pa,  $\tau = 4$  h the most gradual change of the carbon and nitrogen content in the carbonitrided zone of the layer occurs.
5. Increased amount of carbon has been found both in the combined and in the diffusion zone of the carbonitrided layer.
6. After carbonitriding in low temperature plasma, difference between the values of the residual compressive stresses, obtained by the three ways of defining diffraction angles (the method of maximum intensity -  $\sigma^{\text{ps}}$ , the cord method -  $\sigma^{\text{pc}}$ , and the method of the body centre -  $\sigma^{\text{pb}}$ ) has been established.
7. It has been established that, after the process of ion carbonitriding, the residual compressive stresses formed on the surface of the alloyed steel 25CrMnSiNiMo have a considerably higher value, than the value of these stresses in Armco-Fe.
8. It has been proved that in the process of ion carbonitriding of the investigated materials, the increase in the ammonia and carbon pressure in the vacuum chamber leads to a decrease in the value of the residual compressive stresses.
9. A probable mechanism of glow discharge carbonitriding in a medium of ammonia, carbon dioxide and argon is suggested. As a consequence of the dissociation and

ionization of the ammonia molecules and the carbon dioxide molecules, close to the cathode in the zone of the negative glowing diffusion capable nitrogen and carbon are obtained, which impact the surface and diffuse at a certain distance into the material. The process of saturation of the metal surface depends only on the concentration of the atomic carbon and nitrogen in the plasma and the temperature of the article, while the electron/ion impact plays role for ensuring the necessary temperature of the details.

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