ANNALS OF THE FACULTY OF ENGINEERING HUNEDOARA
2006, Tome IV, Fascicole 3, (ISSN 1584 – 2673)
FACULTY OF ENGINEERING HUNEDOARA,
5, REVOLUTIEI, 331128, HUNEDOARA

# ON THE INFLUENCE OF THE PROCESS OF CARBONITRIDING IN SMOULDERING DISCHARGE ON THE PROPERTIES OF 25CrMnSiNiMo STEEL

Angel ZIUMBILEV[1], Ilia ZIUMBILEV[1], Krasimir NIKOLOV[2]

[1] TU SOFIA – PLOVDIV BRANCH,
SECTION MATERIAL SCIENCE AND TECHNOLOGIES, PLOVDIV, BULGARIA

[2] DOC DORTMUNDER OBERFLÄCHENCENTRUM GMBH,
DORTMUND, GERMANY

**Abstract:**
The aim of this paper is to investigate the influence of the processes of nitriding and carbonitriding in smouldering discharge on the parameters of the obtained layers and on certain mechanical and technological properties of 25CrMnSiNiMo steel (GOST).

The influence of the two processes has been examined under three considerably different modes of treatment. Ammonia and propane-butane in certain percentage proportion at different time and constant temperature are used as saturating gases.

The results show that at the same temperature (550 $^0$C) and time of treatment (4h), but at different saturating gas media ($NH_3$, $C_3H_8$ – $C_4H_{10}$), the layers formed after ion carbonitriding are with lower thickness and micro hardness than the ones formed after ion nitriding. It has been established that after conducting the processes of carbonitriding and nitriding in low temperature plasma, the impact strength of 25CrMnSiNiMo steel reduces by 15 %. Bigger reduction of the relative extension of 25CrMnSiNiMo steel is observed after carbonitriding. After ion carbonitriding the heat resistance of 25CrMnSiNiMo steel is higher than after nitriding.

**Keywords:**
processes of nitriding and carbonitriding, layers,
mechanical and technological properties, steel

## 1. INTRODUCTION

Nitriding and carbonitriding are basic methods for surface strengthening of details and tools made of iron-carbon alloys, during which nitrogen only or nitrogen and carbon are built in the surface layer.

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.

When the processes of carbonitriding and nitriding are conducted in the plasma of a smouldering discharge, these difficulties are avoided, which is the main advantage of the method. Using a smouldering electrical discharge for details processing is a perspective method for materials nitriding and carbonitriding in the modern machine building.

The nitrided and carbonitrided layers are characterized with high values of hardness and wear resistance. Together with their positive sides, however, the layers have an essential disadvantage, namely, their high brittleness. The carbide and nitride particles formed in the diffusion layer act as concentrators of the pressures. These zones can be regarded as the most dangerous from the point of view of the brittleness, since cracks originate in them. The nitrided and carbonitrided details are a multi-layer system, consisting of a basic material (core) and a layer [3,11]. The results obtained from testing the nitrided (carbonitrided) samples to strain characterize the joint deformation and the hardness of the covering layer and the core. The testing defines the properties of the test samples with layers in comparison to samples without layers.

In works [1,2,3,5] mainly the mechanism of building, the structure and properties of the nitrided layers obtained in low temperature plasma are considered, while papers [3,4,6 ] reveal basic problems related to carbonitriding in conventional gas furnaces, and [7,12,15] describe carbonitriding in smouldering electrical discharge. There is lack of complete data in the examined literature of comparative investigations about the influence of nitriding and carbonitriding in low temperature plasma on the basic characteristics of the obtained surface layers.

The aim of the present work is to investigate the influence of the processes of nitriding and carbonitriding over the parameters of the obtained layers and certain mechanical and technological properties of 25CrMnSiNiMo steel.

## 2. METHODOLOGY OF THE INVESTIGATIONS

### 2.1. Materials under investigation

25CrMnSiNiMo steel, which is actually a complex steel alloy with low carbon percentage, was chosen to be used for the investigations. The chemical composition of the steel mentioned above was examined by means of equipment for automatic analysis "Spectrotest". The results are given in table 1. From the steel test samples with sizes 15x10 x10 mm and surface roughness $R_a$ = 0.63 µm are made

Table 1. Chemical composition of the investigated steel

| Steel | Chemical elements, weight percentage | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | C | Si | Mn | Cr | Ni | S | P | Mo |
| 25CrMnSiNiMo | 0.24 | 1.45 | 1.28 | 0.87 | 1.36 | 0.002 | 0.002 | 0.12 |

### 2.2. Modes of thermal treatment, ion nitriding and carbonitriding

The test samples were treated thermally in a chamber furnace in an oxidative medium according to the modes, presented in table 2.

Table 2. Modes of preliminary thermal treatment

| Steel | t hard., ° C | Cooling medium | t temp., ° C | Cooling medium |
|---|---|---|---|---|
| 25CrMnSiNiMo | 900 | Oil | 600 | Air |

The samples were nitrided and carbonitrided in a "Ion-20" installation according to the modes, presented in table 3. Ammonia ($NH_3$) and propane-butane ($C_3H_8$ - $C_4H_{10}$) in different percentage ratios were used as saturating gases. Both nitriding and carbonitriding were conducted at temperature 550 °C.

### 2.3. Metallographic investigations

In order to establish the morphological peculiarities of the nitrided and carbonitrided layers metallographic analysis was carried out. The distribution of nitrogen and oxygen in depth of the layer was examined by optical spectroscopy with the help of the device GDA 750, produced by Spectruma-Analytic GmbH.

Table 3. Modes of nitriding and carbonitriding

| № Of the mode | Treatment | $\tau_1$ h | $P_1$ $NH_3$ Pa | $P_2$ $NH_3$ Pa | $\tau_2$ h | $P_3$ $C_3H_8$ $C_4H_{10}$ Pa | Total P Pa | Total $\tau$ h | Voltage. U V |
|---|---|---|---|---|---|---|---|---|---|
| 1 | nitriding | 4 | 400 | - | - | - | 400 | 4 | 530 |
| 2 | carbonitriding | 4 | 360 | - | - | 40 | 400 | 4 | 620 |
| 3 | carbonitriding | 2 | 400 | 360 | 2 | 40 | 400 | 4 | 570 |
| 4 | nitriding | 4 | 200 | - | - | - | 200 | 4 | 560 |
| 5 | carbonitriding | 4 | 180 | - | - | 20 | 200 | 4 | 670 |
| 6 | carbonitriding | 2 | 200 | 180 | 2 | 20 | 200 | 4 | 630 |

In the process of clearing out the structure, the parameters and the thickness of the nitrided layers a microscope "Axioskop" was used and metallographic pictures were taken by means of it.

Measuring the micro hardness of the nitrided samples was carried out by means of a micro-hardness meter "Shimadzu" with a load of 0.49N following the "Vikers" method. During the process of defining the heat resistance of the layers, the level of hardness of the additionally tempered nitrided and carbonitrided samples was measured by the Vikers method with a load of 49.05N.

The impact strength of the thermally treated, ion nitrided and carbonitrided 25CrMnSiNiMo steel was defined by using standard samples with sizes of 55 x 55x10 mm and a V-shaped opening. The test for impact three-point bending was done with a fly hammer IO 5003 with maximum energy of 150 J.

In testing 25CrMnSiNiMo steel at strain standard cylindrical samples with given sizes ($l_0$ = 75 mm,$d_0$ = 7.5 mm ) were used in accordance with ISO 6892-1984. The procedure of testing the samples at strain was carried out with the help of an universal machine "INSTRON-1343" type at the following conditions: traverse velocity -1mm/min, perceptor - tensor resistant, dynamic with sensitivity 2.5mv/mm, base - 25mm and running - 2.5mm.

Defining the heat resistance of the nitrided and carbonitrided layers was done after measuring the hardness (HV5) of the additionally tempered at different temperatures ($550^0$, $600^0$, $650^0$C) nitrided and carbonitrided test samples. The additional tempering of the samples lasted 4 hours. The heat resistance was defined through the limiting temperature of additional tempering, at which hardness of 5500 HV5 was retained for 4 hours.

## 3. EXPERIMENTAL RESULTS AND DISCUSSION

### 3.1. Preliminary thermal treatment

The results from measuring the hardness after the thermal treatment are given in table 4.

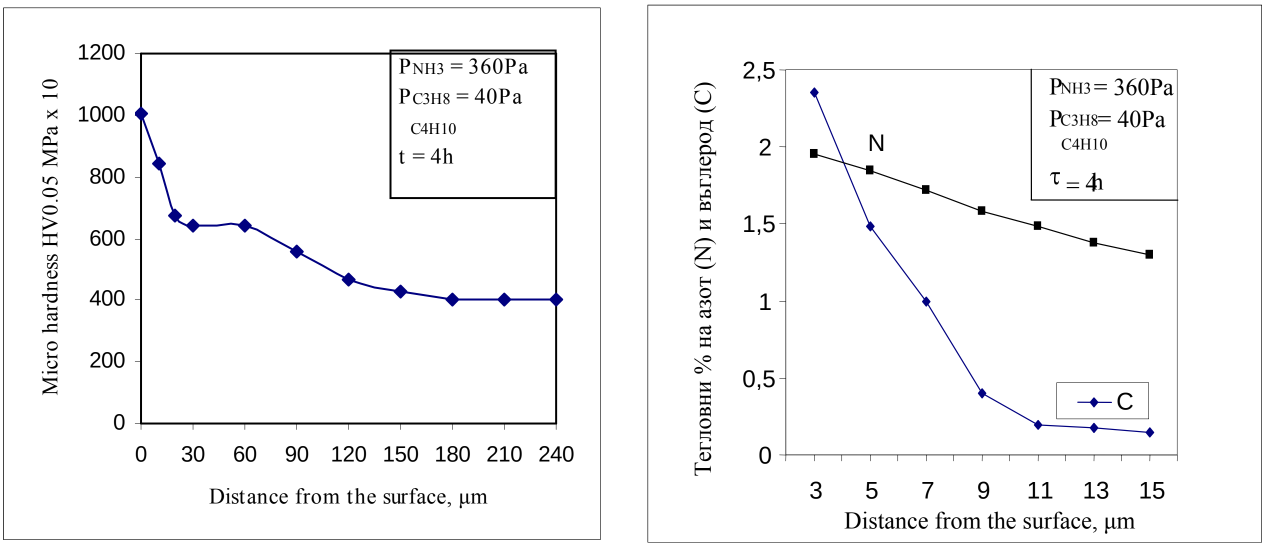
Table 4. Results from the preliminary thermal treatment

| Steel | Hardness, HRC | |
|---|---|---|
| | Hardening | Tempering |
| 25CrMnSiNiMo | 47 | 35 |

### 3.2. Ion nitrided and carbonitrided samples

### 3.2.1. Metallographic amalysis

By means of measuring the micro hardness of the thermally treated, ion nitrided and carbonitrided samples in depth, the maximum surface hardness – $HV_{0,05}$ and the total thickness of the nitrided (carbonitrided) layer δtot (Fig.1a) are found, and with the help of a metallographic microscope the thickness of the compound zone - δcz is defined. The results are given in table 5.



a b

Figure 1. Distribution of the micro hardness (a) and the amount of nitrogen and hydrogen (б) in depth of the layer

Table 5. Results from ion carbonitriding and nitriding

| № of the mode from table 3 | $HV_{0.05}$ MPa | δcz µm | δtot µm | Rm MPa | $R_{P0,2}$ MPa | A % | Heat resistance 5500 HV5/4h $^0$C | KCV MJ/m$^2$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 10720 | 9 | 270 | 895 | 800 | 2.7 | 570 | 0.35 |
| 2 | 10060 | 5 | 180 | 780 | 740 | 2 | 590 | 0.32 |
| 3 | 9460 | 8 | 210 | 850 | 775 | 2.4 | 565 | 0.30 |
| 4 | 10060 | 7 | 240 | 800 | 750 | 2.6 | 560 | 0.31 |
| 5 | 8410 | 3 | 120 | 910 | 820 | 1.5 | 585 | 0.38 |
| 6 | 8410 | 6 | 180 | 875 | 780 | 1.7 | 560 | 0.33 |
| Not nitrided sample | 3500 | — | | 930 | 760 | 2.8 | — | 0.42 |

From table 5 it can be noticed that after ion nitriding of 25CrMnSiNiMo steel under the modes 1 and 4 a nitrided layer with different surface micro hardness, total thickness and combined zone thickness is obtained. Under the two modes of nitriding of 25CrMnSiNiMo steel high value of hardness is obtained, which can be explained with the content of alloying constituents in the steel, participating actively in forming nitrides and in hardening the surface layer. They impede the diffusion of the nitrogen in depth and, as a result, thinner layers with thicker combined zone are obtained. Steel nitriding at a higher level of ammonia pressure - 400Pa (first mode, table 3) is the reason for the higher micro hardness and thickness of the layer, than they are at ammonia pressure of 200Pa. With the higher ammonia pressure we have a smaller coefficient of pulverizing, which, in turn, contributes to the reverse diffusion of the nitrogen.

During the process of carbonitriding of 25CrMnSiNiMo steel in a medium of 90% $NH_3$ +10 % $C_3H_8$ -$C_4H_{10}$ at 400Pa pressure (mode 2, table 5) a layer with lower micro hardness ($HV_{0.05}$ = 10060MPa), total thickness (180 μm) and combined zone thickness is formed than after the process of niriding. This is probably due to the small content of propane-butane ($C_3H_8$ -$C_4H_{10}$) in the gas medium (10%), which increases the voltage of the discharge and consequently the coefficient of pulverizing grows up. At the higher coefficient of pulverizing the length of the free run of the pulverized atoms is bigger and the opportunity for a reverse diffusion of carbon and nitrogen is smaller. A carbonitrided layer with lower concentration of nitrogen but higher concentration of carbon is obtained. The more active pulverizing does not give any chances for the combined zone to grow, since it contains less nitrogen and more carbon (Fig.1 b).

With the decrease of the time of saturation with ammonia (2h) and the increase of the duration of treatment with propane-butane (2h) at 400Pa pressure (table 5, mode 3) carbonitrided layers with higher total thickness (210-250 μm) and combined zone thickness (8-6μm) than during the second mode of carbontriding of the two types of steel are formed. This is due to the initial saturation of the test samples with ammonia only within 2 hours. The availability of a certain amount of nitrogen on the surface leads to accelerating the diffusion of carbon at the second stage of the simultaneous saturation with nitrogen and carbon, as a consequence of which thicker carbonitrided layers are obtained.

After ion carbonitriding of the steel at lower ammonia and propane-butane pressure (modes 5 and 6, table 3) carbonitrided layers with lower total thickness and combined zone thickness are obtained than at the higher pressure of the two gases - 400Pa (modes 2 and 3, table 3). This can be explained with the higher work voltage of the discharge (U= 630-670V, table 5), which is caused by the lower pressure of the two saturating gases (200Pa), leading, in turn, to an increase in the coefficient of pulverizing and thus to limiting the reverse diffusion of the nitrogen and carbon on the surface of the sample.

The compound zone thickness, obtained during the process of ion nitriding is always bigger than the one, formed during the simultaneous saturation of the two steels with nitrogen and carbon at the same pressure if the gases in the vacuum chamber. This can be explained by the following fact: when propane-butane enters the vacuum chamber, the voltage of the discharge increases by more than 10% (table 3) and, as a result, the coefficient of pulverizing increases, which, in turn, increases the amount of the detached carbon and nitrogen atoms from the surface of the test samples. The replacement of the nitrogen atoms by carbon ones in the ε – phase grid leads to the decrease of the amount of feeding nitrogen for the chosen time of treatment (4 h), and consequently the concentration gradient of the nitrogen – the basic factor in the diffusion process - decreases .

During the process of 25CrMnSiNiMo steel treatment with additionally introduced into the ammonia medium, surface hardness and combined zone thickness are obtained, than in the process of nitriding. This is due to the heightened content of carbon on the surface (Fig.1) directly delivered from the propane-butane. Obviously the availability of carbon on the surface of the carbonitrided layer and the carbon from the steel impede the diffusion of nitrogen into the interior of the material.

In consequence of the two processes going on in the plasma – dissociation and ionization, carbon and nitrogen atoms are formed, which combine with the pulverized iron in the smouldering discharge and probably make up iron carbonitride [Fe(NC)]. It precipitates in the form of a thin layer on the surface of the sample and decompounds, thus leaving carbon and nitrogen, which diffuse in depth. After a certain period of time a ε – phase is formed and part of the nitrogen atoms are replaced by the bigger hydrogen atoms, which causes an increase in the parameters of the ε-carbonitride. This is possible for two reasons: approximately the same radius of the nitrogen [$r_{ion}$ = 13(5+1)pm, $r_{ion}$ = 16(3+1)pm] and carbon [$r_{ion}$ = 16(4+1)pm], and the possibility for the carbon atoms to take the vacant spaces between the knots of the grid. The change of the periods of the hexagonal grid is not the same: the biggest increase is observed with the parameter – a, thanks to which the ratio c/a for the carbonitride ε-phase decreases. The reduction of the micro hardness of the carbonitrided 25CrMnSiNiMo steel can be explained with forming a ε-carbonitride, for which smaller elastic distortions are observed, since the ratio between the parameters of the grid c/a of the ε-carbonitride are smaller than for the ε-nitride [8,9].

It can be noted that using propane-butane together with ammonia in the process of ion carbonitriding leads to increase in the voltage of the discharge in the plasma, which depends on their ratio. With introducing propane-butane in the chamber, the voltage of the discharge increases (table 3). In order to achieve the required temperature of carbonitriding in this case, it is necessary to decrease the current of the discharge. Thus the power of the plasma is retained. The increase in the voltage leads to an increase in the pulverizing action of the plasma in the vacuum camera, which increases the kinetic energy of the ions though their amount stays the same, which, in turn, leads to a decrease in the combined zone thickness.

### 3.2.2. Mechanical and technological properties of nitrided and carbonitrided samples

Heat resistance

The results, obtained for the heat resistance of the nitrided and carbonitrided test samples are given in table 5. From the table it can be noticed that all the modes of nitriding and carbonitriding increase the heat resistance of 25CrMnSiNiMo steel, leading to a higher value with the carbonitrided samples (table 5), compared to the nitrided ones. The highest value of heat resistance ($590^0$C) is observed after ion carbonitriding at: $t = 550^0$C, $P_{NH3}$ = 360Pa and $P_{C3H8 - C4H10}$ = 40 Pa,$\tau$ = 4 h.

The changes in the carbonitrided layer are caused mainly by the two processes – de-nitriding and homogenization. The process of de-nitriding can be explained as a consequence of the difference between the activity of the nitrogen in the hard phase and in the gas medium at the corresponding temperature. De-nitriding mainly concerns the surface zones of the layer and causes intensive pore forming. In all cases the combined zone is considerably reduced or is missing in general, and the total length of the layer has increased. These morphological changes of the nitrided and carbonitrided layer have an unfavorable effect on the rest of the characteristics and on the exploitation behavior of the nitrided (carbonitrided) surfaces. The homogenization is expressed in the striving of the layer for taking all the interstitial states at the new thermodynamic conditions, and at the same time it causes certain motion at the borders between the separate zones towards the interior.

It can be noted that the positive influence of the two processes (nitriding, carbonitriding) on the heat resistance of 25CrMnSiNiMo steel is related to alloying constituents(chromium, molybdenum) in the hard solution, the heightened resistance of the solution containing nitrogen and carbon and the slower coagulation of the carbonitride and nitride particles. All of this slows down the processes of de-hardening of the nitrided (carbonitrided) layer and determines its heightened heat resistance.

Impact strength

The results, obtained from testing the ion nitrided and carbonitrided test samples at impact three-point bending are given in table 5.

From table 5 it can be noticed that at all modes of ion nitriding and carbonitriding the impact strength of the investigated steel decreases. This is due to the layer, formed on the surface of the sample, which has a higher brittleness and a higher module of elasticity than the basic material [2,3,4,11]. For all modes of treatment elements of brittle destroying are registered on the surfaces and such elements can be seen in the not carbonitrided part of the material as well– Fig.3 c,d. In the periphery of the surface a white facet ring clearly stands out and its thickness is compatible with the thickness of the carbonitrided (nitrided) layer. The nitride (carbonitride) precipitations in the diffusion zone of the nitrided (carbonitrided) layer are a concentrator of the pressures, which favorably influences the origin and the propagation of the crack, since strain forces perpendicular to the direction of movement are created. From the table it can be seen that mode 5 of carbonitriding has the least influence on the reduction (15%) of the impact strength of the steel. This is due to the lower total thickness of the carbonitrided layer $\delta_{tot}$ = 120μm and the thinner compound zone $\delta_{cz}$ = 3μm.

Tensile strength, limitation of flow and relative extension

From table 5 it can be seen that after ion nitriding and carbonitriding of 25CrMnSiNiMo steel its tensile strength decreases (Rm), as does its relative extension after destroying (A), while, depending on the mode of treatment, the arbitrary border of flow ($R_{P0,2}$ ) increases with over 5%. This can be explained with the high module of elasticity of the nitride and carbonitride particles formed. At a certain deformation the pressures originating in these particles are significant, which favors the rise of micro cracks. As a consequence, the multi-layer body (layer, core) is destroyed at lower pressures.

The increase of the arbitrary border of flow at certain modes of nitriding and carbonitriding can be explained with the higher module of elasticity of the multi-layer system and the lower concentration of pressures on the top of the carbonitrided particle because of the lower voltage applied (the linear part of the diagram), during the process of testing the sample to strain. The anisotropy of the material properties along the cross-section plays an obvious role because of the availability of the nitrided (carbonitrided) layer formed on the surface.

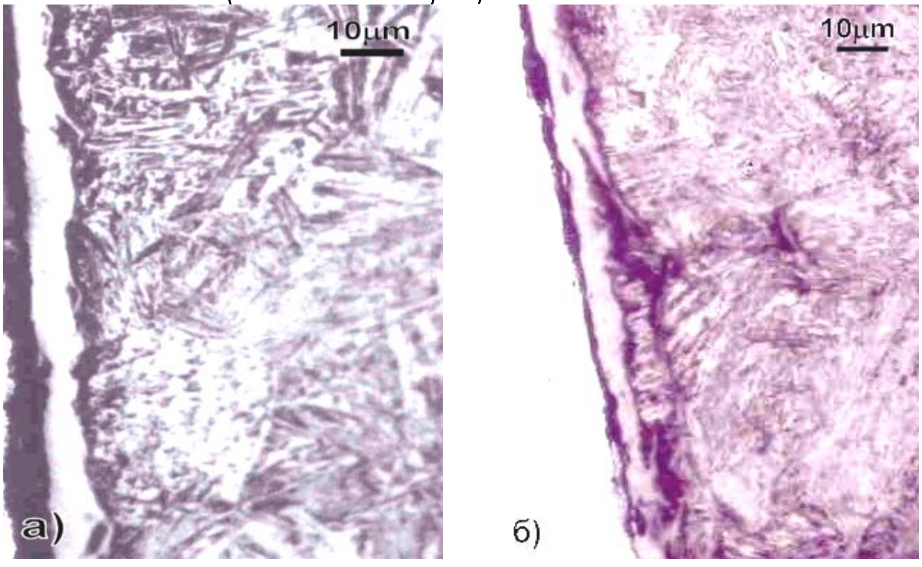


Figure 2. Microstructure of nitrided and carbonitrided 25CrMnSiNiMo steel
a –nitrided at: t = 550˚C, $P_{NH_3}$ = 400Pa, τ = 4h ; b-carbonitrided at: t = 550˚C, $P_{NH_3}$ = 400 Pa, τ = 2h; $P_{NH_3}$ = 360 Pa, $P_{C_3H_8-C_4H_{10}}$ = 40 Pa, τ = 2h

The presence of this hardened layer does not give a chance to localize the deformation and thus impedes from forming a journal on the otherwise plastic material under the layer. As a consequence, a specific surface with a strict macro fracture is obtained. The availability of a facet ring on the surface is an evidence of brittle destroying in the area of the carbonitrided (nitrided) layer – Fig. 3 a,b. The influence of the layers formed on the surface over the relative extension of the sample is stronger, and, depending on the mode of treatment, it decreases by over 50% (table 5, mode 5). After ion carbonitriding a bigger decrease of the relative extension of the samples is observed (45%), than after nitriding (5%). This can be explained by the bigger amount of carbonitride precipitations in the carbonitrided layer – Fig. 2.

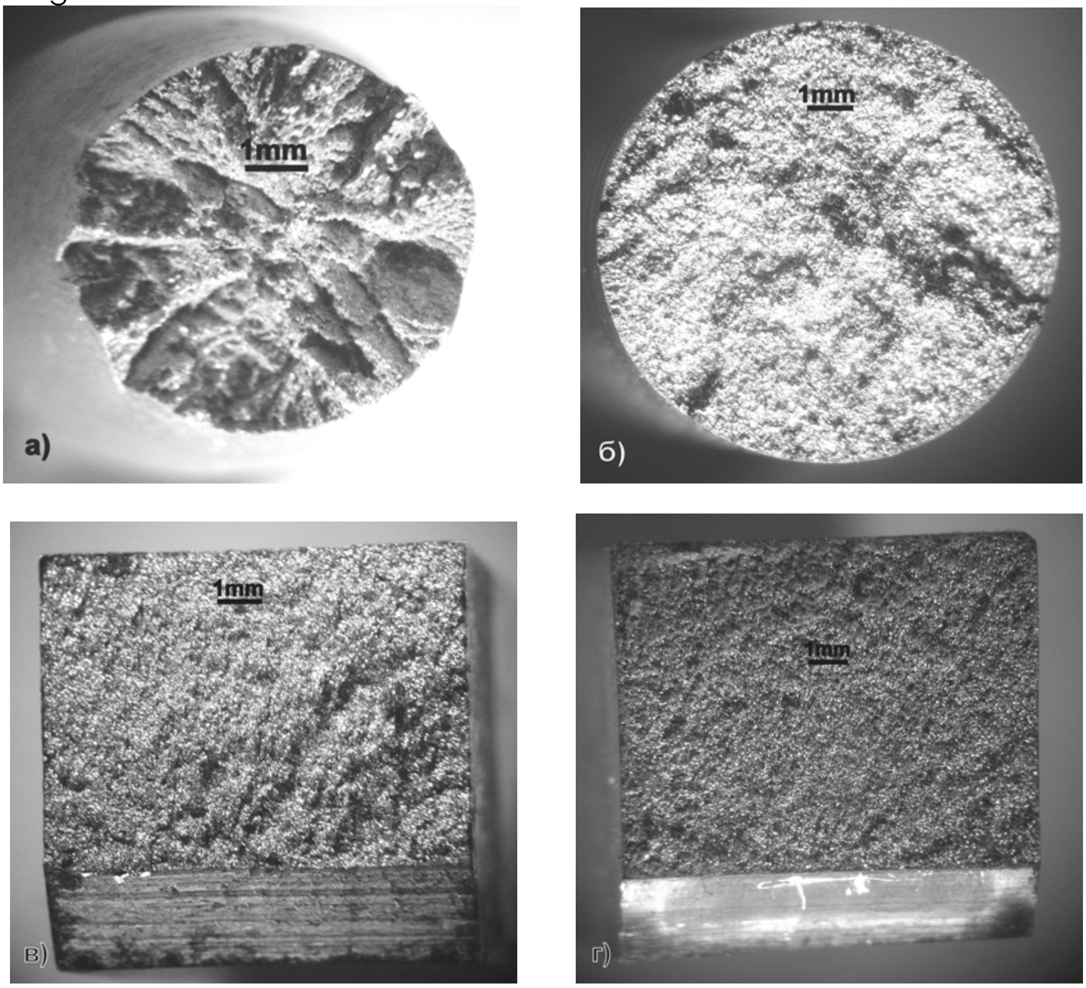


Figure 3. Fracture diagrams of test samples surfaces
a-tested at strain thermally treated sample; b- tested at strain carbonitrided ( $t = 550^{\circ}C$, $P_{NH3} = 360$ Pa, $P_{C3H8 - C4H10} = 40$ Pa, $\tau = 4$) sample; c–tested at impact three-point bending thermally treated sample; d-tested at impact three-point bending carbonitrided ( $t = 550$; $P_{NH3} = 360$ Pa, $P_{C3H8 - C4H10} = 40$ Pa, $\tau = 4h$) sample

## 4. CONCLUSIONS

- It is established that at the same temperature (550 $^{0}$C) and time of treatment (4h) but different saturating gas media ($NH_3$, $C_3H_8$ – $C_4H_{10}$) the layers, obtained after ion carbonitriding are with lower thickness than they are after ion nitriding.
- It is proved that the biggest decrease (up to 45 %) in the relative extension of 25CrMnSiNiMo steel is observed after carbonitriding, while after nitriding it reaches 5%.

- It is established that after ion carbonitriding the heat resistance of 25CrMnSiNiMo steel is higher than it is after nitriding.
- It is proved that for the two processes of carbonitriding and nitriding in low temperature plasma decrease of the impact strength of 25CrMnSiNiMo steel with 15 % is observed.
- It is established that the concentration of nitrogen in the combined zone of the nitrided layer is bigger than it is in the carbonitrided layer and it depends on the percentage ratio of the two saturating gases – ammonia and propane-butane.

---

## REFERENCES

[1.] Toshkov V., Theoretical and practical aspects of the process of nitriding iron and iron-carbon alloys in low temperature plasma, Thesis, Sofia, 1997.

[2.] Toshkov V., Nitriding in low temperature plasma, King, 2004.

[3.] Fisher-ChatterjeeP.,W.Eysell,u.a.,Nitrieren und Nitrocarburieren, Sindeifingen, Expert Verbag, 1994 .

[4.] Rusev R., Theoretical and experimental analysis of the system Fe-N-C and its application in the carbonitriding technologies, Thesis, Varna, 1998.

[5.] Hocman R.F., Effects of Nitrogen in Metal Surfaces, Proceeding of an Internacional Conference on Ion Nitriding, Clevland, Ohio, USA 15-17, September 1989, pp 23-30.

[6.] Rusev R., Peculiarities, mechanism of forming and morphology of carbonitrided layers, obtained in ammonia and carbone dioxide medium, Thesis, Varna, 1979.

[7.] Varhoshkov E., Carbonitriding of steels in smouldering discharge, Thesis, Sofia, 1985.

[8.] Lahtin Y., Difussion bases of the process of nitriding,МиТОМ, №7,1995, c.14-17.

[9.] Zumbilev A., K. Nikolov, Nitriding and carbonitriding of 20 and 25CrMnSiNiMo steels, Amtech 9-11 November 2005, Rousse.

[10.] Sommers M., Micro structural transformation of the combined zone during the process of nitriding and carbonitriding – the role of carbon, 11th congress of MOTO, 19.10.1998, Florence.

[11.] Samsonov G., V. Shatinskij, V. Kopylov. Physical and chemical processes in plasma covering and in destroying materials with covers, Kiev, Naukova Dumka, 1983

[12.] Huchel U., J.Crummenauer, S.Stramke, Nitrocarburieren und Oxidieren im Plasma, ELTRO GmbH , Baesweiler, 2003.

[13.] Nitriding and Nitrocarburising, Contract Heat Treatment Association, Aston University, Birmingham, 1996.

[14.] Gontiyo L., R.Machado, L. Casteletti and P. Nascente, Evaluation of the Effect of Cooling Speed fn the Layer Formation fn Stainless Steel by Plasma Carbonitriding, Acta Microscopica, Volume 12, № 1, December, 2003.

[15.] Schnatbaum F.,A. Melber. Plasma carburizlng of steel in pulsed DC glow discharges Technical Information-Leybold Durferrit, 1993.