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RAMAX S – STEEL NITRIDING AND CARBONITRIDING IN SMOULDERING DISCHARGE PLASMA

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ABSTRACT

The aim of the present work is to investigate the influence of the processes of nitriding and carbonitriding in low-temperature plasma in ammonia and argon medium (82% Ar and 18% CO) over the surface hardness and total thickness of the nitrided and carbonitrided layers of RAMAX S steel (420 F, modified – AISI).

The results from the experimental work show that after ion carbonitriding of RAMAX S steel at the same temperature of treatment and time for saturation but at different percentage of the two gases in the vacuum chamber (NH_3 – 50, 70, 90, 100% and corgon – 50, 30, 10%), the obtained layers have lower thickness and micro hardness, than after the process of ion nitriding. It has been also established that during the process of ion nitriding of steel 420, layers without combined zone are formed, while at the modes of carbonitriding the combined zone is thin and broken, with thickness up to 2.5 μm.

KEYWORDS

Nitriding, carbonitriding, low-temperature, plasma, ammonia and argon medium

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 nitriding and carbonitriding materials in the modern machine building.

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 there are also descriptions of the process of carbonitriding in a smouldering electrical discharge [7,9,10,11,12,14]. There is lack of data in the examined literature about carbonitriding in the plasma of a smouldering discharge in ammonia and corgon medium (82 % Ar and 18% CO_2), and complete data about comparative investigations of the two processes – nitriding and carbonitriding – are also missing.

Works [4,7,8] point that when in the process of carbonitriding propane-butane is used as a carbon carrier, the phase composition of the combined zone of the carbonitrided layer cannot be precisely regulated. Better results are obtained if methane-argon mixture is used [7]. In metal welding corgon is often used as a protective gas since it contains argon and carbon dioxide in a particular ratio.

The objective of the present work is to investigate the possibility to use corgon not only in welding but to use it as an indirect carbon carrier in the process of simultaneous saturation of the metal surface with nitrogen and carbon (carbonitriding) at low temperatures. The small percentage of carbon dioxide (18%) in the gas corgon enables the possibility to regulate the amount of the carbon, introduced into the vacuum chamber. There is lack of data in the examined literature about nitriding and carbonitriding of materials in the plasma of a smouldering discharge in ammonia and corgon medium (82 % Ar and 18% CO_2).

RAMAX S steel (420 F, modified – AISI) is with a heightened content of chromium (17%), which makes it corrosion resistant. In most cases the steel is delivered in thermally treated state of hardness 32-35 HRC. It can be well processed mechanically at this level of hardness because of the availability of the heightened content of sulphur in its chemical composition. This steel is mainly used for making syringe forms for producing details from polyvinylchloride. Data about plasma nitriding and carbonitriding of RAMAX S steel are not found [10,11,12,13,14].

The aim of the present work is to investigate the influence of the processes of nitriding and carbonitriding in low-temperature plasma in ammonia and corgon medium (82 % Ar and 18% CO_2) over the surface hardness and total thickness of the nitrided and carbonitrided layers of steel 420F.

2. MATERIALS UNDER INVESTIGATION AND MODES OF THERMAL TREATMENT, ION NITRIDING AND CARBONITRIDING

Corrosion-resistant steel 420F was chosen for the purpose of the investigation. The chemical composition of the steel was studied by means of equipment for automatic analysis “Spectrotest”. The data are given in Table 1.

Table 1. Chemical composition of the steel

Steel	CHEMICAL ELEMENTS, WEIGHT PERCENTAGE									
	C	Si	Mn	Cr	Ni	S	P	Cu	Nb	V	Mo
420F	0,34	0,4	1,4	17,1	0,55	0,12	0,02	-	-	0,47	0,17

The necessity for a preliminary thermal treatment of the steel is imposed mainly by the following two considerations: to achieve good mechanical parameters and a structure, enabling uniform distribution of the nitrogen and carbon in depth, on one hand; to enable favorable passing of the diffusion, on the other hand.

The steel 420F samples were thermally treated in a chamber furnace in oxidative medium, following the modes, shown in Table 2.

TABLE 2. MODES OF PRELIMINARY THERMAL TREATMENT

STEELS	T_{hard}, °C	Cooling medium	$T_{temp.}$, °C	Cooling medium
420F	1030	Oil	620	Air

The samples of the steel under investigation were nitrided and carbonitrided in the installation “Ion – 20” according to the modes, presented in Table 3. Ammonia

(NH_3) and corgon (82 % Ar и 18% CO_2) in different percentages were used as saturating gases. The temperature of treatment was 550°C.

Table 3. Modes of nitriding and carbonitriding

№ of the mode	Treatment	τ h	P_1 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	2	200	200	400	415
6	carbonitriding carbonitriding nitriding	6	200	200	400	415
7		4	280	120	400	435
8		4	400	-	400	530

3. METHODOLOGY OF THE INVESTIGATION

In order to establish the morphological peculiarities of the nitrided and carbonitrided layers metallographic analysis was conducted.

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

The thickness of the nitrided layer was defined by measuring the depth at which hardness equal to the core plus 500 MPa is achieved.

Measuring the micro hardness of the nitrided samples is carried out by means of a micro- hardness meter "Shimadzu" with a load of 0.49N following the “Vikers” method.

4. EXPERIMENTAL RESULTS AND ANALYSIS

4.1. Preliminary thermal treatment

The results from measuring the hardness after carrying out the thermal treatment are given in Table 4.

Table 4. Results from the preliminary thermal treatment

Steel	Hardness, HRC	
	Hardening	Tempering
420F	52	35

After hardening and tempering the structure of 420F steel is sorbate-troostite with sulphide particles observed in it. (FeS) – Fig 1.

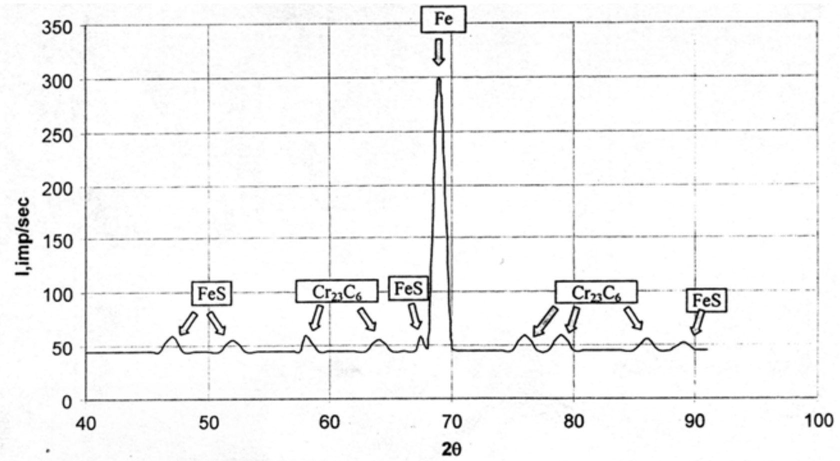

Figure 1. Roentgenogram of a thermally treated sample

They are irregularly distributed and have different form and size – Fig.2. This could be explained by the higher percentage of sulphur (0.12 % - Table1) in the steel.

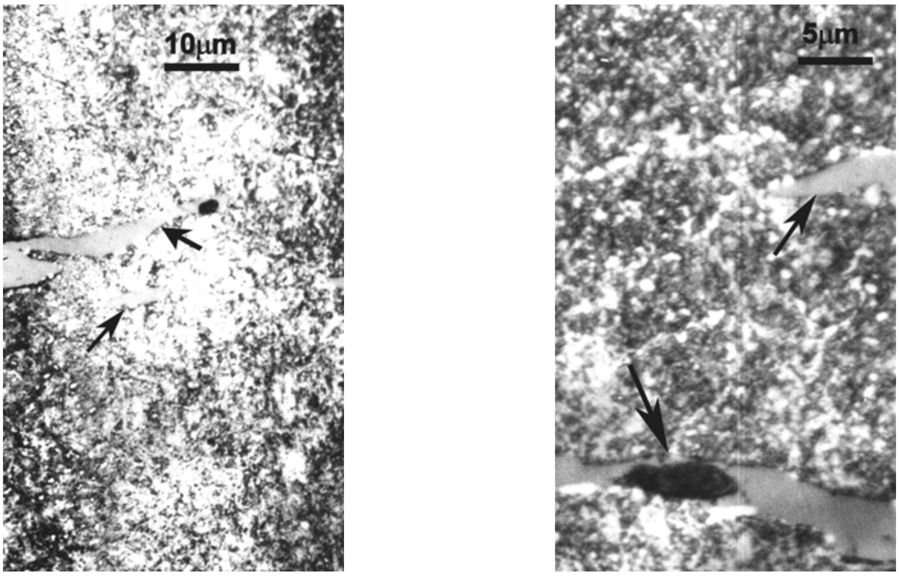

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Figure 2. Microstructure of 420F steel after hardening and tempering

4.2. Ion nitrided and carbonitrided samples

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 combined zone - δcz for the two layers is defined. The results are given in Table 5.

Table 5. Results from ion nitriding and carbonitriding of 420F steel samples

№ of the mode from Table3	420F			Pressure
	$HV_{0,1}$ MPa	δ_{tot} μm	$\delta_{c.z}$ μm	U V
1	11200	60	-	530
2	11000	50	1.5	470
3	12000	80	2	470
4	12500	95	-	530
5	10500	55	1	415
6	11100	85	2.5	415
7	11300	60	1.5	435
8	11700	75	-	530

After nitriding of 420F steel at temperature of 550°C, ammonia pressure of 400 Pa and duration of 2 hours a layer with thickness 60 μm and maximum micro hardness $HV_{0.1}$= 11200 MPa is obtained. A nitride (white) zone is not observed on the surface – Fig 2. From Table 5 it can be seen (modes 1,8 and 4) that with prolongation of the time of treatment from 2 h to 4 and 6 hours the surface micro hardness does not increase considerably ($HV_{0.1}$= 11200- 11700 MPa) but the total thickness of the layer does increase (60 - 95 μm). With prolongation of the time of treatment a combined zone in the nitrided layer is not formed as well – Fig. 3. It is easy to see a sulphide particle (FeS) under the layer, which is pointed by the arrow in the picture.

When except for ammonia also 10% of gas corgon containing 82 % Ar и 18% CO_2 (Table 5, modes 2 and 3) are additionally introduced into the chamber, a carbonitrided layer with lower micro hardness and lower total thickness of the layer and the forming combined zone is obtained.

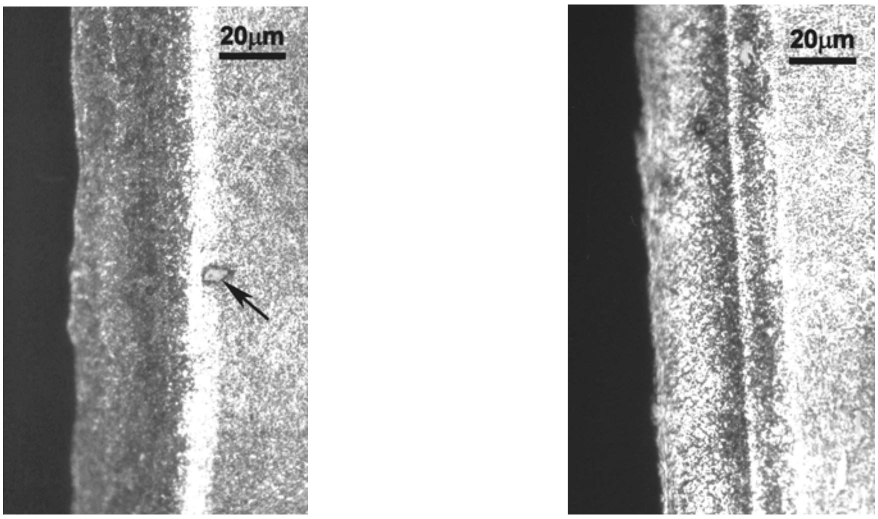

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Fig.3. Microstructure of 420F steel after nitriding
at: $t_{nitr.}$= 550˚C, P_{NH3} = 400Pa , a - т = 2h ; б - т = 4h

At the shorter time of treatment of 420F steel a layer with lower micro hardness ($HV_{0.1}$= 11000MPa), lower total thickness (50μm) and combined zone (1.5μm - фиг.4a) is obtained, than at the longer duration of the process of carbonitriding (Table 5, mode 3).

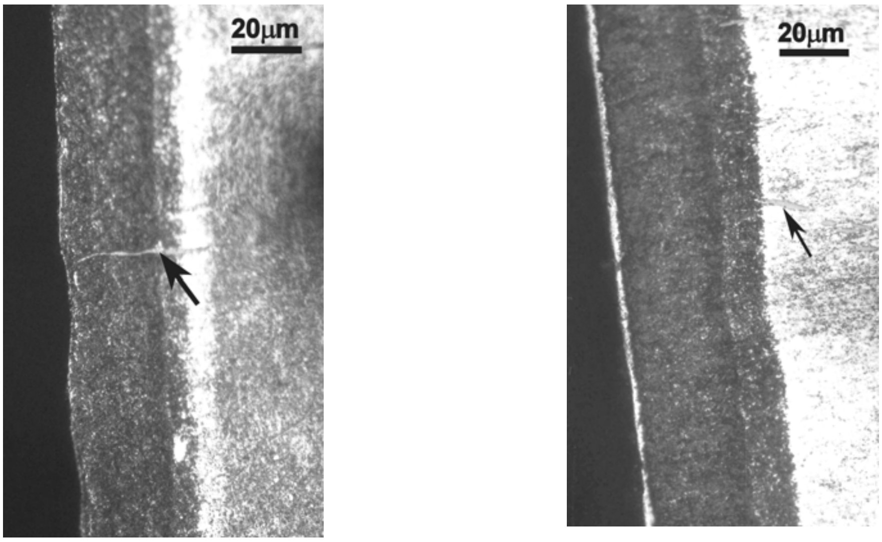

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Fig.4. Microstructure of 420F steel after carbonitriding
at: t = 550˚C, a- P_{NH3} = 360Pa , $P_{82\%\,Ar\,+18\%\,CO2}$ = 40Pa , т = 2h;
б-P_{NH3} = 200Pa , $P_{82\%\,Ar\,+18\%\,CO2}$ = 200Pa

On Fig.4 the carbonitrided layer stands out well and a sulphide inclusion (pointed at by an arrow) is observed in it.

With prolongation of the time of treatment of the samples from 2 h to 6 h a layer with higher maximum surface hardness $HV_{0.1}$= 12000 MPa, higher total thickness of 80 μm and thickness of the combined zone 2 μm is obtained.

It could be noted that after carbonitriding in a medium of 90% NH_3 + 8.2% Ar + 1.8 % CO_2 at 400Pa pressure a layer with lower micro hardness and total thickness is obtained than after the process of nitriding without adding carbon containing gases. After conducting metallographic analysis a combined zone is not observed in the nitrided layers formed. This is probably due to the availability of corgon in the saturating medium, which, obviously, appears to be an indirect carrier of carbon atoms, as well as to the small percentage of argon in the medium, which, 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 reverse diffusion of the nitrogen is smaller. A carbonitrided layer with lower concentration of carbon and nitrogen is the result. The more active pulverization does not allow the combined zone to grow and a combined zone, which is more deficient in nitrogen and carbon is formed.

After 420F steel carbonitriding following mode 5 from Table 5 with bigger pressure of the corgon ($P_{82\% Ar + 18\% CO2}$ = 200Pa) a layer with total thickness of 55μm, maximum surface micro hardness $HV_{0.1}$= 10500MPa and combined zone thickness of 1 μm is obtained. The combined zone is uneven and broken. With prolongation of the time of treatment from 2 h to 6 h at the same content of the saturating gas (mode 6 - 50% NH_3 + 41% Ar + 9 % CO_2) the micro hardness of the layer increases ($HV_{0.1}$= 11100 MPa) as well as its total thickness (85 μm) and the thickness of the combined zone (2.5 μm), which is uniform and stands out well – Fig. 4b.

It can be noted that with the increase in the corgon pressure to 200Pa and the decrease in the pressure of ammonia to 200Pa in the saturating gas medium, carbonitrided layers with lower surface micro hardness, with approximately the same total thickness and combined zone thickness are obtained. This is due to the heightened activity of the process of pulverization as the amount of the argon in the gas medium is bigger - 41%. The higher degree of pulverization leads to reducing the probability for a collision between the atoms and ions, in consequence of which smaller amounts of carbon and nitrogen atoms are delivered to the surface. Except for the bigger content of argon, the saturating medium is richer with CO_2, which is an indirect carrier of carbon atoms. They impede the diffusion of the nitrogen in depth and de-stabilize the γ'- phase, thus creating conditions for forming the ε- phase.

After 420F steel carbonitriding following mode 7 from Table 5 in a gas medium composed of 70% NH_3 + 24.6%Ar + 5.4 % CO_2 at the pressure of 400Pa a layer with thickness of 60μm, maximum micro hardness $HV_{0.1}$= 11300 MPa and combined zone thickness of 1.5 μm is obtained.

After 420F steel treatment with additionally introduced into the ammonia medium carbon-containing gas (corgon) at different percentage ratio, layers with lower surface micro hardness and lower total thickness are obtained than after the process of nitriding. This is due to the increased content of carbon on the surface, indirectly delivered from the CO_2 in the following probable mechanism: the carbon, pulverized from the steel probably binds in the smouldering discharge to the available in the chamber CO_2 following the reaction $C + CO_2 \rightarrow CO$. The carbon oxide in its turn dissociates, and during this process carbon dioxide and atomic carbon are formed. Most probably another reaction passes as well, during which carbon oxide is formed and the reaction is as it follows: as a consequence of the processes of dissociation and ionization of ammonia nitrogen and hydrogen are obtained. The resultant hydrogen in the smouldering discharge probably interacts with the available CO_2 following the reaction: $CO_2 + H_2 \rightarrow CO + H_2O$. Under certain conditions the iron in the plasma of the discharge can bind with the carbon oxide obtained and can form cementite ($Fe+CO+H_2 \rightarrow Fe_3C+H_2O$). The carbon and nitrogen atoms formed bind with the pulverized iron in the smouldering discharge and form iron-carbonitride. It precipitates on the surface of the material and decompounds, thus producing carbon and nitrogen atoms, which diffuse in depth. Part of the nitrogen atoms are replaced by the bigger carbon atoms, which causes an increase in the parameters of the ε-phase. This is possible for two reasons: approximately the same ion 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 fill in the vacant interknits. The change in the periods of the hexagonal grid is not the same: the biggest increase is observed in the parameter - a, thanks to what the ratio c/a for the carbonitride ε-phase decreases. Apparently the availability of carbon on the surface impedes the nitrogen diffusion in depth the metal. The decrease in the micro hardness of the carbonitrided 420F steel can be explained by forming ε - carbonitride, during which smaller elastic distortions are observed, since the ratio of the grid parameters c/a for the ε - carbonitride is smaller than it is for the ε - nitride [8,9].

After conducting the process of carbonitriding with corgon (82 % Ar + 18 % CO_2) and ammonia for 420F steel, layers with incompact and broken combined zone of up to 2.5 µm are obtained.

It can be noted that during the process of carbonitriding with using corgon together with ammonia leads to decreasing the voltage in the plasma discharge, which depends on their ratio. With introducing of corgon into the chamber, the voltage of the discharge decreases (Table 3). In order to achieve the required temperature of treatment in this case it is necessary to increase the current of the discharge. This way the energy of the plasma is preserved. The increase in the current density leads to raising the pulverizing action of the plasma, despite the low voltage. This is explained by the bigger amount of ions, bombing the surface of the detail. The higher density of the current does not lead to an increase in the kinetic energy of the ions. The decrease in the pressure of the gases in the chamber results in an increase in the discharge voltage, and the kinetic energy of the ions also increases without any change in their amount. Thus the coefficient of pulverizing can also be increased, which would lead to a decrease in the combined zone thickness, or to its absence in certain cases.

5. CONCLUSIONS

5.1.It has been established that, after ion nitriding under the folloing conditions: t_{nitr} = 550˚C; P_{NH3}= 400 Pa; and τ = 6h, 420F steel has the highest surface micro hardness $HV_{0.1}$= 12500 MPa and biggest total thickness of the layer 95 µm .

5.2.It has been proved that after ion carbonitriding under the following conditionst: t = 550˚C; P_{NH3} = 360 Pa; $P_{82\% Ar +18\% CO2}$ = 40Pa; $P_{tot .}$= 400Pa ; and τ = 6h, 420F steel possesses the highest micro hardness $HV_{0.1}$= 12000MPa in comparison to the other modes of treatment .

5.3. It has been proved that at the same temperature (550°C) and duration of treatment (2,4,6 h), but with different content of the saturating gas medium [NH_3, (82 % Ar + 18 % CO_2)], and at total pressure of 400Pa, the layers obtained after ion carbonitriding of 420F steel are with lower thickness and micro hardness than the ones, obtained after ion nitriding.

5.4. It has been established that during the process of ion nitriding of 420F steel, layers without a combined zone are formed, while in the modes of carbonitriding the combined zone is thin and broken, reaching up to 2.5 µm.

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