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## X-RAY DIFFRACTION ANALYSIS OF A CARBONITRIDED LAYER OF ARMCO-IRON

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**Abstract:** Nitriding and carbonitriding are basic processes for surface hardening of details and tools made of iron-carbon alloys, during which either nitrogen only or both carbon and nitrogen are simultaneously introduced into the surface layer. In case of conducting these two processes in conventional gas furnaces or salt baths, it is impossible to regulate in a reliable way the thickness and the composition of the obtained layers, what necessitates varying with the potentials of nitrogen and carbon in the gas mixture or in the liquid medium. The aim of the present work is to study the influence of the gas corgon on the formation of the phase composition of the combined zone after ion carbonitriding of Armco-iron. The conducted roentgenographuc structural analysis of the carbonitrided materials in a medium of ammonia and corgon does not register cementite in the phase composition of the carbonitrided zone. The obtained results also show that the oxide phases -  $Fe_2O_3$ ,  $Fe_3O_4$  - are found in the formed carbonitrided layer.

**Keywords:** carbonitrided layers, x-ray diffraction, armco-iron

### 1. INTRODUCTION

Nitriding and carbonitriding are basic processes for surface hardening of details and tools made of iron-carbon alloys, during which either nitrogen only or both carbon and nitrogen are simultaneously introduced into the surface layer [3,4,5,6,9]. In case of conducting these two processes in conventional gas furnaces or salt baths, it is impossible to regulate in a reliable way the thickness and the composition of the obtained layers, what necessitates varying with the potentials of nitrogen and carbon in the gas mixture or in the liquid medium.

The conventional nitriding of working parts is accomplished in an atmosphere of partially dissociated ammonia or in a cyanide-cyanate salt bath at a temperature of 500-850 °C. Both methods not only have great potential for pollution of the environment, but also tend to cause serious industrial accidents (including with operators) during the time of treatment. The big difficulties in controlling the white zone in the layer are another disadvantage of these methods [1,2,7,9].

In the processes of carbonitriding and nitriding in glow-discharge plasma these difficulties are resolved, and this is the major advantage of the method. The use of glow electric discharge for treating details is a perspective method of nitriding and carbonitriding various materials in modern machine building.

The nitrided and carbonitrided layers are characterized by certain wear-resistance, by which they excel the carburized layers. Significant role for the high wear-resistance plays the nitrided (carbonitrided) zone, formed on the surface, which imparts two new functions to this surface, subjected to wearing, in addition to its increased hardness. The first one is the decrease in the coefficient of friction due to the availability of the highly nitrous  $\epsilon$ - phase with a hexagonal lattice (HL). The low coefficient of friction strongly reduces the adhesive strengths and improves the anti-blocking qualities of the carbonitrided surface. The second is that the carbonitrided zone is more stable to oxidation than the base material, what raises the heat resistance of the wearing surface and does not allow oxidative wearing. The phase composition of the layer is also of importance for its wear-resistance but the data on this topic are contradictory. Special importance for the surface properties of the carbonitrided layer has the structure of the carbonitried zone in the richest with nitrogen and close to the surface areas, where almost always finer or hoarser pores are formed. The porosity of the  $\epsilon$ - phase in the carbonitrided zone reduces its hardness, leads to worse roughness, increases as a whole the active surface of the material, but strongly decreases the coefficient of friction and the contact friction metal surface under conditions of wearing [8,10].

This paper aims at studying the influence of the gas corgon on forming the phase composition of the combined zone after ion carbonitriding of Armco-iron.

## 2. METHODOLOGY OF THE STUDY

### 2.1. Studied materials and modes of heat treatment

Armco-iron with chemical composition, presented in Table 1, was studied. Its chemical composition was defined by means of the equipment for automatic analysis "Spectrotest". Samples from Arco-iron with dimensions 15 x 15 x 10 mm were produced with surface roughness  $R_a = 0.63 \mu\text{m}$ .

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

Materials	Chemical element, weight percentages							
	C	Si	Mn	Cr	Ni	S	P	Mo
Armco-iron 99.8 %	0.02	0.01	0.07	0.02	0.03	0.002	0.002	0.02

The sample bodies were ion nitrided and carbonitrided in the installation "Ion – 20" under modes, presented in Table 2. Two media were used as saturating gases: only ammonia ( $\text{NH}_3$ ), and a mixture of ammonia and corgon (82%Ar and 18% $\text{CO}_2$ ) in different percentages. The temperature of treatment for both processes was 550 °C.

**Table 2.** Modes of ion carbonitriding and nitriding

Nº of the mode	Treatment	$\tau$ h	$P_1 \text{ NH}_3$ Pa	$P_2 \text{ corgon}$ Pa	P total Pa	U V
1	nitriding	2	400	-	400	530
2	carbonitriding	4	280	120	400	435
3	carbonitriding	2	350	350	700	380
4	carbonitriding	6	350	350	700	380

### 2.2. Metallographic and Roentgen studies

Metallographic analysis was carried out in order to clear out the morphological peculiarities of the nitrided and carbonitrided layers. The thickness of the nitrided and carbonitrided layers was defined by the depth at which hardness, equal to the core plus 50 was achieved. Measuring the micro-hardness of the obtained layers was accomplished by means of a micro hardness-meter "Shimadzu" at a load of 0.98 N(100g), following the Vickers' method. The samples were developed with 3% nitric acid solution in ethyl alcohol. The Roentgen analysis of the samples was conducted in Cr-K $\alpha$  radiation with average wave length  $\lambda = 2.291002 \text{ \AA}$  by means of an XR diffract-meter URS-50IM at  $U = 25 \text{ kV}$ ,  $I = 6 \text{ mA}$ , filter -V and mode of scanning – velocity  $\omega = 1 \text{ deg/min}$  and step  $\Delta\theta = 0,25 \text{ deg}$ . For defining the available phases on the surface combined zone of the nitride and carbonitrided samples qualitative XR structural analysis was carried out. In our particular case we used chrome X-ray radiation Cr - K $\alpha$  with wavelength  $\lambda = 2.29 \text{ \AA}$ . Information about the formed phases in the carbonitrided layer can be obtained at 11 $\mu\text{m}$  from the surface of the nitrided or the carbonitrided surface. The obtained diffractograms are given in Figure 1 and Figure 2.

### 3. EXPERIMENTAL RESULTS AND ANALYSIS

The maximum  $HV_{0,1}$  and the total thickness ( $\delta_{tot}$ ) of the nitrided and carbonitrided layers were defined by means of the measured micro-hardness of the thermally treated, ion nitrided and carbonitrided samples, while by means of a metallographic microscope the thickness of the combined zone ( $\delta_{c.z.}$ ) of the two layers was defined. The obtained results are given in Table 3.

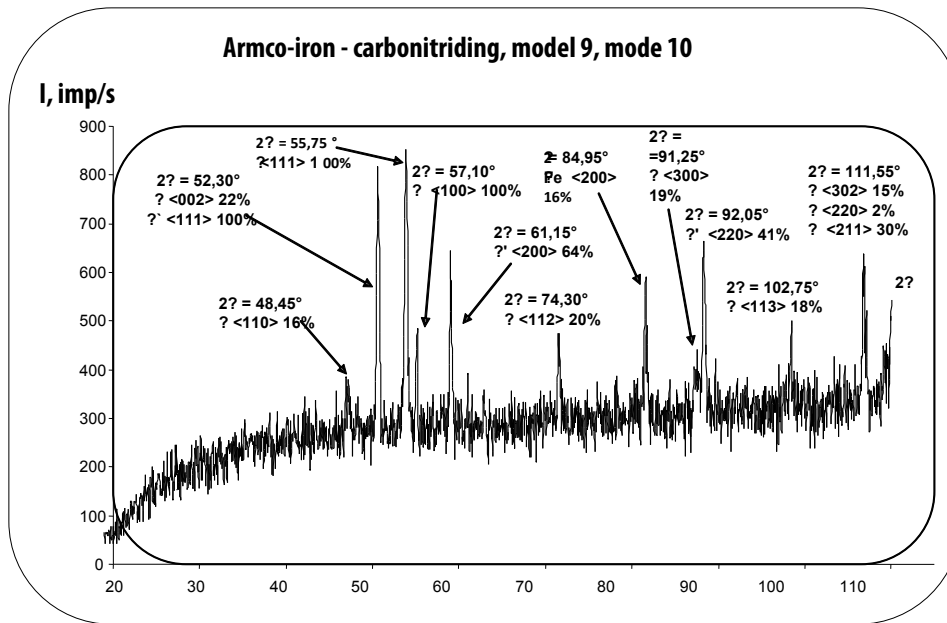
Table 3 presents data from the quantitative analysis of the phases, registered in the nitrided and carbonitrided layers.

From Table 3 it can be noted that when gas corgon is used as an indirect carbon carrier, the amount of the  $\epsilon$ -phase in the carbonitrided layer increases – Figure 1. It is necessary to note that under the following mode:  $t = 550 \text{ }^\circ\text{C}$ ,  $P_{ammonia} = 350 \text{ Pa}$ ,  $P_{corgon} = 350 \text{ Pa}$ ,  $\tau = 6 \text{ h}$  of carbonitriding (Table 3), the greatest amount of  $\epsilon$ - carbonitride - 54,65% - is observed, containing nitrogen and carbon, as it has been established by the author by means of optic spectral analysis with glow discharge.

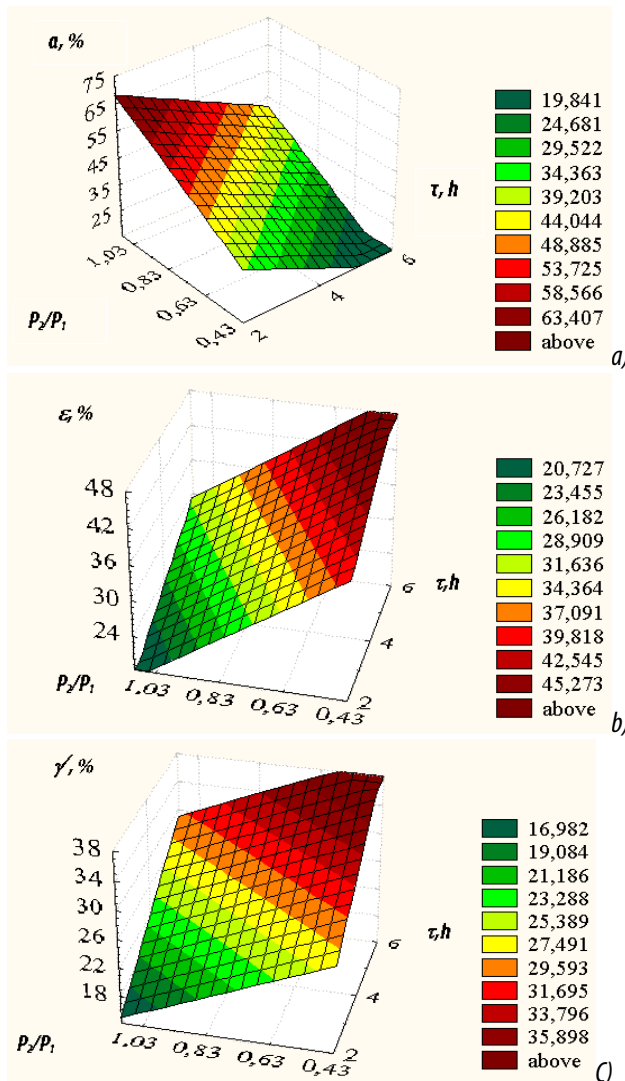
**Table 3.** Phase and quantitative analysis of the formed layers

Modes from Table 2	$HV_{0,1}$	$\delta_{tot}$ $\mu\text{m}$	$\delta_{c.z.}$ $\mu\text{m}$	$\alpha$ -Fe %	$\epsilon$ %	$\gamma$ %	$P_2/P_1$ %
1	380	220	6.8	26.7	15.8	57.4	-
2	480	280	6.5	18.0	41.1	40.7	0.43
3	540	210	4	8.1	47.1	44.6	1
4	560	320	8	12.3	54.6	33	1

Figure 1 and Table 3 show the phases, found by the Roentgen structural analysis in Armco-iron. When Armco-iron is ion carbonitrided under these parameters:  $t = 550 \text{ }^\circ\text{C}$ ,  $P_{ammonia} = 350 \text{ Pa}$ ,  $P_{corgon} = 350 \text{ Pa}$ ,  $\tau = 6 \text{ h}$ , a layer is formed with the following phase composition:  $\epsilon$ ,  $\gamma$  and  $\alpha$ . According to [1, 2, 3, 4] the phase  $\xi$  cannot be found in nitrided (carbonitrided) layers by an X-ray structural analysis but by metallographic and chemical analyses. Thus line 10 most probably gives information about the nitrous ferrite –  $\alpha$  and it is shifted toward higher values of the angle of measuring due to the saturation of  $\alpha$  with nitrogen and carbon. The  $\alpha$ -phase is also present with its theoretically highest peak at  $2\theta_{meas.} = 57.10^\circ$ , which provides unique information about this phase. This allows for drawing the conclusion that the reflection at  $2\theta_{meas.} = 111.55^\circ$  (line 10) is not by  $\xi$  or  $\epsilon$ , but by the nitrous ferrite - $\alpha$ .



**Figure 1.** X-ray of Armco-iron after carbonitriding at:  $t = 550\text{ }^{\circ}\text{C}$ ,  $P_{\text{ammonia}} = 350\text{ Pa}$ ,  $P_{\text{corgon}} = 350\text{ Pa}$ ,  $\tau = 6\text{ h}$



**Figure 2.** Change in the quantity of the ε-phase, γ'-phase and α-iron depending on the availability of gas corgon in carbonitriding Armco-iron

The ε-phase shows its theoretically highest peak (line 3 at  $2\theta_{\text{meas.}} = 55.75^{\circ}$ ), as well as three separate peaks (1, 6 and 9 from Table 4.1). Theoretically the strongest line of γ' duplicates with the reflection by the ε-phase, but the γ'-phase also has separate lines at  $2\theta_{\text{meas.}} = 92.05^{\circ}$  and  $2\theta_{\text{meas.}} = 61.15^{\circ}$ , what confirms its presence in the changed layer after carbonitriding.

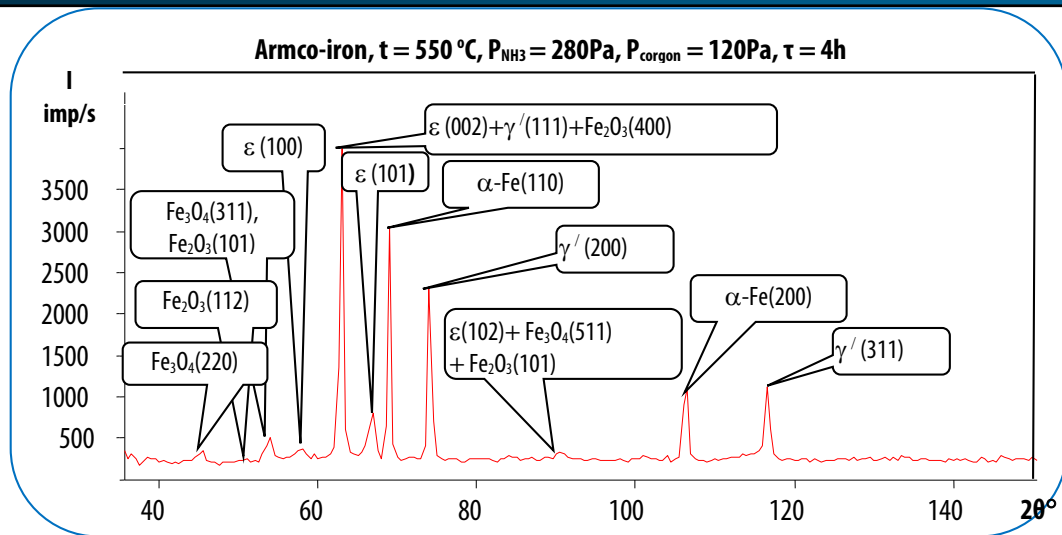
Figure 2 presents the graphs of changing the amounts of the ε-phase, γ'-phase and α-iron in the carbonitrided layer of Armco-iron.

From Fig. 2 it can be seen that the amount of α-iron increases together with the decrease in the time of carbonitriding and with the increase in the ratio between the pressure of the gases corgon/ammonia in the chamber. The amounts of the ε-phase and γ'-phase increase together with the increase in the time of saturation with the gases and decrease in the ratio between the pressures of the gases corgon/ammonia in the considered range.

Based on the conducted qualitative X-ray structural analysis of the sample bodies made of Armco-iron, various phase composition in the obtained layers is established, which depends on the mode of carbonitriding.

After ion carbonitriding of Armco-iron (under the mode:  $t=550^{\circ}\text{C}$ ,  $P_{\text{ammonia}}=280\text{ Pa}$ ,  $P_{\text{corgon}}=120\text{ Pa}$ ,  $\tau= 4\text{ h}$ ), in the surface layers except for ε, γ', α-Fe, oxides of the type  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  are observed – Figure 3.

Oxides are not observed in the nitrided layers. The availability of oxides in the carbonitrided layers is a proof that oxygen together with the nitrogen and carbon also diffuses in the surface of the treated sample. Instead of carbonitriding this process should be called oxycarbonitriding.



**Figure 3.** X-ray of Armco-iron after carbonitriding at:  $t = 550\text{ }^{\circ}\text{C}$ ,  $P_{\text{ammonia}} = 280\text{ Pa}$ ,  $P_{\text{corgon}} = 120\text{ Pa}$ ,  $\tau = 4\text{ h}$

According to [2], the availability of a certain amount of oxygen in the system leads to acceleration of the diffusion of carbon and nitrogen. The availability of carbon and oxygen in the phases in the system "iron-nitrogen" reduces the brittleness of the oxycarbonitrided layer [4]. The conducted X-ray structural analysis of the carbonitrided materials in a medium of ammonia and corgon does not register cementite in the phase composition of the carbonitrided zone. This can be explained by the lower concentration of carbon in the surface layer.

#### 4. CONCLUSIONS

It has been proved that after ion nitriding under the following mode:  $t=550\text{ }^{\circ}\text{C}$ ,  $P_{\text{ammonia}}= 280\text{ Pa}$ ,  $P_{\text{corgon}} = 120\text{ Pa}$ ,  $\tau = 4\text{ h}$  in the carbonitrided layer except for  $\epsilon$  and  $\gamma'$  phase, also the oxide phases  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  are observed.

It has been established that with increasing the time of treatment and reducing the ammonia pressure in the chamber, the content of  $\epsilon$  and  $\gamma'$  phase in the carbonitrided layer increases.

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