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DETERMINING OF RESIDUAL STRESSES IN THE CARBONITRIDED LAYERS X RAY DIFFIRACTION TECHNIQUES

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ABSTRACT:
The aim of the present investigation is to examine the influence of carbonitriding in low temperature plasma over forming macro-residual stresses on the surface of the materials.
Particular modes of ion carbonitriding are considered, in which layers of different depth and different surface micro-hardness are obtained. The residual stresses in the carbonitride layers are determined by the method of $\sin^2 Y$.
The results show that at different modes of ion carbonitriding residual macro-stresses with different sizes are obtained and they depend on the mode of treatment (ammonia pressure, temperature of carbonitriding, duration of treatment) and the depth of the carbonitride zone.
Keywords: Ion carbonitriding, residual compressive stresses

1. INTRODUCTION

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 [1,2,3,4]. A task of present interest with a view to increasing the effectiveness of the technologies, developed on the purpose, is the investigation of internal stresses in the materials, resulting from the corresponding treatment [5, 6].

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 [7].

The Roentgenograhic method allows registering submicroscopic changes in the distances between the atoms corresponding to the measured planes in the crystal lettuce 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 $l \leq 20\mu m$, 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 lettuce is normally about several nanometers. The wave length λ 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 [8,9].

The aim of the present work is to investigate the influence of the carbonitride layers over the type and the size of the residual stresses resulting from the process of carbonitriding of Armco-iron and 25CrMnSiNiMo steel.

2. METHODOLOGY OF INVESTIGATION

2.1. INVESTIGATED MATERIALS AND 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" and given in Table 1. The low percentage of sulphur /< 0,015%/ in them guarantees a high level of hardness and toughness of the investigated materials.

Table 1. Chemical composition of the 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 2. Modes of preliminary thermal treatment

Material	$t_{hard.}$ (°C)	Cooling medium	$t_{temp.}$ (°C)	Cooling medium
25CrMnSiNiMo	900	Oil	600	Air

Table 3. Modes of ion carbonitriding

Mode. №	Sample №	Material	τ [h]	P_1 ammonia [Pa]	P_2 corgon [Pa]	P [Pa]	U [V]
1	33	Armco-Fe	4	280	120	400	435
2	8	25CrMnSiNiMo	4	280	120	400	435
3	90	25CrMnSiNiMo	2	200	200	400	415
4	444	25CrMnSiNiMo	2	350	350	700	380

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, given in Table 2. Treated this way, the samples are then subjected to ion carbonitriding in the installation "Ion – 20", according to the modes, given in Table 3. Ammonia (NH_3) and corgon (82 % Ar и 18% CO_2) in different percentages are used as saturating gases. The temperature of treatment for the two processes – nitriding and carbonitriding - is 550°C.

2.2. METALLOGRAPHIC INVESTIGATIONS

Microscope "Axioscope" is used for the metallographic analysis. The thickness of the carbonitride layers is defined by the depth at which hardness, equal to the core plus 50, is obtained. Measuring the micro-hardness is carried out by means of a micro-hardness meter – Shimadzu. The Vikers' method with a load of 100g is used.

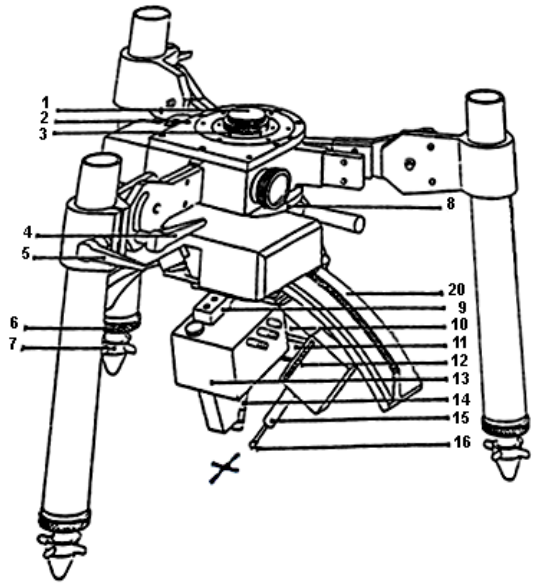

FIGURE 1. Diffraction-meter SET-X ENSAM
1-blocking screw, 2-manually operated breaker, 3-adjustment roll 4-handle for tightening, 5- handle for tightening, 6-blocking roll, 7-leg, 8-crutch of the measuring head, 9-angular crutch for the pipe and the detector, 10-X-ray tube, 11- window opening, 12-height marks (diodes) 13-detector, 14-collimator, 15-metal rod for precise measurements, 16-lever and и point (sharp blade), 17-control panel, 18-X-rays generator, 19-cooling system, 20-cam-comb gear

2.3. 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 „sin²Ψ" method. The working node of the diffraction-meter is given in Figure 1.

To illustrate the action of the diffraction-meter, the exact location of its measuring instruments with respect to the angles of rotation of the sample is shown in Fig.2 and Fig.3.

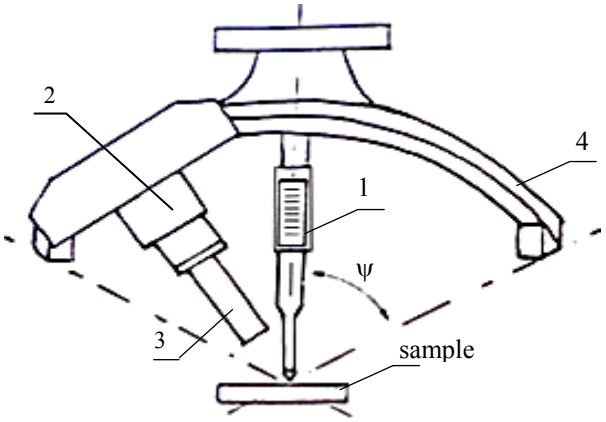

FIGURE.2. Defining the angle Ψ
1-metal tubule for precise measurements, 2-detector, 3-collimator, 4-cam-comb gear

When the sample rotates, the angle Ψ changes in the following sequence: 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°.

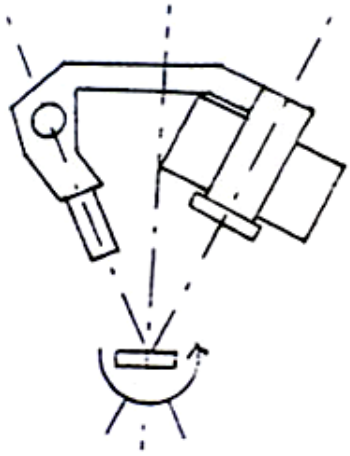

FIGURE.3. Defining the angle 2θ
1-detector, 2-collimator

The angle φ changes from 0° to minus 90° - Fig.4

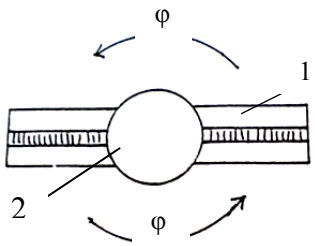

FIGURE.4. Defining the angle *φ*. 1-cam-comb gear, 2- sample

Thanks to the angles Ψ and φ, found by the diffraction-meter, it is possible to measure more accurately the corresponding diffraction angles θ_{hkl} and to define the residual stresses formed on the surface of the sample.

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 6μm from the surface of the sample in a plane α - Fe {2 1 1}

By means of the Roentgen diffraction-meter the diffraction angles in the carbonitride layers are measured. The data are introduced into the program „MATHLAB-2008". Through graphical representation of a straight line, built in the coordinates „2θ - sin² Ψ", the value of the diffraction angle 2θ at sin² 90 is defined.

The residual stresses are defined by the following dependence:

$$\sigma_{\varphi}=\frac{E}{2(1+\mu)}\cdot\cot\Theta\,(2\theta_{\varphi=0}-2\theta_{\varphi=90})\,\frac{\pi}{180}$$

The values of the elasticity constants in the given formula are chosen for non - carbonitrided steel: Poisson's ratio μ = 0,29, elasticity modulus E = 210 Gpa. The master diffraction angle is 2θ = 156°30', and θ = 78°15'. The miscount at defining stresses depends on the relative mistake Δθ/θ at defining the angle θ. Because of the lack of data in the literature concerning the elasticity constants of a carbonitride layers - μ and E, their replacement with data, concerning non- carbonitrided steel, also leads to inaccuracy in defining the residual stresses.

3. EXPERIMENTAL RESULTS AND ANALYSIS

3.1. THERMALLY TREATED AND ION CARBONITRIDED SAMPLES

Samples hardness, measured after their thermal treatment, is given in Table 4.

The total thickness of the carbonitrided layer - δtot is defined by the depth at which hardness, equal to the core plus 50 is obtained, and by means of a metallographic analysis the combined zone thickness δcz is determined. The results are given in Table 8.

Table 4. Hardness after thermal treatment

Material	Hardness (HRC)	
	Hardening	Tempering
25CrMnSiNiMo	47	35
Note: The hardness of Armco-Fe is 75HB		

It can be noted from Table 8 that depending on the modes of carbonitriding the materials 25CrMnSiNiMo steel and Armco-iron obtain a carbonitrided layer with different surface micro-hardness, total thickness and combined zone thickness. Under the three modes of carbonitriding, 25CrMnSiNiMo steel has a higher micro-hardness but a lower total thickness and a thicker combined zone than Armco-iron. It can be explained by the availability of alloying elements in the steel, which actively take part both in forming carbonitrides and in the surface layer hardening. They impede the diffusion of the nitrogen in depth, as a result of which thinner layers with thicker combined zone are obtained.

3.2. ROENTGENOGRAPHIC DEFINING OF INTERNAL STRESSES

By means of the Roentgen diffraction-meter the diffraction angles (Table 6, Table 7) at different angles of rotation of the sample - Ψ и φ – 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 2θ for sin²Ψ, at Ψ=90° are calculated - Fig.5, Fig.6.

Table 6. Diffraction angles, measured after rotating the sample 90 at angles Ψ and φ

φ	ψ	sin²ψ	2θs	2θc	2θb
0	0	0	153,617	154,12	154,091
0	14,96	0,07	154,015	154,205	154,214
0	21,42	0,13	154,441	154,355	154,341
0	26,57	0,2	154,605	154,567	154,501
0	31,09	0,26	154,824	154,708	154,661
0	35,26	0,33	154,92	154,852	154,779
0	37,23	0,36	155,02	154,974	154,899
0	-10,52	0,03	153,847	154,205	154,14
0	-18,43	0,09	154,058	154,396	154,375
0	-24,09	0,16	154,464	154,528	154,523
0	-28,88	0,23	154,71	154,643	154,675
0	-33,21	0,29	154,669	154,824	154,757
0	-37,27	0,36	154,93	154,979	154,868
-90	0	0	153,546	154,033	154,014
-90	14,96	0,07	154,061	154,19	154,204
-90	21,42	0,13	154,232	154,394	154,303
-90	26,57	0,2	154,32	154,601	154,557
-90	31,09	0,26	154,73	154,702	154,698
-90	35,26	0,33	154,877	154,961	154,823
-90	37,23	0,36	154,99	154,937	154,848
-90	10,52	0,03	153,803	154,098	154,092
-90	18,34	0,09	154,219	154,292	154,33
-90	24,09	0,16	154,526	154,589	154,549
-90	28,88	0,23	154,695	154,679	154,665
-90	33,21	0,29	154,874	154,818	154,793
-90	37,27	0,36	154,894	155,025	154,927

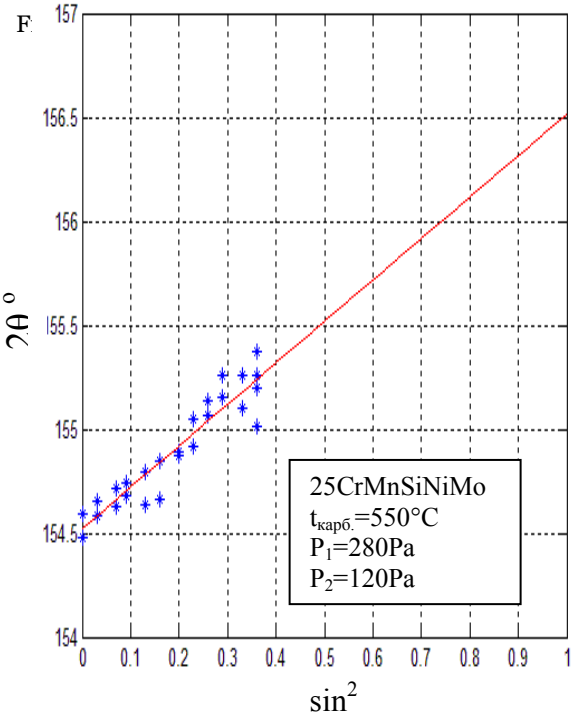

Figure.5. Graph for defining the angle 2θˢ at Ψ= 90° for sample № 90

Table 7. Diffraction angles measured after the rotation of sample 33 at angles Ψ and φ

φ	ψ	sin²ψ	2θs	2θc	2θb
0	0	0	155,025	156,021	155,897
0	14,96	0,07	155,933	156,212	155,899
0	21,42	0,13	155,939	156,193	155,902
0	26,57	0,2	155,94	156,203	155,904
0	31,09	0,26	155,998	156,185	155,901
0	35,26	0,33	156,075	156,178	155,907
0	37,23	0,36	155,942	156,194	155,914
0	-10,52	0,03	155,047	156,173	155,916
0	-18,43	0,09	156,054	156,18	155,899
0	-24,09	0,16	155,911	156,199	155,91
0	-28,88	0,23	155,894	156,187	155,898
0	-33,21	0,29	156,04	156,172	155,903
0	-37,27	0,36	155,978	156,149	155,906
-90	0	0	155,863	156,189	155,89
-90	-10,52	0,03	156,065	156,211	155,943
-90	-18,34	0,09	155,904	156,235	155,958
-90	-24,09	0,16	155,943	156,207	155,946
-90	-28,88	0,23	155,965	156,213	155,933
-90	-33,21	0,29	155,944	156,193	155,906
-90	-37,27	0,36	155,871	156,205	155,905
-90	14,96	0,07	155,986	156,224	155,971
-90	21,42	0,13	155,986	156,243	156,017
-90	26,57	0,2	155,982	156,235	156,005
-90	31,09	0,26	155,971	156,241	155,985
-90	35,26	0,33	155,983	156,207	155,99
90	37,23	0,36	155,872	156,247	155,98

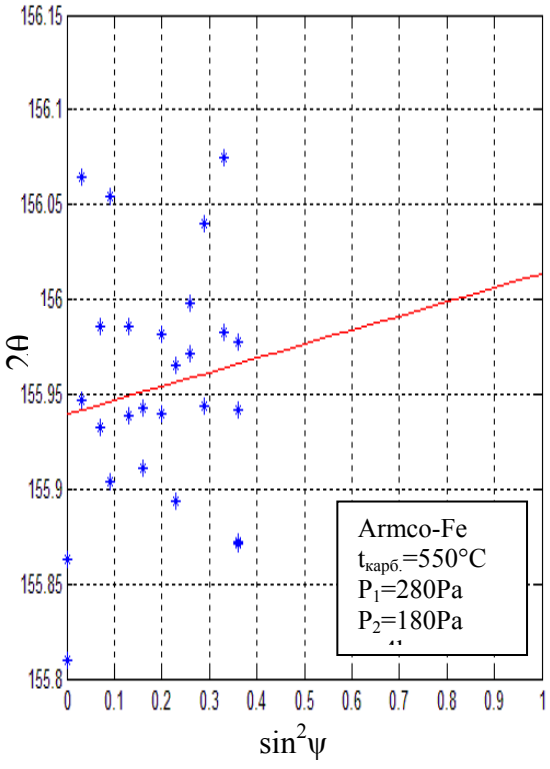

Figure 6. Graph for defining the angle 2θˢ at Ψ= 90° for sample № 33

After defining the angle $2\theta^s$ at $\Psi = 90^o$ for all carbonitrided samples, the calculation of the residual compressive stresses in the carbonitrided layers is done and given in Table 8 . Three ways of defining the diffraction angles are used: the maximum intensity method - $\sigma^{\varphi s}$, the chord method - $\sigma^{\varphi c}$, and the body centre method - $\sigma^{\varphi b}$.

Table 8. Results from the obtained residual stresses

Material	τ [h]	P_1 ammonia [Pa]	P_2 corgon [Pa]	$HV_{0,1}$	$\delta_{об}$ [μm]	$\delta_{c.з}$ [μm]	$\sigma^{\varphi s}$ [MPa]	$\sigma^{\varphi c}$ [MPa]	$\sigma^{\varphi b}$ [MPa]
Armco-Fe	4	280	120	480	280	6.5	-21	-6	-6
25CrMnSiNiMo	4	280	120	930	210	6.3	-578	-627	-530
25CrMnSiNiMo	2	200	200	890	150	4.5	-871	-719	-661
25CrMnSiNiMo	2	350	350	740	140	4.1	-84	-61	-31

It can be seen from Table 8 that after ion carbonitriding of Armco-iron (sample № 33, Table 3) at $t_{nitr.} = 550°C$, $P_{NH_3} = 280Pa$, $\tau = 4h$, a nitrided layer with total thickness $\delta tot = 280\mu m$, combined zone thickness $\delta_{cz} = 6,5\ \mu m$ and maximum micro-hardness of 480HV0.1 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 ($\sigma^{\varphi s} = -21MPa$) results. The compressive stresses, resulting after the ion carbonitriding in the surface layer of Armco-Fe are much lower than those of 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 Armco-Fe layer.

After ion carbonitriding of 25CrMnSiNiMo-steel at $t_{nitr.} = 550°C$, $P_{NH_3} = 200Pa$, $P_{corgon} = 200Pa$, $\tau = 2h$, a carbonitrided layer with total thickness $\delta tot = 150\mu m$, combined zone thickness $\delta_{cz} = 4.5\mu m$ and maximum micro-hardness of 890HV0.1.is obtained. In the so formed carbonitride (combined) zone in the carbonitrided layer residual compressive stresses with highest value are formed $\sigma^{\varphi s} = -871$ MPa .

With prolongation of the time of 25CrMnSiNiMo-steel carbonitriding from 2 to 4 hours and reducing the corgon pressure from 200 to 120 Pa while increasing ammonia pressure from 200 to 280 Pa, a carbonitrided layer with higher total thickness $\delta tot = 210\mu m$, higher combined zone thickness $\delta cz = 6,3\ \mu m$, and higher maximum micro-hardness - 930HV0.1. - is formed. The resultant compressive stresses on the carbonitrided surface are lowered to $\sigma^{\varphi s} = 578$ MPa.

Together with increasing ammonia and corgon pressure from 200 to 350Pa for 2 hours time of treatment (sample 444, mode 4, Table 3) a carbonitrided layer with total thickness $\delta_{об} = 140\mu m$, combined zone thickness $\delta_{c3} = 4,1\mu m$ and maximum micro-hardness 740HV0.1 is obtained. In the white zone of the carbonitrided layer, formed this way, the smallest residual compressive stresses are formed $\sigma^{\varphi s} = -84MPa$. The high pressure of the two saturating gases $P_{tot} = 700$ Pa does not activate the process of pulverizing and therefore a bigger amount of nitrogen and carbon is delivered to the surface.

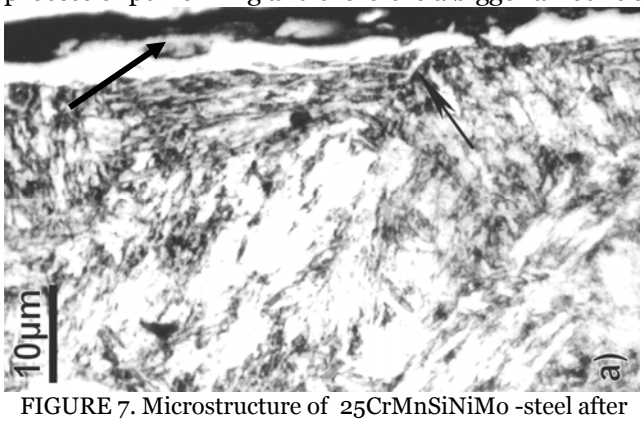

FIGURE 7. Microstructure of 25CrMnSiNiMo -steel after carbonitriding at: $t = 550^\circ C$, $P_{NH_3} = 350Pa$, $P_{82\%\ Ar\ +18\%\ CO_2} = 350Pa$, $\tau = 2h$

This probably leads to forming a bigger amount of micro-pores in the white zone (Fig.7), as a consequence of which the specific volume of the carbonitrided surface formed is smaller than the one in the core material.

In the process of 25CrMnSiNiMo -steel ion carbonitriding the increase of ammonia pressure (P_{MH_3} = 200-350 Pa) in the saturating medium forms a carbonitrided layer with approximately the same total thickness ($\delta_{об}$ = 140-150μm) and combined zone thickness (δ_{c3}= 4,1 – 4,5μm), but with lower micro-hardness (890 – 740 HV0,1). This leads to a considerable decrease of the residual compressive stresses on the carbonitrided surface ($\sigma^{\varphi s} = 871 – 84$ MPa).

It can be easily noted that under the same modes of ion carbonitriding (modes 1 and 2, Table 3) the two materials under investigation form different residual compressive stresses on their surfaces ($\sigma^{\varphi s} = 21–578$ 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 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 carbonitride zone, 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.

4.CONCLUSIONS

- It has been proved that there is certain difference between the values of the residual compressive stresses, obtained by the three ways of defining diffraction angles: the method of maximum intensity - $\sigma^{\varphi s}$, the cord method - $\sigma^{\varphi c}$, and the method of the body centre - $\sigma^{\varphi b}$.
- It has been established that the residual compressive stresses formed after ion carbonitriding on the surface of the alloyed steel 25CrMnSiNiMo have a considerably higher value, than those of Armco-Fe.
- It has been proved that in the ion carbonitriding of the investigated materials, the increase in the ammonia and corgon pressure in the vacuum chamber leads to a decrease in the value of the residual compressive stresses.
- A methodology for defining residual compressive stresses formed in layers after ion carbonitriding has been suggested.

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