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Obtaining the Controlled Sulphonitrocarburized Layer Phase Compositions, by the Variation of the Solid Powdery Medium Components

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Abstract. *Simultaneous saturation of the metallic surface with sulphur, nitrogen and carbon – named sulphonitrocarburizing (SNC) process - may be carried out in a multitude of variants, differ in media state of aggregation which provide the elements in native state, or differ in phase composition. The most commonly used media in SNC process are liquid or gaseous and from standpoint of phase composition, there are media made of compounds generator of the cyanides, representing important source of carbon and nitrogen, and as a sulphur source, may be used iron sulphide, sodium sulphide, sodium thiocyanides or ammonium. Carbamide/urea (CON_2H_4) it is frequently used in the media composition met in nitro-carburizing or carbo-nitriding process, alongside being added carbonates (sodium or potassium carbonate), thus resulting in cyanides (primary sources of the elements helping superficial saturation of the metallic products), as a result of the reactions which take place at the operating temperature of process. The medium toxicity decreased, based on carbamide used in nitrocarburizing and in particular, SNC process, being possible by carbonates replacing with ammonium chloride. This paper quantify the possibility of using solid powder mixture constituted of carbamide, in order to achieve SNC process of the iron matrix and effects quantification varying the percentage of the solid powdery mixture, so that it becomes possible to control the layer phase composition, by modifying the phase composition of the powder mixture used in thermo chemical processing.*

Keywords*: sulphonitrocarburizing, solid medium, carbamide, layer, experimental programming*

1. Introduction

The SNC process applied to steel and cast iron products, at temperatures below the eutectic transformation according to the Fe-N diagram, can be performs in a variety of technological variants, differing in terms of phase composition of media provider by the elements in native state and of aggregation state [1-16]. The most commonly solutions that have been called starting with process implementation, are those in liquid media and in this case, the melts which contain components with high toxicity used in initial melting are predominant [1-8,13]. The toxic-salt components found in the SNC mix are: sodium cyanide-NaCN, sodium thiocyanate-NaSCN, potassium cyanide-KCN, potassium thiocyanate-KSCN, potassium ferrocyanide-$K_4Fe(CN)_6$, ammonium thiocyanate-NH_4SCN; their proportion goes beyond frequently up to 50 %. Beside them, or alone, in salt bath SNC are found non-hazardous components, but extremely active during the process (neutral salts) acting as an accelerator in chemical reactions to produce the cyanides in salt bath and therefore in kinetic of layers generation.

Gaseous and respectively plasma media are frequently using in SNC processes: gas mixture (ammonia-NH_3 + carbon disulfide-CS_2) or those gases that result from the organic compounds instillation containing sulphur [3-5].

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The information concerning solid powder mixture used in SNC are quite rare, one of these indicating the environments containing $K_4Fe(CN)_6$ [7], a hazardous component, and another more recent, representing a pattern request [10, 16], which calls for carbamide as active component, a direct source of nitrogen and carbon and to powder Sulphur. Another component it is the ammonium chloride having double role in process, active component (source of ammonia), but also by the surface cleaner/activator.

Effects quantification by varying the components percentage of mixing used in order to achieve this desideratum has a special interest since it enables the optimal lead of the process, assuring a kinetic highest overall, under the conditions of a predefined phase composition of the SNC layer.

2. Materials and methods

Metallic matrices subjected to thermochemical processing have been making from commercially pure iron (Armco-Fe) to highlight, without other influences, the effects of SNC application in different processing conditions established by programming method.

The solid powdery components used as sources of nitrogen, carbon, and sulphur are as follows:

- Carbamide (technical urea) manufactured by AZOMURES Romania, having a granulation of 2-5 mm, with a total nitrogen content of 46 % and a humidity 0.3 % max.;
- Charcoal - broken
- Ammonium chloride of analytical purity, manufactured by Silver Chemicals Romania;
- Sulphur powder manufactured by Jainson Labs (India), with a granulation of 60-70 μm, of purity 99.5 % min. and humidity 0.1% max.

Advanced solid powdery mixture homogenization has been achieve by mixing components in a high energy ball mill for 15 minutes, reporting to a ratio of 11:1, representing the mass of the balls and the powdery mixture. The experimental programming method adopted dictated different proportions of the mixture components in different processing conditions.

Samples with dimensions 10x10x15 mm, were thermochemically heat treated (SNC) under the different processing conditions imposed by the adopted programming method. The Armco-Fe samples have been place in steel boxes and packed in powdery mixture. All experiments have been performing in identical conditions regarding the temperature and time maintaining - heat treating at 560 ^{0}C for 1 h and furnace cooling to 100 ^{0}C, then air. The samples have been degreasing with isopropyl alcohol.

Clay latches to limit the tendency of the gases to leave the boxes sealed. In this way, a box slight overpressure ensured. An automatic furnace with silicon carbide heating elements, type AUTOMATICA-Romania, for thermal processing carried out.

The samples for metallographic and scanning analysis have been: sectioned (DELTA AbrasiMet Cutter), mounted (SimpliMet 2000 Mounting Press) in ProbeMet compression mounting powder, grinded and polished (Phoenix Beta & Power Head) and finally etching by using Nital 2 % chemical reagent. The BUEHLER Company produces all the machines and consumables used for the metallographic samples preparation.

The results were investigated by light optical microscopy (LOM) using an imaging system consist of Reichert Univar microscope and OmniMet Enterprise software from BUEHLER and by scanning electronic microscopy (SEM), including Energy-Dispersive X-ray Spectroscopy analysis (SEM-EDS), using Quanta SEM Inspect F50.

3. Results and discussions

Effects quantification by varying the phase composition of the solid powder mixture used to carry out the SNC process have been making possible through experimental programming [17, 18]. It was used a second-order non-compositional programming method based on X_1 as sulphur native (%), X_2 as carbamide (%), X_3 as ammonium chloride (%) as independent variable and the remaining minced

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charcoal powder, up to 100 %, for each experiment (Table 1). As dependent variable were chose Y_1 as total thickness of the SNC layer and Y_2 as compound zone thickness.

Table 1. Correspondence between factors values stated as natural and codified units

Factor	S, [%]		CON_2H_4, [%]		NH_4Cl, [%]		Charcoal[1], [%]
	natural units, ***Zi***	codified units, X_1	natural units, ***Zi***	codified units, X_2	natural units, ***Zi***	codified units, X_3	natural units
Base level	$Z_0 = 15$	0	$Z_0 = 35$	0	$Z_0 = 3.5$	0	46.5
Range of variation	$\Delta Z = 5$	-	$\Delta Z = 15$	-	$\Delta Z = 1.5$	-	21.5
Higher level	$Z_0+\Delta Z = 20$	+1	$Z_0+\Delta Z = 50$	+1	$Z_0+\Delta Z = 5$	+1	25
Lower level	$Z_0-\Delta Z = 10$	-1	$Z_0-\Delta Z = 20$	-1	$Z_0-\Delta Z = 2$	-1	68

[1] *Observation: %Charcoal = 100 - Σ (%S + %CON_2H_4 + %NH_4Cl)*

Table 2 emphases the experiments and the results under conditions imposed by the second-order non-compositional programming method:

Table 2. Operating conditions of the experiments and results

Exp. no.	Independent variable Xi, [%]										Y, [μm]	
	X_0	X_1 (S)	X_2 (CON_2H_4)	X_3 (NH_4Cl)	X_1X_2	X_1X_3	X_2X_3	X_1^2	X_2^2	X_3^2	δ_{tot}	δ_{comp}
1	+1	+1	+1	0	+1	0	0	+1	+1	0	**195.0**	**4.034**
2	+1	+1	-1	0	-1	0	0	+1	+1	0	**59.9**	**8.5**
3	+1	-1	+1	0	-1	0	0	+1	+1	0	**202.9**	**5.099**
4	+1	-1	-1	0	+1	0	0	+1	+1	0	**22.5**	**4.8**
5	+1	+1	0	+1	0	+1	0	+1	0	+1	**62.3**	**3.8**
6	+1	+1	0	-1	0	-1	0	+1	0	+1	**196.0**	**2.664**
7	+1	-1	0	+1	0	-1	0	+1	0	+1	**245.1**	**1.98**
8	+1	-1	0	-1	0	+1	0	+1	0	+1	**33.0**	**0.99**
9	+1	0	+1	+1	0	0	+1	0	+1	+1	**235.8**	**1.752**
10	+1	0	+1	-1	0	0	-1	0	+1	+1	**188.6**	**1.0**
11	+1	0	-1	+1	0	0	-1	0	+1	+1	**66.81**	**0.8**
12	+1	0	-1	-1	0	0	+1	0	+1	+1	**165.5**	**1.45**
13	+1	0	0	0	0	0	0	0	0	0	**127.7**	**0.99**
14	+1	0	0	0	0	0	0	0	0	0	**131.4**	**1.52**
15	+1	0	0	0	0	0	0	0	0	0	**144.4**	**1.068**

Statically processing of the information obtained because of experimental cycle (Table 3), has led to the next coded particular forms (1, 2) of the regression equations, respectively the decoded forms (3, 4):

- Total thickness of SNC, (coded) - Y_1:

$$Y_1 = \delta_{tot} = 134.5 + 64.8X_2 - 11.3X_1X_2 - 86.4X_1X_3 + 36.47X_2X_3 - 22.2X_1^2 + 21.8X_3^2 \quad (1)$$

- Compound zone thickness, (coded) - Y_2:

$$Y_2 = \delta_{comp} = 1.192 + 0.766X_1 - 0.458X_2 + 0.275X_3 - 1.191X_1X_2 + 2.762X_1^2 + \\ + 1.654X_2^2 - 1.59X_3^2 \quad (2)$$

- Total thickness of SNC layer, (decoded) - δ_{tot}:

$$Y_2 = \delta_{tot} = -582.7 + \%S(72.27 - 0.89\%S) + \%CON_2NH_4(0.9 + 1.62\%NH_4Cl - 0.15\%S) + \\ + \%NH_4Cl(48.3 - 11.52\%S + 96.9\%NH_4Cl) \quad . \quad (3)$$

- Compound zone thickness, (decoded) - δ_{comp}:

$$Y_2 = \delta_{comp} = 16.1 + \%S(0.11\%S - 2.59) + \%CON_2H_4(0.00735\%CON_2H_4 - 0.0158\%S - 0.307) + \\ + NH_4Cl(5.13 - 0.708\%NH_4Cl) \quad (4)$$

Table 3. Statistical processing of experimental data on the effect of the composition variation of the pulverulent solid medium used in the snc process

Crt. no.	*Y₁* Total thickness of layer, [μm]	$t_{\alpha;\,N}$	*Y₂* Compound zone thickness, [μm]
1	$S_0^2 = 76.9$	$t_{0.05;15} = 2.131$	$S_0^2 = 0.0545$
2	$S_{b0}^2 = 25.63 \rightarrow S_{b0} = \pm 5.06 \rightarrow \Delta_{b0} = \pm 10.78$		$S_{b0}^2 = 0.0181 \rightarrow S_{b0} = \pm 0.134 \rightarrow \Delta_{b0} = \pm 0.286$
3	$S_{bi}^2 = 9.61 \rightarrow S_{bi} = \pm 3.1 \rightarrow \Delta_{bi} = \pm 6.6$		$S_{bi}^2 = 0.00681 \rightarrow S_{bi} = \pm 0.0825 \rightarrow \Delta_{bi} = \pm 0.1758$
4	$S_{bii}^2 = 25.6 \rightarrow S_{bii} = \pm 5.06 \rightarrow \Delta_{bii} = \pm 10.78$		$S_{bii}^2 = 0.018148 \rightarrow S_{bii} = \pm 0.1347 \rightarrow \Delta_{bii} = \pm 0.287$
5	$S_{bij}^2 = 19.22 \rightarrow S_{bij} = \pm 4.38 \rightarrow \Delta_{bij} = \pm 9.34$		$S_{bij}^2 = 0.0136 \rightarrow S_{b\,ij} = \pm 0.1167 \rightarrow \Delta_{bij} = \pm 0.248$

Checking the agreement of the calculated nonlinear models equations (1, 2) - see Table 4, led to the conclusion that they are adequate ($F_{calc} < F_{tab}$), expressing with a high probability (~ 95%; α = 0.05) the correlation between the dimension total sulfonitrocarburizing layer, respectively the size of the compound area and the composition of the solid powdery medium used for sulfonitrocarburizing.

Table 4. Checking the presumption about the agreement of both nonlinear calculated patterns with the results obtained via experimental research

$Y=f(X_1;\,X_2;\,X_3)$	S_{conc}^2	F_{calc}	F_{tab}
$Y_1=f(X_1;\,X_2;\,X_3)$ - eq. 1	634.99	8.25	19.37
$Y_2=f(X_1;\,X_2;\,X_3)$ - eq. 2	0.5508	10.10	19.35

The first two regression equations graphical representations (Figure 1, 2) allows, together with the regression equations, either in coded (1, 2) or decoded (3, 4) form, as well as independently, to determine the direction in which the solid powdery medium composition used for SNC has to be modified. So, in this respect results a certain ratio of the saturated layer dimensions simultaneously with the three elements.

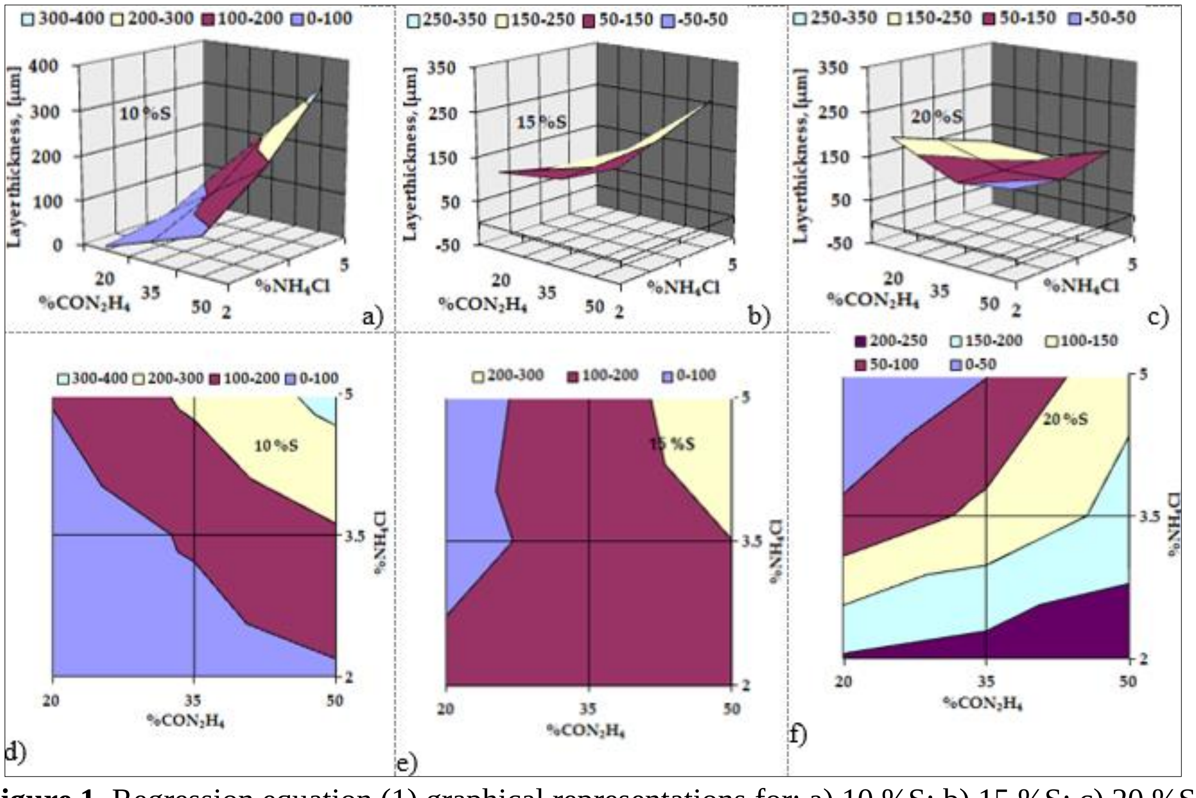

Figure 1. Regression equation (1) graphical representations for: a) 10 %S; b) 15 %S; c) 20 %S, and their domains of ownership (areas of equal overall layer size), for the same %S: d) 10 %S; e) 15 %S; f) 20 %S. SNC in pulverulent solid medium composed of: *CON_2H_4-Charcoal-NH_4Cl-S*

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The experimentally obtained results have being corroborate, in order to be understood, with the information provided by the reactions that take place in the solid powdery mixture, (CON_2H_4+ Charcoal NH_4Cl+S) and which lead to the formation of the active state elements.

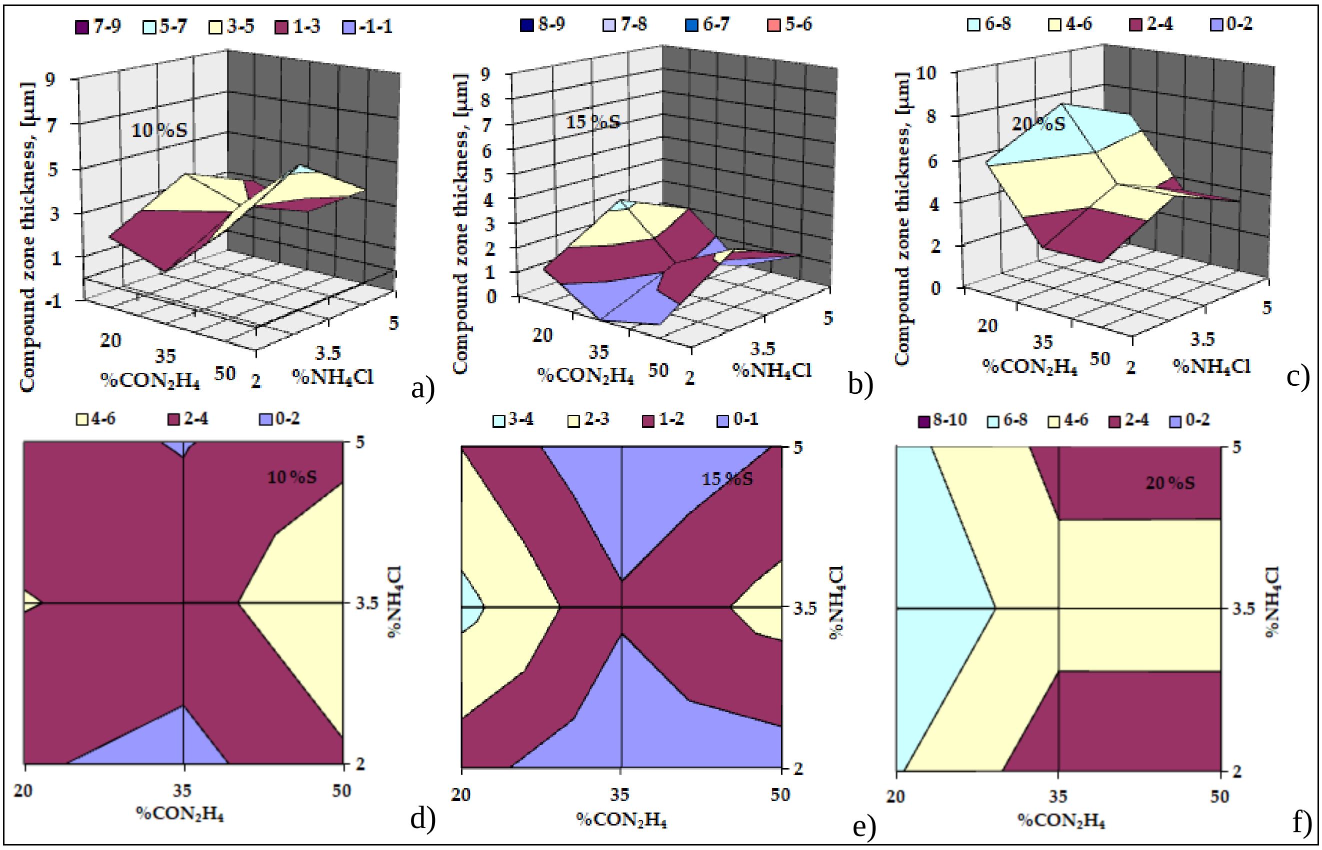

Figure 2. Regression equation (2) graphical representations for: a) 10 %S; b) 15 %S; c) 20 %S, and their domains of ownership (areas of equal overall layer size), for the same %S: d) 10 %S; e) 15 %S; f) 20 %S. SNC in pulverulent solid medium composed of: *CON_2H_4-Charcoal-NH_4Cl-S.*

$$2CON_2H_4 + O_2 = 2CO_2 + 2NH_3 + N_2 + H_2 \quad (5)$$
$$NH_3 = N^* + 3/2H_2 \quad (6)$$
$$CO_2 + C = 2CO \rightarrow C^* + CO_2 \quad (7)$$
$$H_2 + O_2 = 2H_2O \quad (8)$$
$$CO + 3H_2 = CH_4 + 2H_2O \quad (9)$$
$$CH_4 \rightarrow C^* + 2H_2 \quad (10)$$
$$NH_4Cl \rightarrow NH_3 + HCl \quad (11)$$
$$\downarrow (reaction \quad 6)$$

The sulphur element participate directly to the formation of mono (FeS) or iron disulphide (FeS_2) in adsorbed state as it shown in reactions (12, 13) or indirectly through carbon disulphide (CS_2), as it shown in reactions (15, 16):

$$S + Fe = FeS \downarrow ads \quad (12)$$

Alternatively, at higher sulphur concentrations:

$$S + Fe = FeS_2 \downarrow ads \quad (13)$$
$$2S + C = CS_2 \quad (14)$$

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$$CS_2 + 2Fe + O_2 = 2FeS \downarrow ads + CO_2 \quad (15)$$

Or $\downarrow (reaction\ \ 7)$

$$CS_2 + Fe + O_2 = 2FeS_2 \downarrow ads + CO_2 \quad (16)$$

$\downarrow (reaction\ \ 7)$

$$C + O_2 = CO_2 \quad (17)$$

$\downarrow (reaction\ \ 7)$

Or,

$$2C + O_2 = 2CO \quad (18)$$

$\downarrow 2(C^* + CO_2)$

$$C + 2H_2 = CH_4 \rightarrow C^* + 2H_2 \quad (19)$$

All these reactions lead to the formation of the three active elements (S, C, N), which by diffusion form the SNC layer with a desired phase composition. This is possible refer thermodynamic standpoint, their enthalpies being negative at the operating temperature: 560 ^oC.

LOM micrographs (Figure 3, 4) and SEM images (Figure 5) highlight the typical aspects of the SNC layers obtained on matrices of Armco-Fe. Thus, the area adjacent to the surface where there are iron carbonitrides but also sulphides (especially FeS), the sulphur concentration being dependent on its proportion in the environment used, but also on that of carbamide, respectively ammonium chloride. In the diffusion zone the γ' (Fe_4N) nitride separations are noted.

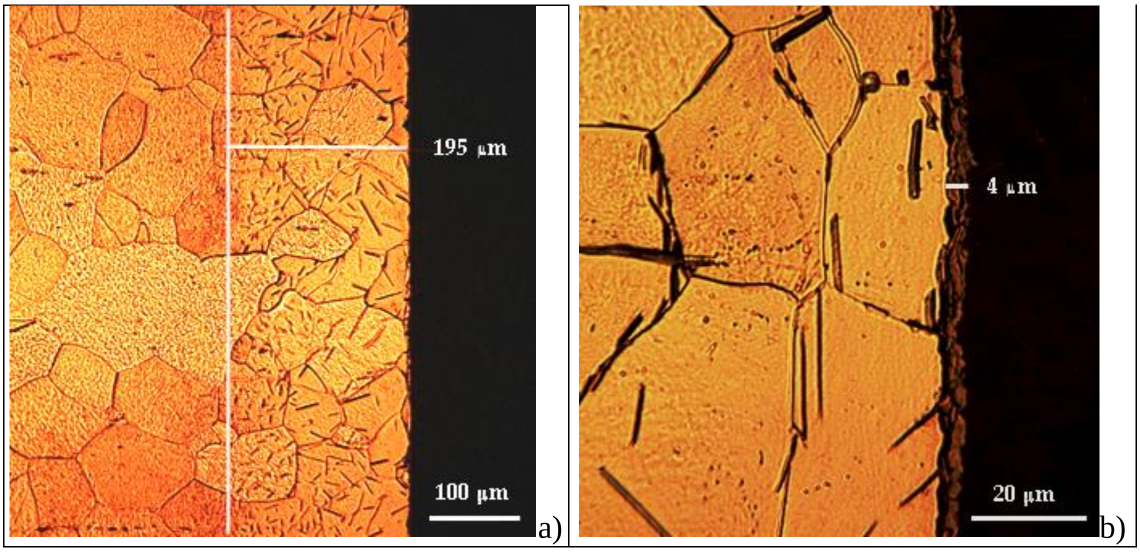

Figure 3. LOM microfraphs of Armco-Fe matrix subjected to SNC process using S-CON_2H_4-NH_4Cl-Charcoal (20 %-50 %-3.5 %-26.5 %) - *First experiment*; Etchant: Nital 2%; In layer: 11 %S, 0.94 %N; Layer features: δ_{tot} = 195 µm; δ_{comp} = 4 µm. *Note: The metallographic appearance of the SNC layer is extremely similar to the nitrocarburizing layer*

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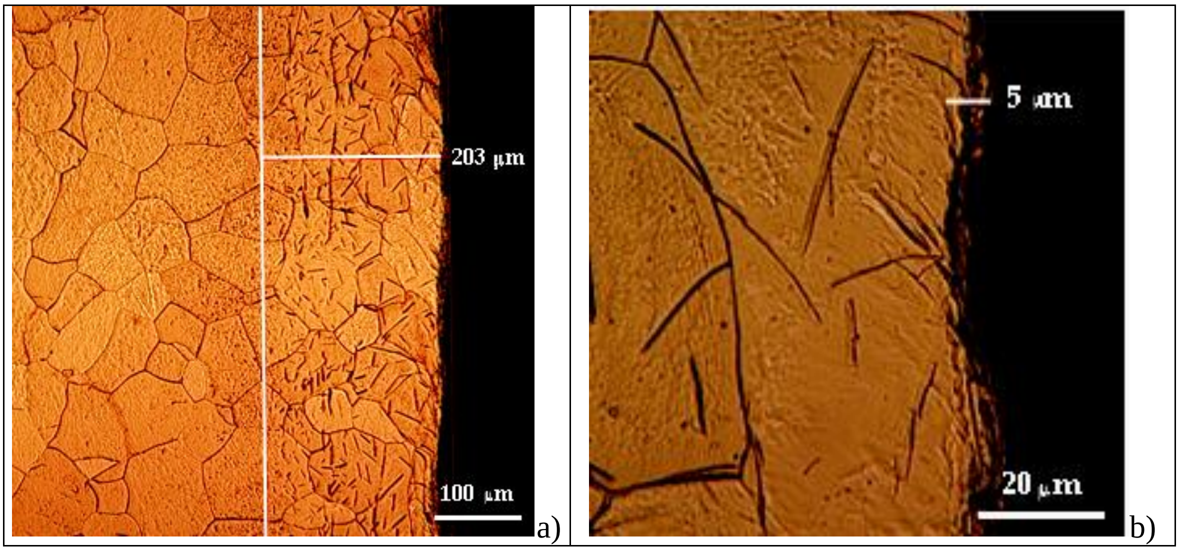

Figure 4. LOM micrographs of Armco-Fe matrix subjected to SNC process using S-CON_2H_4-NH_4Cl-Charcoal (10 %-50 %-3.5 %-36.5 %) - *Third experiment*; Etchant: Nital 2%; In layer: 2.30 %S, 2.36 %N; Layer features: δ_{tot} = 203 µm; δ_{comp} = 5 µm

The investigation results of SEM-EDS analyses (Figure 5) lead to the conclusion that the concentration values of those three elements (S, N, C) diffused in iron matrix and found in compound area by means of sulphide and carbonitride, are strictly linked to components percentage providing these elements which can be found in powdery media.

Thus, in case of constant carbamide and ammonium chloride in environment used for SNC, to further increase of nascent sulphur will be recorded an increasing of sulphur proportion by means of iron sulphide in compound layer and a decreasing of adsorbed nitrogen. The proportions evolution of these two elements in the compound area is antagonistic. So, by increasing the carbamide percent in powdery media (the rest components maintaining constant), the adsorbed sulphur percentage will be diminish and that of nitrogen will be increased.

The results must be in conjunction with the elements activity in environments used for SNC and respectively with the diffusion coefficient value in matrix - Fe_α at the operating temperature. Thus, for values in the same range of diffusion coefficient for sulphur and nitrogen respectively in Fe_α matrix, about 10^{-13} m^2/s ($D_S^{Fe\alpha}$ = 1.9×10^{-13} m^2/s [19], comparative with $D_N^{Fe\alpha}$ = 8.76×10^{-13} m^2/s [20]), the growth activity of one of two elements used in SNC process will determine an increase of this in superficial layers over the other.

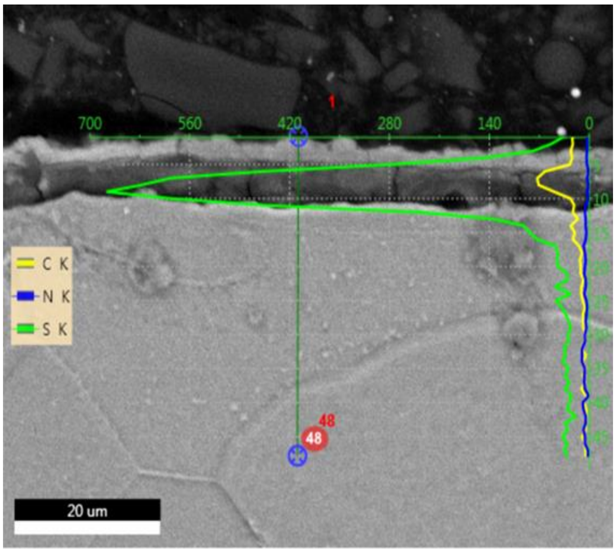

Figure 5. SEM-EDS image of Armco-Fe matrix subjected to SNC process using S-CON_2H_4-NH_4Cl-Charcoal (20 %-35 %-5 %-40 %) - *Fifth experiment*; Etchant: Nital 2%; In layer: 6.59 %S; 1.83 %N; Layer features: δ_{tot}=62.3µm; δ_{comp}=2.67µm.

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By varying the environment components, proportion ratio used in SNC clearly affects the kinetics forming of the total layer and compound area thickness, as it shown in Figure 6.

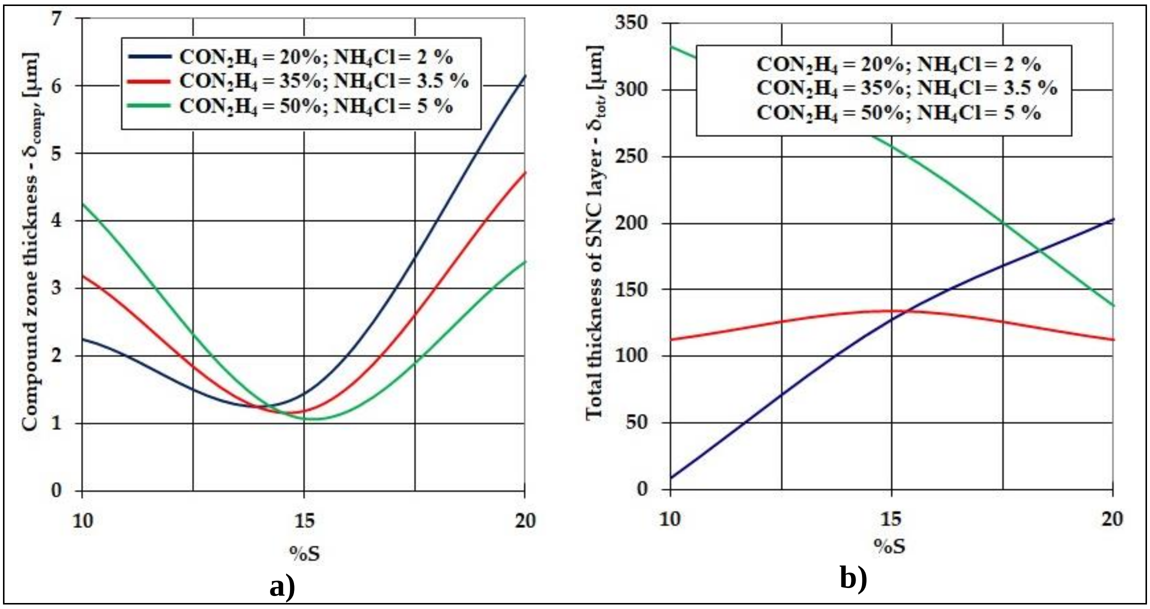

Figure 6. SNC layer total thickness variation (a) and compound zone (b) determined by the change in the percentages of the powdered solids components ratio used for the thermochemical processing

We can see that, at proportions of sulfur of more than 15 % in the powdered solid mixture used for sulfonitrocarburizing, the kinetics intensity of the compound area formation increases as the proportion of carbamide (the main source of nitrogen and partially carbon) decreases in the mixture. On the other hand, increasing the proportion of carbamide, together with that of sulphur, generates a decrease in the area of compounds and a decline in the diffusion zone kinetics. The explanation of the phenomena is related to the antagonistic effects determined by the simultaneous presence of the two elements, sulphur and nitrogen, in the superficial layer areas.

4. Conclusions

The presence of sulfur-providing components can provide simultaneous saturation with nitrogen, carbon, and sulfur, by processing at temperatures below the eutectoid transformation temperature of the Fe-N system.

The adjustment of the superficial layers phase composition, in accordance with the demands to which the product in operation is subject, can be possible by a strict control of the solid powdery components proportions, environments providing elements in active state, at a certain temperature.

The mathematical models of the interactions between the components of solid powdery medium (CON_2H_4-C-NH_4Cl-S), used in the SNC process, determined by the programming of experiments, are particularly useful tools for controlling the phase composition of the formed layers.

The thickest SNC layer and that of the compound area, respectively, for mixed sulphur concentrations around 10%, while carbamide and ammonium chloride are at the maximum level adopted from the experimental research program (0% and 5% respectively) obtained.

The kinetics of the compound area formation is accelerating substantially by the carbamide and ammonium chloride proportion decreasing in the solid powdery mixture.

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