

## QUANTIFICATION THE EFFECTS OF CHANGE THE PHASE COMPOSITION OF POWDERY MEDIA UTILISED FOR CARBONITRIDING-ANTIMONIZING OF STEELS

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**Abstract.** The cementation with antimony (antimonizing) of metallic matrixes has as main effect the increase of their corrosion resistance against sea water and aqueous solutions of hydrochloric acid or sulphuric acid. The concomitant increase of C, N and Sb contents in the superficial layers, e.g. by means of carbonitriding-antimonizing, is expected to improve also the wear and seizing resistances of these zones. The paper shows the mathematical models of the interactions between the components of the powdery medium (utilised for carbonitriding-antimonizing) and the corrosion resistance, respectively the total case depth of 21NiCrMo2 case-hardening steel. The mathematical models have been developed by means of the experiment programming method.

Energy-dispersive X-ray spectroscopy (EDS) was applied in order to evaluate quantitatively the antimony concentrations in the carbonitrided-antimonized layers. The kinetics and the corrosion resistances in (synthetic) sea water of the carbonitrided-antimonized samples have been corroborated with the concentrations of the three elements available in the superficial layers of steel considered (with highlighting the influence of Sb concentration).

**Keywords:** carbonitriding-antimonizing in powdery medium, corrosion resistance in (synthetic) sea water, layer growth kinetics, 21NiCrMo2 case - hardening steel.

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### 1. Introduction

The ability of antimony to enhance the corrosion resistance of cast-irons, steels and non-ferrous alloys, or to act as corrosion inhibitor is well known (Minkevici, 1965; Chen *et al.*, 2012; Mago & West, 1974; Le *et al.*, 2008). Based on this observation, an increase of the corrosion resistance of steel matrixes, respectively the increase of their corresponding wear and seizing resistances, can be ensured by controlling the antimony content, either in the elaboration stage, or by means of superficial saturation (thermochemical treatment) (Minkevici, 1965; Gorson, 1936). To reach this goal can be used either solid medium (rarely utilised) or liquid, gaseous or plasma media which are more likely to be utilised for high temperature carbonitriding-antimonizing in the presence of a controlled amount of antimony containing components. In the case of antimonizing in powdery medium, the antimony oxides could be the suppliers of antimony. As far as the authors know, there is a lack of literature related to this field. The manuscript aimed to quantify the effects of concomitant increase of C, N and Sb contents in the superficial layers of a case-hardening alloy steel (by means of

carbonitriding-antimonizing in powdery medium) on the growth kinetics and corrosion resistance in (synthetic) sea water of these zones.

To keep unaltered the steel resistance characteristics in the presence of antimony, it is necessary to control rigorously the proportion of the components supplying antimony in the carbonitriding-antimonizing medium. It is advisable to optimize the ratio between the proportions of the components of the carbonitriding-antimonizing medium such as to maximize the layer case depth, concomitantly with the increase of wear, seizing and corrosion resistances without altering other resistance characteristics.

## 2. Methodology, materials and equipment used in the research

The quantification of the effects of change the phase composition of powdery media selected for the carbonitriding-antimonizing experimental researches was achieved by programming the experimental cycles (Taloi *et al.*, 1983; Dimitriu & Taloi, 2014).

The 2<sup>nd</sup> order non-compositional programming method was utilised and the independent variables considered were  $X_1$ -%Sb,  $X_2$ -%NH<sub>4</sub>Cl,  $X_3$ -%Na<sub>2</sub>CO<sub>3</sub>. The fourth component of the powdery mixture (utilised for the superficial saturation with antimony, carbon and nitrogen) was the carbon graphite, in a proportion representing the difference up to 100% (see Table 1). The following dependent variables, Y, have been chosen:  $Y_1$ -the total case depth of the carbonitrided - antimonized layer, [ $\mu$ m] and  $Y_2$ -the gravimetric index, which is associated to the specific corrosion rate in (synthetic) sea water medium [mg/cm<sup>2</sup>h]. The chemical composition of the synthetic sea water medium was: 5g KI, 10g KBr, 30g NaCl at 1000 ml water (Minkevici, 1965). The homogenising of the powdery medium was achieved by mixing of it for 15 min in balls mills with the useful volume of about 2,5l; the ratio between the mass of the milling bodies and the powdery mixture mass was about 11:1. The metallic matrix subject to thermochemical processing was a case - hardening alloy steel 21NiCrMo2 in normalized state.

The correspondence between the values of the factors expressed as natural units and as codified units is presented in table 1.

**Table 1.** Correspondence between the values of the factors expressed as natural units and as codified units

Factor	%Sb		%NH <sub>4</sub> Cl		%Na <sub>2</sub> CO <sub>3</sub>		%Carbon graphite
	Natural units, $Z_i$ ,%	Coded value, $X_1$	Natural units, $Z_i$ ,%	Coded value, $X_2$	Natural units, $Z_i$ ,%	Coded value, $X_3$	Natural units, %
Base level	$Z_0=3$	0	$Z_0=1,5$	0	$Z_0=15$	0	80,5
Variation range	$\Delta Z=2$	-	$\Delta Z=0,5$	-	$\Delta Z=5$	-	7,5
Superior level	$Z_0+\Delta Z=5$	+1	$Z_0+\Delta Z=2$	+1	$Z_0+\Delta Z=20$	+1	73
Inferior level	$Z_0-\Delta Z=1$	-1	$Z_0-\Delta Z=1$	-1	$Z_0-\Delta Z=10$	-1	88

Note:  $X_1$ ;  $X_2$ ;  $X_3$ - represent the process independent variables

$$\% \text{Carbon graphite} = 100 - \sum (\% \text{Sb} + \% \text{NH}_4\text{Cl} + \% \text{Na}_2\text{CO}_3)$$

All the experiments have been developed in identical conditions e.g. the temperature and holding time were 930°C/60min and the cooling was performed in the powdery mixture where the samples were packed (cooling in furnace). The samples have not been subjected to further thermal processing after the thermochemical treatment. The investigations have been realized on the thermochemically processed samples.

The thermochemical processing was realized in a heat treatment furnace endowed with automatic temperature control and adjustment. The tests necessary to determine the corrosion rate in (synthetic) sea water, evaluated by means of the gravimetric index  $\Delta m/S.t.$ , have last for 216 hours.

The investigations of the layers have been made by optical microscopy (Reichert Univar microscope and OmniMet Enterprise software from BUEHLER) and electronic microscopy (SEM/ EDS microscopy-Quanta SEM Inspect F50).

### 3. Results. Interpretation

The development of the experimental cycle under the conditions imposed by the 2<sup>nd</sup> order non-compositional programming method and the results obtained are presented in the Table 2.

**Table 2.** 2<sup>nd</sup> order non-compositional programming matrix (k=3);  
The conditions for the development of the experiments and the results obtained

No. exp	Independent variables ( $X_i$ )										Y	
	$X_0$	$X_1$ %Sb	$X_2$ %NH <sub>4</sub> Cl	$X_3$ %Na <sub>2</sub> CO <sub>3</sub>	$X_1X_2$	$X_1X_3$	$X_2X_3$	$X_1^2$	$X_2^2$	$X_3^2$	$\delta_{tot}$ , $\mu m$	$\Delta m/S.t.$ , $\times 10^{-3}$ mg/cm <sup>2</sup> h
1	+1	+1	+1	0	+1	0	0	+1	+1	0	55,68	2,59
2	+1	+1	-1	0	-1	0	0	+1	+1	0	59,9	6,16
3	+1	-1	+1	0	-1	0	0	+1	+1	0	60,74	5,12
4	+1	-1	-1	0	+1	0	0	+1	+1	0	22,5	5,043
5	+1	+1	0	+1	0	+1	0	+1	0	+1	59,26	4,703
6	+1	+1	0	-1	0	-1	0	+1	0	+1	59,13	2,73
7	+1	-1	0	+1	0	-1	0	+1	0	+1	58	7,12
8	+1	-1	0	-1	0	+1	0	+1	0	+1	20,96	8,80
9	+1	0	+1	+1	0	0	+1	0	+1	+1	36,45	5,072
10	+1	0	+1	-1	0	0	-1	0	+1	+1	29,23	5,84
11	+1	0	-1	+1	0	0	-1	0	+1	+1	38,43	5,81
12	+1	0	-1	-1	0	0	+1	0	+1	+1	19,03	6,48
13	+1	0	0	0	0	0	0	0	0	0	57,8	6,01
14	+1	0	0	0	0	0	0	0	0	0	59,9	6,43
15	+1	0	0	0	0	0	0	0	0	0	59,3	6,52

The statistical processing of information on carbonitriding-antimonizing layers case-depths and gravimetric indexes is presented in table 3.

**Table 3.** The statistical processing of the experimental data related to the effects of change the phase composition of the powdery media utilised for carbonitriding-antimonizing

No.	Y <sub>1</sub> - Total size of the layer, μm	t <sub>α;N</sub>	Y <sub>2</sub> -Indicator of the corrosion in synthetic sea water, Δm/S.t, mg/cm <sup>2</sup> .h
1	S <sub>o</sub> <sup>2</sup> =1,17	t <sub>α;N</sub> =2,131	S <sub>o</sub> <sup>2</sup> =7,41.10 <sup>-8</sup>
2	S <sub>bo</sub> <sup>2</sup> =0,39;S <sub>bo</sub> =±0,624; Δb <sub>o</sub> =±1,33		S <sub>bo</sub> <sup>2</sup> =2,47.10 <sup>-8</sup> ;S <sub>bo</sub> =±1,57.10 <sup>-4</sup> ;Δb <sub>o</sub> =±3,35.10 <sup>-4</sup>
3	S <sub>bi</sub> <sup>2</sup> =0,146;S <sub>bi</sub> =±0,382;Δb <sub>i</sub> =±0,814		S <sub>bi</sub> <sup>2</sup> =0,926.10 <sup>-8</sup> ;S <sub>bo</sub> =±9,62.10 <sup>-5</sup> ; Δb <sub>i</sub> =±2,05.10 <sup>-4</sup>
4	S <sub>bii</sub> <sup>2</sup> =0,389;S <sub>bii</sub> =±0,623; Δb <sub>ii</sub> =±1,329		S <sub>bii</sub> <sup>2</sup> =2,467.10 <sup>-8</sup> ;S <sub>bo</sub> =±1,57.10 <sup>-4</sup> ; Δb <sub>ii</sub> =±3,35.10 <sup>-4</sup>
5	S <sub>bij</sub> <sup>2</sup> =0,292;S <sub>bij</sub> =±0,54; Δb <sub>ij</sub> =±1,15		S <sub>bij</sub> <sup>2</sup> =1,85.10 <sup>-8</sup> ;S <sub>bo</sub> =±1,36.10 <sup>-4</sup> ; Δb <sub>ij</sub> =±2,89.10 <sup>-4</sup>

The following *particular coded expressions of the regression equations* resulted:

- for the total case-depth of the carbonitriding-antimonizing layer, Y<sub>1</sub>;

$$Y_1 = \delta_{tot} = 59 + 8,97X_1 + 5,28X_2 + 7,97X_3 - 10,61X_1X_2 - 9,22X_1X_3 - 3,04X_2X_3 + 4,63X_1^2 - 13,9X_2^2 - 14,28X_3^2 \quad (1)$$

- for the gravimetric index

$$Y_2 = \Delta m/S.t = 10^{-3} [6,32 - 1,246X_1 - 0,617X_2 - 0,931X_1X_2 + 0,913X_1X_3 - 0,785X_1^2 - 0,825X_2^2] \quad (2)$$

respectively, to the following *particular decoded expressions of these*:

- for the total case-depth of the carbonitriding-antimonizing layer, Y<sub>1</sub>;

$$Y_1 = \delta_{tot} [\mu k] = -353,74 + \%Sb(1,15\%Sb - 10,61\%NH_4Cl - 0,92\%Na_2CO_3 + 27,29) + \%NH_4Cl(227,4 - 55,6\%NH_4Cl) + \%Na_2CO_3(23,28 - 0,57\%Na_2CO_3 - 1,21\%NH_4Cl) \quad (3)$$

- for the gravimetric index, Y<sub>2</sub>:

$$Y_2 = \Delta m/S.t [mg/cm^2.h] = 10^{-3} [0,77 + \%Sb(0,58 - 0,93\%NH_4Cl + 0,09\%Na_2CO_3 - 0,2\%Sb) + \%NH_4Cl(11,46 - 3,3\%NH_4Cl) - 0,27\%Na_2CO_3] \quad (4)$$

The results of the verification of the concordance between the two calculated non-linear models and the experimental results are presented in table 4.

**Table 4.** Verification of the concordance between the two calculated non-linear models and the experimental results

Y=f(X <sub>1</sub> ;X <sub>2</sub> ;X <sub>3</sub> )	S <sub>conc</sub> <sup>2</sup>	F <sub>calc</sub>	F <sub>tab.</sub>
Y <sub>1</sub> =f(X <sub>1</sub> ;X <sub>2</sub> ;X <sub>3</sub> )-ec.1	21,12	18,05	19,39
Y <sub>2</sub> =f(X <sub>1</sub> ;X <sub>2</sub> ;X <sub>3</sub> )-ec.2	10,21.10 <sup>-7</sup>	13,77	19,37

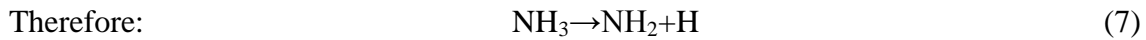
The results confirm the models are true (F<sub>calc</sub><F<sub>tab</sub>) such as these models describe with a high probability (~95%, α=0,05) the correlations between the total case depths of the carbonitrided-antimonized layers and the composition of the carbonitriding-antimonizing powdery medium. The graphical expressions of the regression equations (eq.1-2) (Fig.1a-2a, 5) are eloquent. These graphics together with the related regression equations (either coded -eq.1-2 or decoded -eq.3-4), or independently, define how the powdery medium composition should modify in order to maximize the two independent parameters (the corrosion resistance in (synthetic) sea water and the carbonitrided - antimonized layer case - depth). The iso-property ranges (Fig.1b-2b) simplify substantially the procedures for selection the components proportions in the powdery medium, This way, a faster selection of a proper powdery medium is possible in order

to reach the targeted corrosion resistance in synthetic sea water and total case depth of the layer.

To better understand the experimental results, these need to be compiled with the information provided by the main reactions (eq.5-23) occurring between the powdery components -  $\text{Sb} + \text{NH}_4\text{Cl} + \text{Na}_2\text{CO}_3 + \text{C}_{\text{gr}}$  and which finally generate the elements in active state ( $\text{C}^*$ ,  $\text{N}^*$ )



or, more likely, according to the mechanism proposed by Gräbke (1968), the decomposition of the ammonia takes place in stages, with successive release of hydrogen atoms (Gräbke, 1968; Florian & Cojocaru, 1978; Cojocaru & Florian, 1978; Cojocaru, 1976):



or:

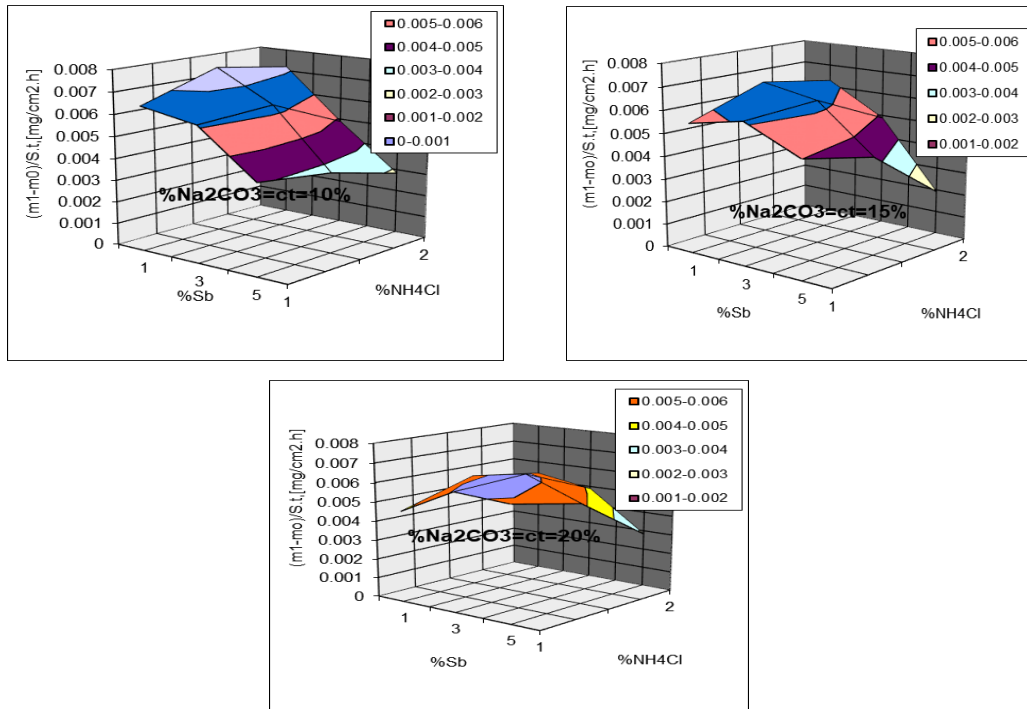


or:



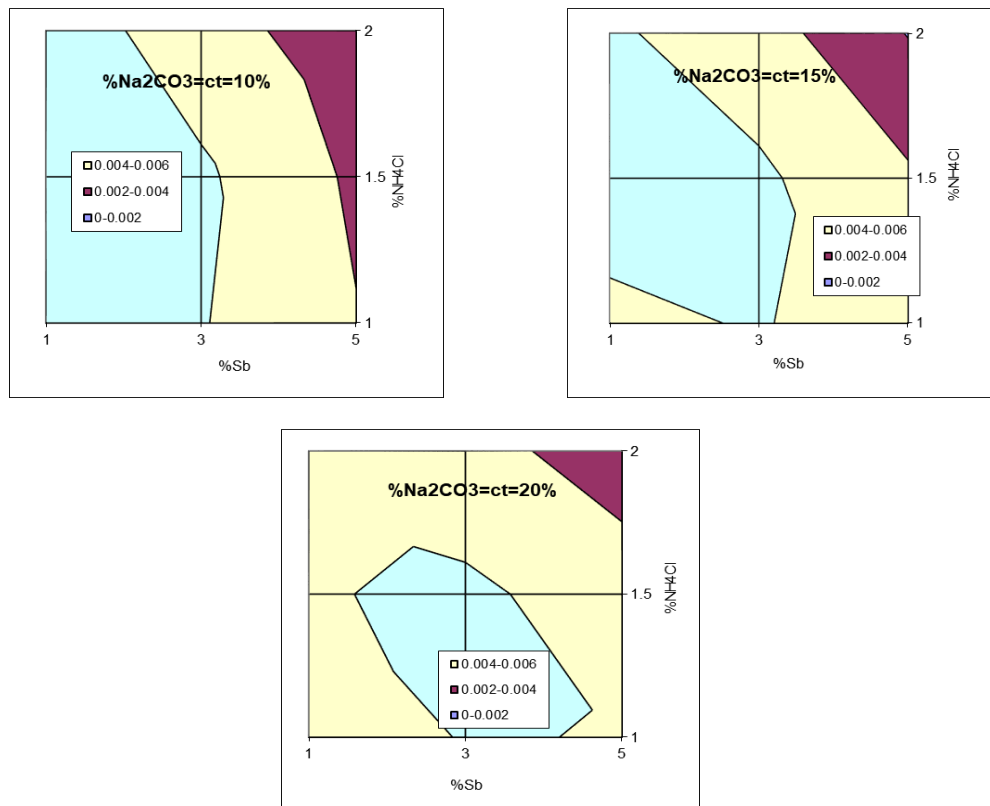
**Note:**

The reaction (eq.15) is less probable by thermodynamic point of view than the reactions (eq.11) or (eq.13). Minkevici (1965) in his experimental researches related to the carbonitriding-antimonizing, described that in the superficial zones of the thermochemically treated products, rich in antimony  $\text{FeSb}$  and  $\text{FeSb}_2$  compounds could appear. However after determination of smaller volumes of these compounds crystalline networks (due to the deficit of iron atoms), he concluded, that these compounds are carbo-antimonized iron like  $\text{FeSb}(\text{C})$ , respectively  $\text{FeSb}_2(\text{C})$  in reality. The presence of nitrogen in the carbonitriding-antimonizing medium makes also possible the existence of carbonitrided-antimonized compounds like  $\text{FeSb}(\text{CN})$ , respectively  $\text{FeSb}_2(\text{CN})$ .

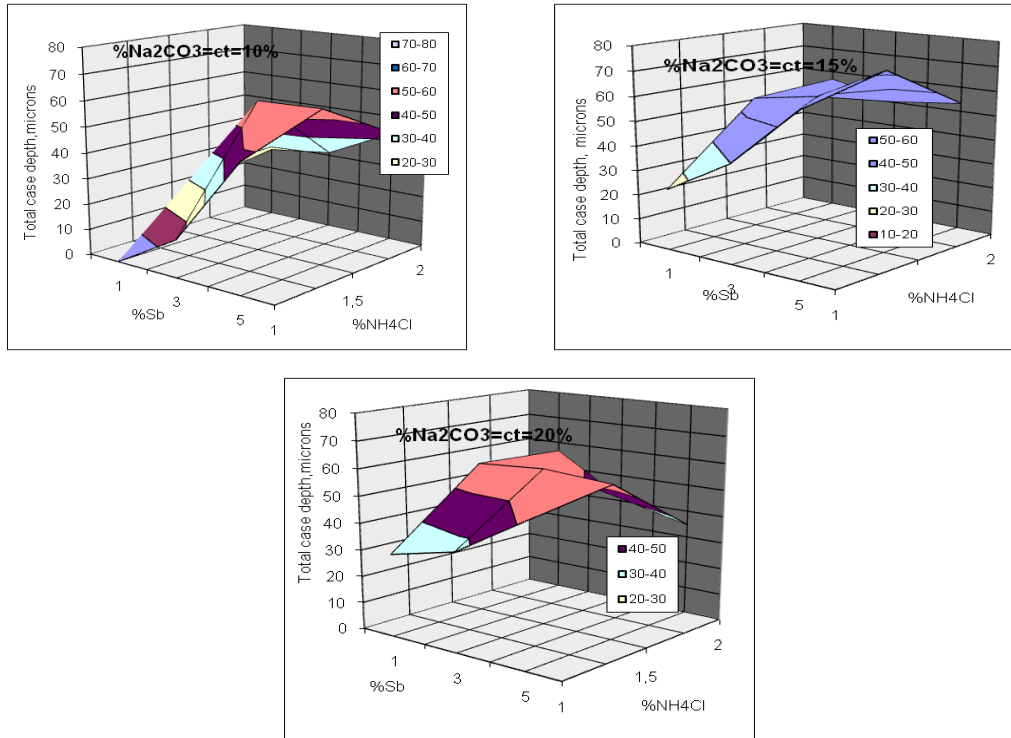


**Fig.1a.** Graphical expression of the regression equation:

$$Y = \Delta m/S.t = 10E(-3)[6,32 - 1,246X1 - 0,617X2 - 0,931X1X2 + 0,913X1X3 - 0,785X1X1 - 0,825X2X2]$$

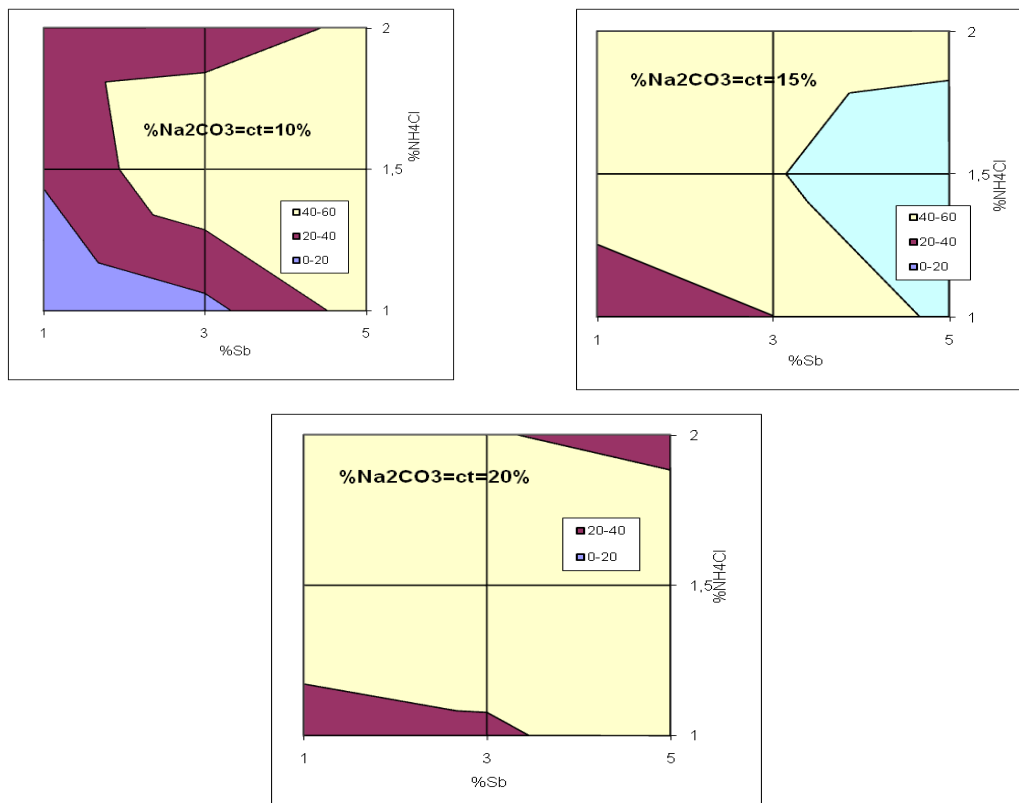


**Fig. 1b.** Iso-property fields (fields where the corrosion resistances in (synthetic sea) water are identical) - carbonitrided-antimonized 21NiCrMo2 steel. Carbonitriding-antimonizing in solid powdery media composed of: carbon graphite-Sb-NH4Cl-Na2CO3



**Fig.2a.** Graphical expressions of the regression equation:

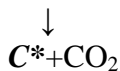
$$Y=59+8,97X_1+5,28X_2+7,97X_3-10,61X_1X_2-9,22X_1X_3-3,04X_2X_3+4,63X_1X_1-13,9X_2X_2-14,28X_3X_3$$



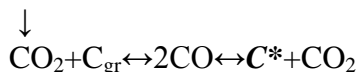
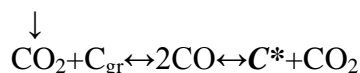
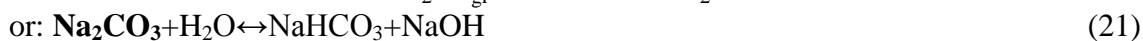
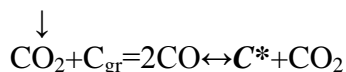
**Fig.2b.** Iso-property fields (fields where the total case depths are identical) - carbonitrided-antimonized 21NiCrMo2 steel Carbonitriding-antimonizing in solid powdery media composed of: carbon graphite-Sb- $\text{NH}_4\text{Cl}$ - $\text{Na}_2\text{CO}_3$



or:



$Na_2CO_3$  is extremely stable up to temperature over 2000K, which are much higher than its melting temperature (Stern & Weise, 1969), such as the reaction  $Na_2CO_3\rightarrow Na_2O+CO_2$  cannot be considered, its role of activator being materialized by means of the reaction products  $CO_2$  (eq. 20) or of  $NaHCO_3$ (eq. 21).



Another important source of carbon is generated through the development of the **water gas reaction** ( $CO_2+H_2\leftrightarrow CO+H_2O$ ), respectively through the **reaction of methane conversion with water vapours** ( $CH_4+H_2O\leftrightarrow CO+3H_2$ ).

All the reactions involved in the generation of the three elements in chemically active state are possible by thermodynamic point of view and consequently led to a carbonitrided-antimonized layer with a certain chemical and phase composition.

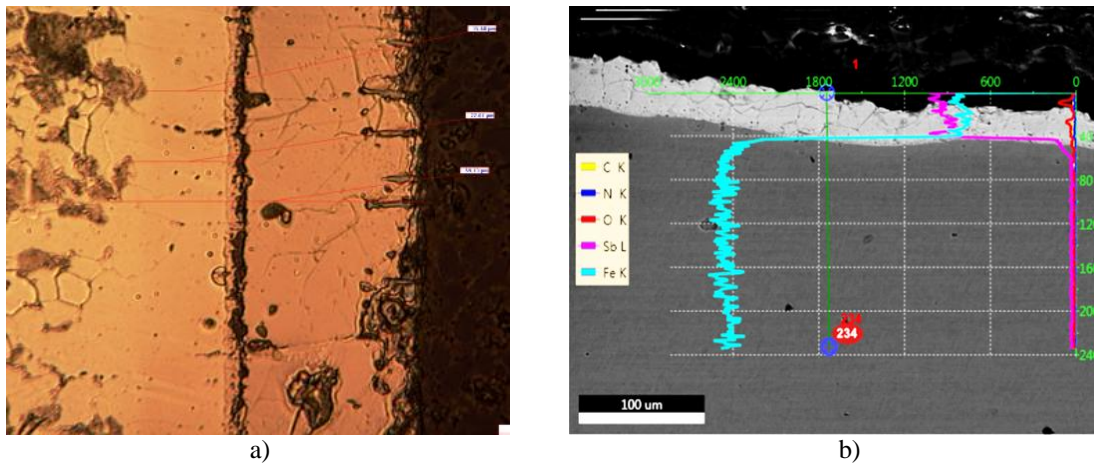
The optical microscopy images (Fig.3-4, a) and the electronic microscopy images (Fig.3-4, b) presented below, reveal the morphological aspects of the carbonitrided-antimonized layer, where could be seen low etched areas, rich in antimony (positioned at the interface with the medium).

The antimony has a diffusion coefficient in austenite with many order of magnitude lower than that of carbon, namely of nitrogen and has the natural tendency to concentrate in the superficial zones of the carbonitrided-antimonized layer (e.g.  $2.25\times 10^{-11}cm^2/s$  at  $950^\circ C$  for Sb diffusion in austenite (Pavlinov, 1983),  $\sim 0.88\times 10^{-7}[cm^2/s]$  for the N diffusion in austenite, respectively  $\sim 1.0\times 10^{-7}[cm^2/s]$  for the simultaneous diffusion also of the carbon in austenite (Prjenosil,1969). Lahtin & Kogan (1976) indicates for the diffusion of the two elements nitrogen and carbon in austenite,, values with one order of magnitude lower than those mentioned by Prjenosil (e.g.  $\sim 10^{-6}[cm^2/s]$ , comparatively with  $10^{-7}[cm^2/s]$  ).

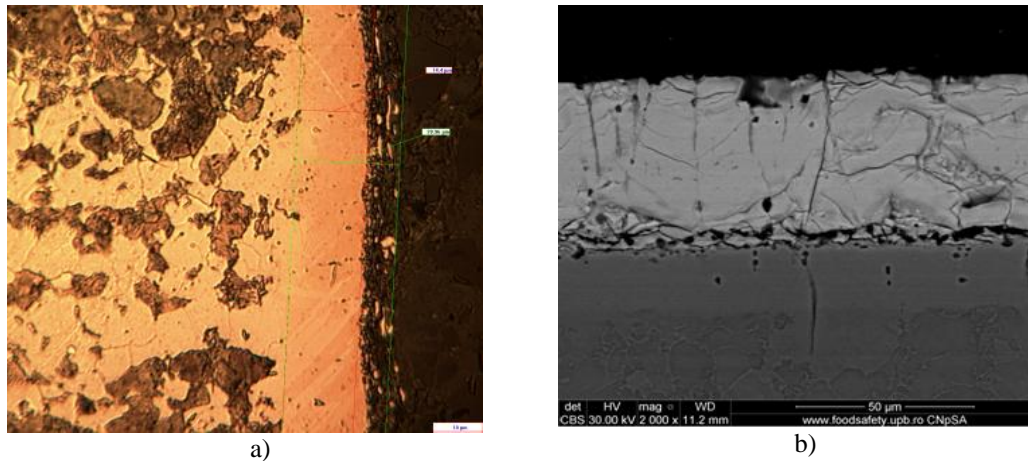
**Note:**

*Independently of reference, the value of the antimony coefficient of diffusion in austenite is clearly lower than the diffusion coefficients of the other two elements considered, therefore it can be found in the superficial layers as carbonitrided-antimonized compound.*





**Fig.3** Optical microscopy(a) and electronic microscopy(EDS)(b) of the carbonitrided-antimonized layer obtained on 21NiCrMo2 steel by thermochemical processing in powdery media composed of **5%Sb**, 1,5% $\text{NH}_4\text{Cl}$ , 10% $\text{Na}_2\text{CO}_3$ , balance  $\text{C}_{\text{gr}}$ (tab.2/6),  $930^\circ\text{C}/60\text{min}$ . Sb max. in layer -56,3%,  $\delta_{\text{tot}}=59,13[\mu\text{m}]$



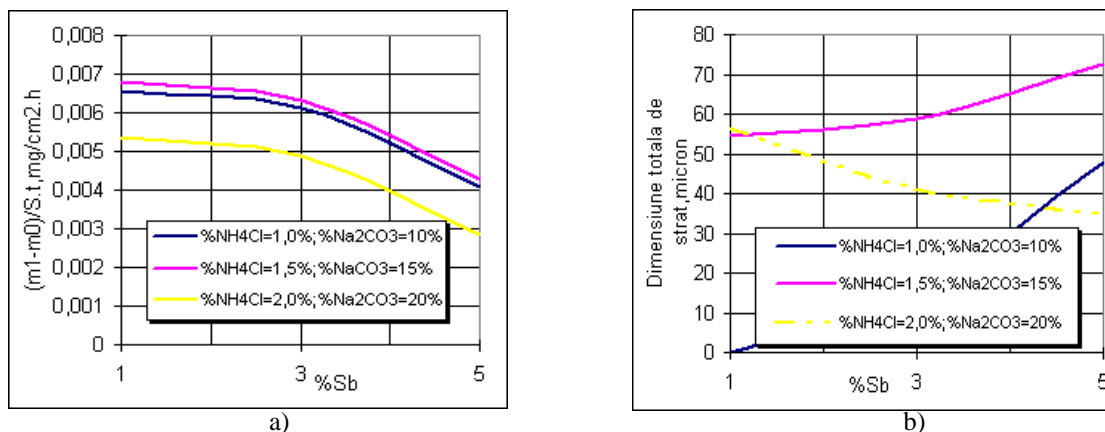
**Fig.4** Optical microscopy(a) and electronic microscopy (EDS)(b) of the carbonitrided-antimonized layer obtained on 21NiCrMo2 steel by thermochemical processing in powdery media composed of **1%Sb**, 1,5% $\text{NH}_4\text{Cl}$ , 10% $\text{Na}_2\text{CO}_3$ , balance  $\text{C}_{\text{gr}}$ (tab.2/8),  $930^\circ\text{C}/60\text{min}$ . Sb max. in layer -13,62%,  $\delta_{\text{tot}}=20,96[\mu\text{m}]$

The metallographic analysis of the carbonitrided-antimonized layer (Fig.3, a) reveals two distinct zones of it:

- an external zone where can be observed the existence of the needle shaped phase  $\epsilon$ . The phase  $\epsilon$  was generated through the decomposition of  $\text{Fe}_3\text{Sb}_2$  and represents a interstitial solid solution of iron in an hypothetical  $\text{FeSb}$  compound (Vol, 1962), or in a  $\text{FeSb}(\text{C})$  compound (in the C presence also). At the extremity of the layer were found carbonitrided-antimonized  $\text{FeSb}(\text{CN})$ , namely  $\text{FeSb}_2(\text{CN})$  and in depth, un-etched area composed of  $\alpha$  solid solution of antimony and carbon in iron was revealed. Under this zone there is a higher carbon concentration following to the generation of the  $\alpha$  solid solution.

The increase of the antimony proportion in the powdery medium utilized for carbonitriding-antimonizing decreases the corrosion rate in the (synthetic) sea water (considered in the experimental researches Fig.5, a). However, this increase needs to be realized in a controlled way because influence the layer growth kinetics and also the mechanical resistance characteristics. It could be observed that an increase of the antimony proportion in the powdery solid medium, concomitantly with an increase of

the other two components  $\text{NH}_4\text{Cl}$  și  $\text{Na}_2\text{CO}_3$  (over the basic level established through the experimental programming matrix), implies a reduction of the total case depth of the carbonitrided-antimonized layer. The diminishing of the total case depth accentuates with the increase of the antimony proportion (Fig.5, b).



**Fig.5.** The influence of phase composition of the carbonitriding-antimonizing powdery media on the gravimetric index (corrosion rate in (synthetic) sea water) (a) and on the total case depth of the carbonitrided-antimonized layer (b).

#### 4. Conclusions

1. The mathematical models of the interactions between the components of the powdery media- $\text{C}_{gr}$ - $\text{Sb}$ - $\text{NH}_4\text{Cl}$ - $\text{Na}_2\text{CO}_3$ , utilised for carbonitriding-antimonizing of the metallic matrixes with a specified composition (in this case, 21NiCrMo2 case-hardening steel), can represent very useful instruments for the control of the thermochemical treatment results.
2. The corrosion resistance in (synthetic) sea water of the 21NiCrMo2 case-hardening steel carbonitrided-antimonized in powdery media increases concomitantly with the increase of the antimony proportion in the thermochemical medium. The increase is most significant if also the proportions of the two other components of the powdery medium - $\text{NH}_4\text{Cl}$  and  $\text{Na}_2\text{CO}_3$  are higher (over 1.5% $\text{NH}_4\text{Cl}$  respectively over 15%  $\text{Na}_2\text{CO}_3$ ).
3. The change of the antimony content in carbonitriding- antimonizing medium has to be correlated strictly with the required total case depth of the layer. It was observed that at higher values of the  $\text{NH}_4\text{Cl}$  and  $\text{Na}_2\text{CO}_3$  (in the limits agreed experimentally), the increase of the antimony concentration in the powdery medium led to the reduction of the carbonitrided-antimonized layer case-depth.

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