THE STRUCTURAL EVOLUTION OF REFRACTORY STEEL SPARE PARTS DURING THE SUCCESSIVE CARBURIZING

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The refractory steel spare parts that work in the heat treatment furnaces are successively subjected to heat treatment cycles identical to those of the processed parts. Durability of spare parts under specific conditions of use depends to a great extent on the composition of the material used and the modifications generated by the successive thermal stress on their structure. Depending on the chemical composition of the steel, the thermal treatment cycle applied, and the cooling fluid used, the distribution of the carbides may change. Starting from these observations, the authors perform an experimental analysis of how the successive heating in the carburizing furnaces affects the structure of the W1.4855 and W1.4849 steels commonly used for the execution of the heat treatment furnaces, by using as parameter of structural assessment the percentage of carbides in the metal matrix. By statistical processing of the experimental data a series of estimation / anticipation solutions of the structural changes of the spare parts made from the two materials are established as a result of the successive thermal treatment of carburization.

Keywords: refractory steels, carburizing, structural evolution, spare parts

1. Introduction

Depending on the field of use, the refractory steels used to make spare parts in the heat treatment industry can be divided into two categories:

- Steels that working in condition of high temperature and thermal and/or mechanical shock (conveyor chains, fixtures, belts, quenching fixtures and trays)
- Steel that working in condition of high temperature and high pressure (combustion tubes, thermo-wells, walking beams, hearth plates radiant tubes, roller and skid rails, muffles, beams, recuperators, conveyor rolls,

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rotary retorts, fans, pit-type retorts and burners.

The most well-known application of refractory steels in heat treatment industry are fixtures and baskets. Fixtures and baskets are special devices used in applications involving operating temperature from 790 C^0 up to 1010° as support for loading of parts to be heat treated in the furnaces. The design of these devices is correlated with the specific application and loading, the heat treatment applied and the furnace equipment type.

The choice of optimum materials for each particular application is usually done on the basis of a set of materials properties determined under standard conditions, properties that will be modified under specifically high temperature conditions. Thus, in concrete exploitation conditions it is possible to have different operating durability in different condition of use for the same type of material. According to [1, 2], the structure of stainless and refractory steels has two main components: the matrix and the minor constituents. The matrix consists of solid solutions α and γ and contains alloying elements in the interstitial position (C and N) or substitution position (Cr, Ni and Ti). Minor constituents include interstitial, intermetallic and inclusion phases. Interstitial phases group are carbides, nitrides or carbonitrides formed with the alloying elements of steel. The most common types of carbide are $M_{23}C_6$. There may also be $Cr_{23}(B, C)_6$ and $Cr_{23}C_6$. $Cr_{23}C_6$ carbide can dissolve elements such as Mo, W, V and Ni. Chromium carbides such as Cr_7C_3, Cr_6C and CrNs and Cr_2N types can also be formed.

In austenitic refractory steels used for the manufacture of fixtures and baskets the matrix consists of austenite (phase γ) and the minor constituents. The structural changes occurring under high-temperature operation consist in changing the proportion, shape and distribution of the minor constituents in the matrix, the group in which the carbides occupy the most important proportion.

The carbon content of the cast austenitic refractory steels, typically used for the executions of the fixtures and baskets, is slightly higher, ranging from 0.15-0.35%. This situation is a factor favoring the chromium carbide precipitation process [3]. Starting from this observation It was performed an analysis of the structural transformations that take place in austenitic refractory steels under real operating conditions specific to devices used in carburizing furnaces.

2. Experimental work

The experimental analysis was made on two steel grades, W1.4855 and W1.4849. As a measure of structural changes, it was used the carbide content of steels. To prove the influence of Nb on the cast steels structure, the two steels were made both with addition and no addition of niobium. The chemical compositions of cast steels subjected to experimental analysis are presented in Table 1.

The experimental work involved the following steps:

- Elaboration of the alloys in an induction furnace with a 250 kg crucible.
- Cast of Y samples in molds made of quartz sand (96%) binded with sodium silicate (6%,) CO2 hardened and coated with zirconium paint.
- Analysis of the chemical composition of cast samples with an optical emission spectrometer ARL QUANTRIS

Table 1

The Chemical composition of cast steels subjected to experimental analysis

	W1.4849 with Niobium	**W1.4849 without Niobium**	**W1.4855 with Niobium**	**W1.4855 without Niobium**
C	0.36933	0.40681	0.33978	0.36642
Mn	0.78009	0.84345	0.71242	0.75401
Si	1.54471	1.46117	1.50230	1.50407
P	0.01250	0.01318	0.02119	0.01763
S	0.01889	0.02417	0.02416	0.03411
Ni	37.18188	37.79135	23.37510	23.63198
Cr	17.70709	18.14052	23.36344	23.62058
Cu	0.15030	0.14876	0.14642	0.13605
Mo	0.13318	0.15055	0.20722	0.21075
V	0.05199	0.04975	0.06125	0.06290
Ti	0.00050	0.00050	0.01121	0.00179
Al	0.00857	0.22155	0.13210	0.05586
Nb	1.70675	0.03924	1.75598	0.00200
W	0.01300	0.01300	0.01300	0.01300
Sn	0.01151	0.00868	0.00905	0.00689
Co	0.12454	0.12811	0.10987	0.12775
B	0.00118	0.00131	0.00141	0.00148
Ca	0.00036	0.00034	0.00016	0.00050
Fe%	Rest	Rest	Rest	Rest

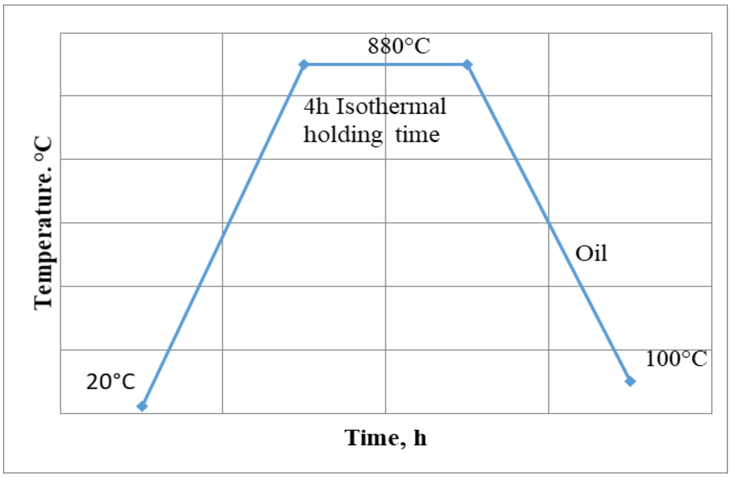


Fig 1 Diagram of the thermal carbide treatment applied in the experimental work

- Successive heat treatment of samples, in a carburizing furnace, according with the diagram presented in fig. 1. The composition of the endothermic atmosphere of the carburization furnace obtained from a mixture air-CH_4, consists of 18-20% CO, 38-40% H_2, 40% N_2, small amounts of H_2O, CO_2, CH_4 residual (<2%) and has a carbon potential of 0,35
- Extract a set of samples after each 20 treatment cycles (a total of 80 hours isothermal maintaining time) and performing the structural analysis with an Olympus microscope, according with the ASTM B487 standard, by using Scentis Software version 1.2 for Windows
- Statistical data processing and determination of the correlation equation between the carbide content of steel and the total time of successive heat treatment.

3. Analysis

To establish a correlation equation between the number of isothermal maintaining hours at successive carburizing and the percentage of carbides in the structure of W1.4849 and W1.4855 with and without the addition of niobium it was used the statistical data processing by passive experiment method [4].

The analysis was performed for each steel composition. For each variant we have only one independent variable (number of isothermal maintaining hours) and one dependent variable (percentage of carbides).

The algorithm for explaining the connection between the independent variable **x,** related to the number of hours of heat treatment and the dependent variable **y,** corresponding to the proportion of the eutectic carbides, involved the following steps:

a. Completing the database of results with the data needed to calculate the partial correlation coefficients τyx and internal $\tau x_i x_j$

b. Calculation the partial correlation coefficients τyx between the independent variables (xi) and the dependence y with the following equation:

$$\tau_{yx} = \frac{n\sum_{i=1}^{n} x_i y_i - \sum_{i=1}^{n} x_i \sum_{i=1}^{n} y_i}{\sqrt{\left[n\sum_{i=1}^{n} {x_i}^2 \, {}^{x^2} - \left(\sum_{i=1}^{n} x_i\right)^2\right]\left[n\sum_{i=1}^{n} y_i^2 - \left(\sum_{i=1}^{n} y_i\right)^2\right]}} \tau_{x_i y_j}$$

c. Calculation of internal correlation coefficients

with the following equation:

$$\tau_{x_i x_j} = \frac{n\sum_{i,j=1}^{n} x_i x_j - \sum_{i=1}^{n} x_i \sum_{j=1}^{n} x_j}{\sqrt{\left[n\sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2\right]\left[n\sum_{j=1}^{n} x_j^2 - \left(\sum_{j=1}^{n} x_j\right)^2\right]}}$$

d. Building the system of standardized equations

General form

$$\begin{cases} B_1 + \tau_{x_1x_2}B_2 + \tau_{x_1x_3}B_3 + \tau_{x_1x_4}B_4 = \tau_{yx_1} \\ B_2 + \tau_{x_2x_1}B_1 + \tau_{x_2x_3}B_3 + \tau_{x_2x_4}B_4 = \tau_{yx_2} \\ B_3 + \tau_{x_3x_1}B_1 + \tau_{x_3x_2}B_2 + \tau_{x_3x_4}B_4 = \tau_{yx_3} \\ B_4 + \tau_{x_4x_1}B_1 + \tau_{x_4x_2}B_2 + \tau_{x_4x_3}B_3 = \tau_{yx_4} \end{cases}$$

Customized form

$$\begin{cases} B_1 + 0.42B_2 - 0.40B_3 - 0.51B_4 = 0.95 \\ B_2 + 0.42B_1 + 0.34B_3 - 0.605B_4 = 0.547 \\ B_3 - 0.40B_1 - 0.34B_2 + 0.77B_4 = -0.489 \\ B_4 - 0.51B_1 - 0.605B_2 + 0.77B_3 = -0.649 \end{cases}$$

e. Calculation of Regression Coefficients

$$b_i = B_i \frac{S_y^2}{S_{x_i}^2} = B_i \frac{S_y}{S_{y_i}}$$

In which average arithmetic deviations S_y, $S_x$can be calculated using relationships:

$$S_y = \sqrt{\frac{n\sum_{i=1}^{n} y_i^2 - \left(\sum_{i=1}^{n} y_i\right)^2}{n(n-1)}}$$ and respectively $$S_x = \sqrt{\frac{n\sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2}{n(n-1)}}$$

f. Calculation of the determination coefficient, R^2

$$R^2 = \left[1 - \frac{n-1}{n-(k+1)}\right] - \frac{n-1}{n-(k+1)}\left[-B_1\tau_{yx_1} - B_2\tau_{yx_2} - B_3\tau_{yx_3} - B_4\tau_{yx_4}\right]$$

4. Experimental results

The carbide contents of steel samples subjected to the analyze are presented in Table 2 and are shown graphically in the figures 2 and 3.
The metallographic structure of samples after successive carburizing, corresponding to a total time of successive heat treatment of 0h, 240h and 400 h are presented in figure 3 (steel W1.4855 with and without niobium) and figure 4 (steel W1.4849 with and without niobium) are presented in table 3 and 4.

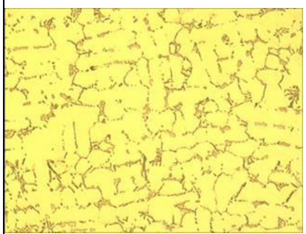
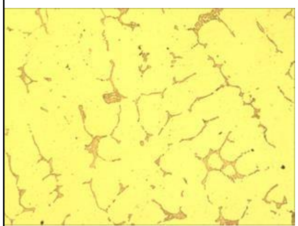
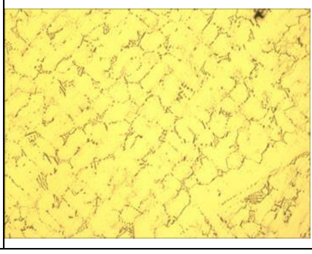
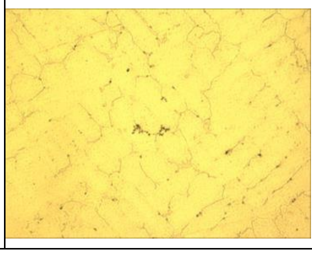
Table 2

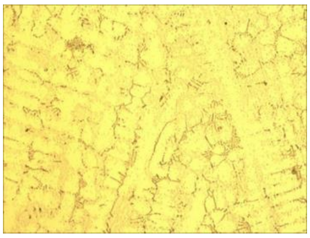
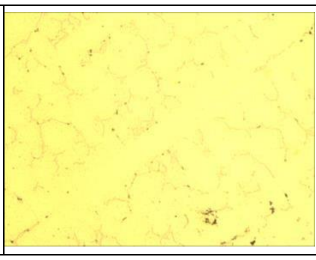
Carbide content of W1.4855 steel samples successively subjected to carburizing heat treatment

Stage	Carbide content, %			
	Alloy 4855 with Niobium	Alloy 4855 without Niobium	Alloy 4849 with niobium	Alloy 4849 without niobium
As casted	13.6	9.6	11.47	8.9
80 hours (20 cycles)	10.1	7.7	9.4	7.1
160 hours (40 cycles)	9.0	6.2	8.6	5.9
240 hours (60 cycles)	7.8	5.1	7.5	4.3
320 hours (80 cycles)	6.1	4.2	5.9	3.5
400 hours (100 cycles)	4.9	3.3	4.2	2.4

Table 3.

Structural evolution of samples made of W1.4855 steel after successive carburizing Attack Murakami, magnitude 100:1

Stage	Alloy W.1 4855, with Nb	Alloy W.1 4855, without Nb
As cast		
240 hours isothermal holding time (60 cycles).		

400 hours isothermal holding time (100 cycles).		

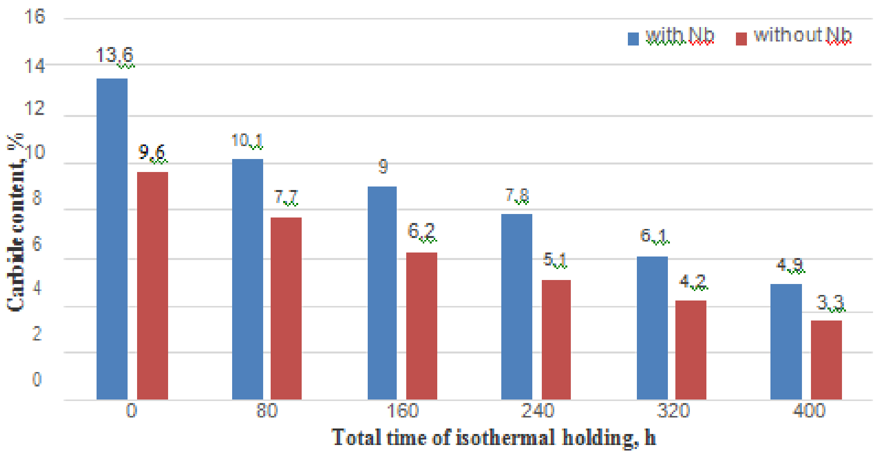
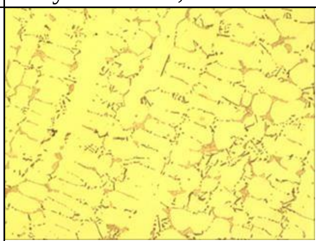
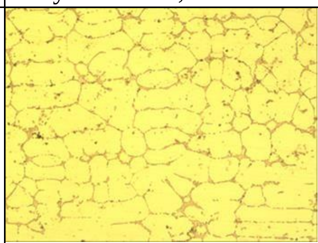
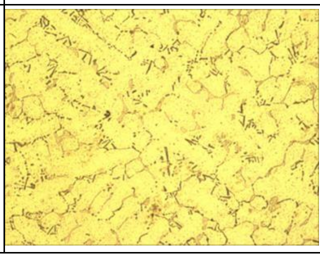
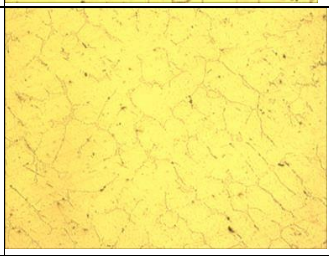
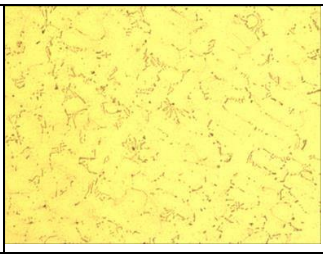
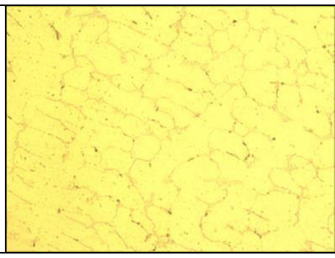


Fig. 2 Carbide content of W1.4855 steel samples successively subjected to carburizing heat treatment

Table 4

Structural evolution of samples made of W1.4849 steel after successive carburizing – Attack Murakami, magnitude 100:1

Stage	Alloy W.1 4849, with Nb	Alloy W.1 4849, without Nb
As cast		
240 hours isothermal holding time (60 cycles).		

400 hours isothermal holding time (100 cycles).		

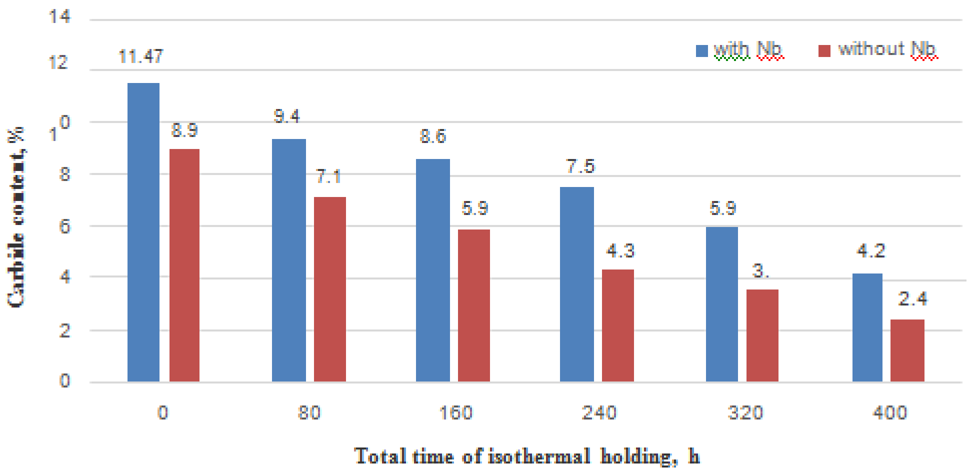


Fig. 3 Carbide content of W1.4849 steel samples successively subjected to carburizing heat treatment

The results for each variant submitted to the analysis are presented below.

Steel W1.4855 with Niobium, carburizing

	x_i no. of isothermal holding hours	y_i carbide%	x_i^2	x_i^3	x_i^4	$x_i y_i$	$x_i^2 : y_i$	$x_i^4 : y_i$
1	0	13.6	0	0	0	0	0	0
2	80	10.1	6400	512000	40960000	40960000	808	64640
3	160	9.0	25600	4096000	655360000	655360000	1440	230400
4	240	7.8	57600	13824000	3317760000	3317760000	1872	449280
5	320	6.1	102400	32768000	$1.048576 * 10^{10}$	$1.0485761 * 10^{10}$	1952	624640
6	400	4.9	160000	64000000	$2.56 * 10^{10}$	$2.56 * 10^{10}$	1960	784000

$\bar{Z}$	1200	51.5	351600	115200000	4.009984 $*10^{10}$	4.009984$*10^{10}$	8032	2152960

$$6b_0 + 1200b_1 + 351600b_2 = 51.5$$
$$1200b_0 + 351600b_1 + 115200000b_2 = 8032$$
$$351600b_0 + 115200000b_1 + 4.009984 \cdot 10^{10}b_2 = 2152960$$

By solving the equation system, it results: b_o=13.01, b_1= -0.029, b_2=+2.33*10^{-5} and the regression equation is $y = 13.01 - 0.029x + 2.33 \cdot 10^{-5}x^2$ or $\%\boldsymbol{carbide = 13.01 - 0.029n - 2.33 \cdot 10^{-5}n^2}$; r_{xy} = -0.98

Steel W1.4855 without Niobium, carburizing

	x_i no. of isothermal holding hours	y_i carbide%	x_i^2	x_i^3	x_i^4	$x_i y_i$	$x_i^2 : y_i$	$x_i^4 : y_i$
1	0	9.6	0	0	0	0	0	0
2	80	7.7	6400	512000	40960000	40960000	616	49280
3	160	6.2	25600	4096000	655360000	655360000	992	158720
4	240	5.1	57600	13824000	3317760000	3317760000	1224	293766
5	320	4.2	102400	32768000	1.048576 $*10^{10}$	1.0485761 $*10^{10}$	1344	430080
6	400	3.3	160000	64000000	2.56$*10^{10}$	2.56 $*10^{10}$	1320	528000
$\bar{Z}$	1200	36.1	351600	115200000	4.009984 $*10^{10}$	4.009984$*10^{10}$	5496	1459840

$$6b_0 + 1200b_1 + 351600b_2 = 36.1$$
$$1200b_0 + 351600b_1 + 115200000b_2 = 5496$$
$$351600b_0 + 115200000b_1 + 4.009984 \cdot 10^{10}b_2 = 1459840$$

By solving the equation system it results: : b_o=9.7, b_1= -0.026, b_2=+2.59*10^{-5} and the regression equation is $y = 9.7 - 0.026x + 2.59 \cdot 10^{-5}x^2$
or $\%\boldsymbol{carbide = 9.7 - 0.026n - 2.59 \cdot 10^{-5}n^2}$ r_{xy} = -0.99

Steel W1.4849 with Niobium, carburizing

	x_i no. of isothermal holding hours	y_i carbide %	x_i^2	x_i^3	x_i^4	$x_i y_i$	$x_i^2 : y_i$
1	0	11.47	0	0	0	0	0
2	80	9.4	6400	512000	40960000	752	60160
3	160	8.6	25600	4096000	655360000	1376	220160
4	240	7.5	57600	13824000	3317760000	1800	432000
5	320	5.9	102400	32768000	$1.048576 * 10^{10}$	1888	604160
6	400	4.2	160000	64000000	$2.56 * 10^{10}$	1680	672000
$\bar{Z}$	1200	47.07	351600	115200000	$4.009984 * 10^{10}$	7496	1988480

$$6b_0 + 1200b_1 + 351600b_2 = 47.07$$
$$1200b_0 + 351600b_1 + 115200000b_2 = 7496$$
$$351600b_0 + 115200000b_1 + 4.009984 \cdot 10^{10} b_2 = 1988480$$

By solving the equation system it results: : b_0=11.12, b_1= -0.015, b_2=- $4.74*10^{-6}$ and the regression equation is: $y = 11.12 - 0.015x - 4.74 \cdot 10^{-6} x^2$ or
$\%carbide = 11.12 - 0.015n - 4.74 \cdot 10^{-6} n^2$ **r_{xy} = -0.994**

Steel W1.4849 without Niobium, carburizing

	x_i no. of isothermal holding hours	y_i Carbid e %	x_i^2	x_i^3	x_i^4	$x_i y_i$	$x_i^2 : y_i$	$x_i^4 : y_i$
1	0	8.9	0	0	0	0	0	0
2	80	7.1	6400	512000	40960000	40960000	568	4544
3	160	5.9	25600	4096000	655360000	655360000	944	1516
4	240	4.3	57600	13824000	3317760000	3317760000	1082	247
5	320	3.5	102400	32768000	$1.04857 * 10^{10}$	$1.0485761 * 10^{10}$	1120	3589
6	400	2.4	160000	64000000	$2.56 * 10^{10}$	$2.56 * 10^{10}$	960	384
$\bar{Z}$	1200	32.1	351600	115200000	$4.00998 * 10^{10}$	$4.009984 * 10^{10}$	4624	7184

$$6b_0 + 1200b_1 + 351600b_2 = 32.1$$
$$1200b_0 + 351600b_1 + 115200000b_2 = 4624$$
$$351600b_0 + 115200000b_1 + 4.009984 \cdot 10^{10} b_2 = 1186560$$

By solving the equation system it results: : b_o=8.54, b_1= -0.016, b_2=-1.6*10^{-7} and the regression equation is: $y = 8.54 - 0.016x - 1.6 \cdot 10^{-7}x^2$

Or $\%carbide = 8.54 - 0.016n - 1.6 \cdot 10^{-7}n^2$, r_{xy} = -0.99

5. Conclusions

The determined regression equations highlight that on the analyzed range (up to 100 cycles of carburization) there is a decrease in the carbides content of samples, with the increase in the number of hours of isothermal maintenance respectively number of successive cycles of carburization.

This result is explained by the fact that, according to the heat treatment diagram, isothermal maintenance is at a temperature in the austenitic range, favorable to carbide dissolution and carbon assimilation in austenite, and oil cooling has a high enough velocity to avoid their recurrence.

The presence of Niobium reveals higher values of the percentage of carbides present in the structure, a phenomenon due to the presence of an additional percentage of elements with high affinity to carbon, capable of forming carbides. Also, in this variant of the composition the carbides are dissolved by successive thermal treatment, but the percentage of carbides remaining in the structure after each stage is twice as high as in the steel without niobium. Therefore, Niobium not only carries a uniform redistribution of carbides, but also because of its high affinity for carbon, it also has the effect of stabilizing it during successive carburizing exposure, with a positive influence on the mechanical characteristics of the steel.

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