THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N°. 1 - 2018, ISSN 1453-083X

PREDICTING OF REMAINING EUTECTIC CARBIDE CONTENT IN W1.4855 STEEL AS FUNCTION OF CARBON CONTENT AND HEAT TREATMENT PARAMETERS

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ABSTRACT

The relationship between the carbon content of W1.4855 steel, and the parameters of heat treatment of solution quenching (maintaining time and maintaining temperature) is investigated. The obtained experimental data are used to perform a statistical processing, resulting in a regression equation, useful for predicting the remaining eutectic carbide content in W1.4855 steel as function of carbon content and heat treatment parameters.

KEYWORDS*:* refractory steel, carbide, carbon content, solution quenching, maintaining time, temperature

1. Introduction

Austenitic refractory steels are widely used in the heat treatment industry to produce components that operate at temperatures in the range of 540 °C-1200 °C. Depending on their field of use, they fall into two broad categories. The first consists of components that work inside the furnaces and are subjected to high mechanical and/or thermal shocks (trays, fixtures, conveyor chains and belts, quenching fixtures). The second category consists of components that operate outside the furnace and are subject to less mechanical and thermal shocks (support beams, hearth plates, combustion tubes, radiant tubes, burners, thermowells, roller and skid rails, conveyor rolls, walking beams, retorts, muffles, recuperators, fans).

Because of the carbon content, most of these components are made from cast steel. In order to homogenize the structure and uniformly distribute the carbides, the cast components are subjected to a heat treatment of solution quenching. Their behavior in exploitation is in direct correlation with the structure, respectively with the content of carbides remaining after heat treatment. The analysis of the influence of the chemical composition on the carbide content of cast steel revealed that the most influential element is carbon [1, 2]. The smallest deviations in the sense of exceeding the prescribed limit of this element may have disastrous effects on the behavior of the material in use as it generates a higher volume of carbons that predominantly distributes to the grain boundary. This effect is even more pronounced as the chromium content of steel is higher, steel W1.4855 being a good example in this respect. Correction of such a situation is possible by heat treatment of solution quenching in the conditions of prolonging the maintaining time at high temperature or use of a higher maintaining temperature, for the purpose of dissolving carbides. However, this solution it is not always efficient to be applied due to too high manufacturing costs.

For this reason, establishing a complex relationship of dependence between the carbon content of steel, and the parameters of heat treatment of solution quenching (maintaining time and maintaining temperature) can be particularly useful for optimizing the whole process to improve their exploitation behavior.

2. Experimental method

The experimental investigations aimed to qualify the effects of the content variation in the carbon content of the steel obtained in W1.4855 (EN 10295-2002) analysis, austenitic stainless steel within the limits imposed by the mark and the thermal and temporal quality parameters for the solution of the proportion of the eutectic carbides remaining in the matrix. The analysis of the steel position in the Schaeffler structural diagram, considering the equivalent content of chromium and nickel respectively by the percentage of the general effects of the alpha- and gamma-phases, leads to the conclusion that regardless of the way of combining the proportion of the chemical elements of the steel within the required concentration limits brand, it remains in the austenitic field. The carbides appearing in the casted steel are inter-dendrite chromium carbides. The experimental researches aimed at explaining the effect of changing the chemical composition of steel on the proportion of carbide in casted state have highlighted that the variation of niobium concentration within the prescribed limits does not significantly influence the proportion of carbide in the cast. The effect of the proportion of this element is proved during subsequent heat transformation heat treatment or welding transformations through the appearance of very fine NbC carbide precipitations. Since Nb gold has a higher alliance than Cr than C, it prevents the formation of chromium carbides and thereby the austenitic build-up during long-term heating. In addition to the stabilizing role, niobium carbides also provide an increase in matrix breaking strength.

Earlier research in the field of carbides content in this casted steel confirm the current influence of carbon on increasing their proportion in steel, clearly superior to that associated with chromium and manganese alloying elements [1].

$$\%Carbide = 2.512 + 24.12\%C + 0.154\%Cr - 0.093\%Mn - 0.074\%Fe \quad (1)$$

This justifies the choice of carbon content as the variable of interest in the study of the proportion of carbide remaining after the steel solution is required.

The other parameters of interest for the statistical processing, namely the temperature at which the heating and the maintenance in order to dissolve the carbide and the isothermal maintenance time were chosen in conjunction with the information required by the standard with the start-up temperature of the grain intensive growth for such a steel.

3. Experimental work

Starting from the standardized composition of W1.4855, %, the C% was varied between 0.1 and 0.19% keeping the other relative ones constant. As a measure of the effect on the structure, the percentage of eutectic carbides was used four alloys, chemical composition variants according to Table 1. All the specimens were manufactured at UTTIS industries SRL.

Elaboration of the alloys was carried out in an induction furnace with a 250 kg crucible. Y-samples were done in molds made of sodium silicate casting (96% quartz sand, 6% sodium silicate) and coated with zirconium paint.

Table 1. *The chemical composition for the group with variable content of Carbon*

Chemical composition	Sample No.		
	1	**2**	**3**
C	0.10894	0.29032	0.49064
Mn	0.76099	0.75832	0.74687
Si	1.03863	1.06435	1.09160
P	0.03976	0.03397	0.03652
S	0.02264	0.01956	0.02263
Ni	24.10008	24.29665	24.36708
Cr	25.58822	25.18587	24.82062
Cu	0.14994	0.16418	0.13577
Mo	0.10307	0.10554	0.11070
V	0.05465	0.05743	0.04933
Ti	0.00050	0.00050	0.00050
Al	0.01963	0.09040	0.15017
Nb	0.00200	0.00200	0.00200
W	0.01300	0.01300	0.01300
Sn	0.00315	0.00359	0.00317
Co	0.14160	0.15711	0.12845
B	0.00105	0.00108	0.00105
Ca	0.00048	0.00037	0.00028
FE %	47.8173	47.7781	47.6758

The experimental analysis was made in the UTTIS laboratory and involved the following steps: - analysis of the chemical composition of cast samples - chemical composition investigations were performed using the optical emission spectrometer ARL QUANTRIS which is a compact, stationary spectrometer for metals analysis, based on the latest high-end CCD (Charge Coupled Device) technology.

Heat treatment of samples - Heat treatment was done in a forced-roaster furnace with a maximum heating limit of 1200 °C. The experimental program implied the variation of two parameters: the isothermal maintenance temperature at 950 and 1100 °C and maintenance time at this temperature, between 1 and 8 hours.

- Cutting and preparing metallographic samples - both electrolyte and mechanical polishing were used to accomplish the critical surface preparation.

- Performing the structural analysis of the analyzed samples and interpreting the data - the structural analysis was made with an Olympus microscope, according with the ASTM B487 standard, by using Scentis Software version 1.2 for Windows and interpreting the data.

- Statistical data processing and determination of the correlation equation between the carbon content, temperature and maintaining time at the heating temperature.

4. Experimental results

The obtained results are presented in Tables 2 and 3 and represented graphically in the Figures 1, 2 and 3.

Table 2. *Carbide content of alloys with different carbon content for 0 to 8 hours maintaining time at 1100 °C and water cooling*

Isothermal maintenance temperature	**Carbide content, %**		
	Alloy with 0.10% C	Alloy with 0.29% C	Alloy with 0.49% C
As casted	4.7	12.52	16.92
1 hour	2.15	10.75	13.09
4 hours	1.59	8.7	10.77
8 hours	0.71	5.77	8.9

Table 3. *Carbide content of alloys with different carbon content for 0 to 8 hours maintaining time at 950 °C and water cooling*

Isothermal maintenance temperature	**Carbide content, %**		
	Alloy with 0.10% C	Alloy with 0.29% C	Alloy with 0.49% C
As casted	4.7	12.52	16.92
1 hour	3.46	11.52	14.16
4 hours	2.49	9.61	12.34
8 hours	1.78	8.32	10.32

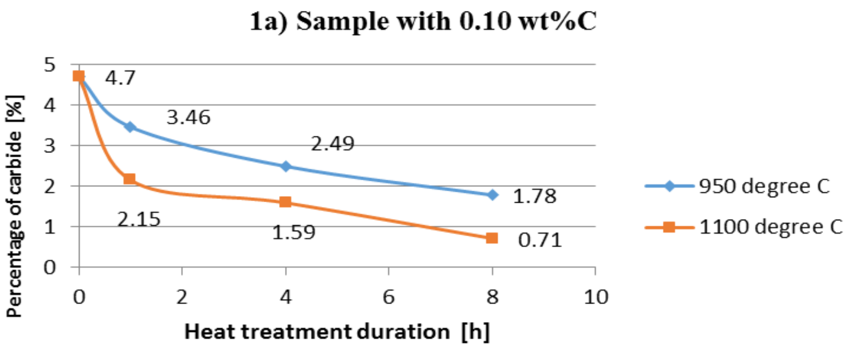

Fig. 1. *The relation between the temperature and maintaining time and the carbide content of steel with 0.10 % C*

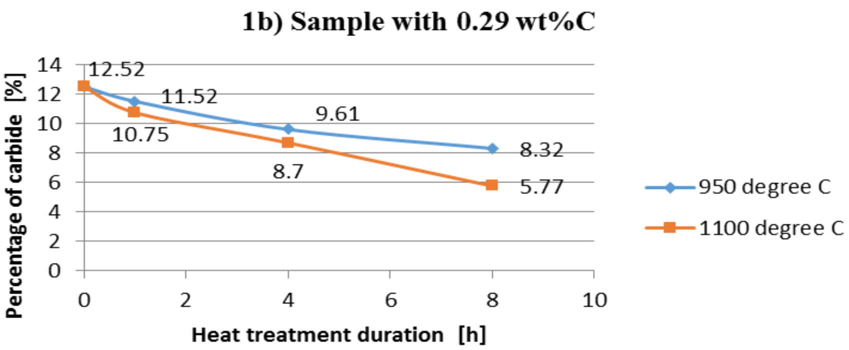

Fig. 2. *The relation between the temperature and maintaining time and the carbide content of steel with 0.29 % C*

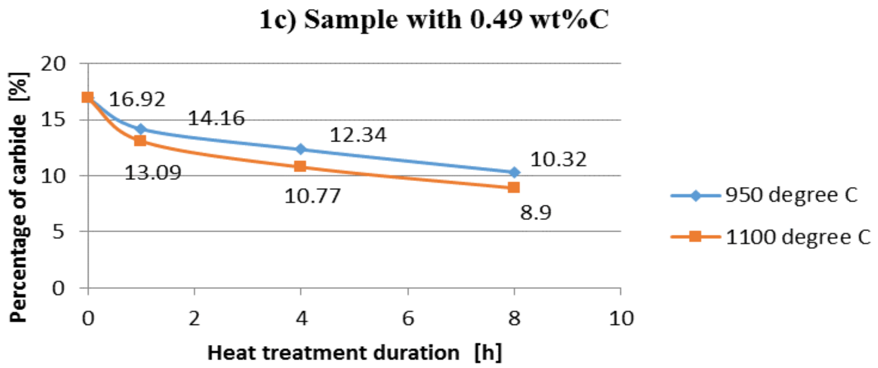

Fig. 3. *The relation between the temperature and maintaining time and the Carbide content of steels with 0.49% C*

Table 4*. Correspondence between factor values expressed in natural units and in coded units*

Factor	(%C)		The temperature of treatment, TPS		Isothermal maintenance time		%Carbide
	Natural units Z1 in %	Coded values X1	Natural units Z2 in %	Coded values X2	Natural units Z3 in %	Coded values X3	Natural units Y, in %
Basic level Δ_{Z_0}	Z0=0.29	$\frac{0.29-0.29}{0.19}=0$	Z0=1025	$\frac{1025-1025}{75}=0$	Z0=4	$\frac{4-4}{3}=0$	-
Variation interval ΔZ_i	ΔZ=0.19	-	ΔZ=75	-	ΔZ=3	-	-
Higher level $Z_{io}+\Delta Z_i$	Z0+ ΔZ= 0.48	$\frac{0.48-0.29}{0.19}=+1$	Z0+ΔZ= 1100	$\frac{1100-1025}{75}=+1$	Z0+ΔZ= 7	$\frac{7-4}{3}=+1$	-
lower level $Z_{io}-\Delta Z_i$	Z0-ΔZ= 0.1	$\frac{0.1-0.29}{0.19}=-1$	Z0-ΔZ= 950	$\frac{950-1025}{75}=-1$	Z0-ΔZ= 1	$\frac{1-4}{3}=-1$	-
	INDEPENDENT VARIABLES						DEPENDENT VARIABLES

Table 5. *Matrix of central orthogonal composite programming for 3 independent variables (K = 3)*

No.	X0	Factors						X1X2	X1X3	X2X3	Y
		X1	X2	X3	X1’	X2’	X3’				
1	+1	+1 0.48	-1 950	-1 1	+0.27	+0.27	+0.27	-1	-1	+1	14
2	+1	-1 0.1	+1 1100	-1 1	+0.27	+0.27	+0.27	-1	+1	-1	2.15
3	+1	-1 0.1	-1 950	+1 7	+0.27	+0.27	+0.27	+1	-1	-1	1.8
4	+1	-1 0.1	+1 1100	+1 7	+0.27	+0.27	+0.27	-1	-1	+1	0.8
5	+1	+1 0.48	-1 950	+1 7	+0.27	+0.27	+0.27	-1	+1	-1	10.1
6	+1	+1 0.48	+1 1100	-1 1	+0.27	+0.27	+0.27	+1	-1	-1	13
7	+1	+1 0.48	+1 1100	+1 7	+0.27	+0.27	+0.27	+1	+1	+1	9.1

8	+1	-1 0.1	-1 950	-1 1	+0.27	+0.27	+0.27	+1	+1	+1	3.46
9	+1	+α=+1.215 0.52	0 1025	0 4	+0.746	-0.73	-0.73	0	0	0	11.8
10	+1	-α=-1.215 0.59	0 1025	0 4	+0.746	-0.73	-0.73	0	0	0	1.2
11	+1	0 0.29	+α=+1.215 1116.1	0 4	-0.73	+0.746	-0.73	0	0	0	8.4
12	+1	0 0.29	-α=-1.215 933.4	0 4	-0.73	+0.746	-0.73	0	0	0	9.9
13	+1	0 0.29	0 1025	+α=+1.215 7.64	-0.73	-0.73	+0.746	0	0	0	7.2
14	+1	0 0.29	0 1025	-α=-1.215 0.355	-0.73	-0.73	+0.746	0	0	0	11.8
15	+1	0 0.29	0 1025	0 4	-0.73	-0.73	-0.73	0	0	0	9

5. Statistical data processing and determination of the correlation equation between the carbon content, temperature and maintaining time at the heating temperature

In order to quantify the variation effects of the parameters of interest (stainless steels carbon content, temperature and isothermal maintenance temperature at the temperature of dissolving the carbide), a method of programming opted for the second orthogonal composite experiment. Statistical methods are used in all stages of the experiment, before developing it. The use of statistical methods in this way aims at establishing the number and conditions of the experiments needed to generate the data obtained after the end of the experimental cycle and the elaboration of the strategies for carrying out new experiments.

This way of dealing with the problem is called the active experiment, and it involves programming the experiment [3].

The correspondence between the values of the factors - independent variables-expressed in natural units and respectively in the coded units is mentioned in Table 4, and the actual matrix of the programming containing the actual conditions in which it will be experimentally performed in Table 5.

The relationship between the natural value (Zi) and the coded (X_i) of a dependent variable is:

$$X_i = \frac{Z_i - Z_{io}}{\Delta Z_i} \qquad (2)$$

Calculation the caloric coefficient of regression bo and bi, bij, bii;

The regression equation will have the following general form:

$$\tilde{y} = b'_0 + \sum_{i=o}^{k} b_i x_i + \sum_{\substack{i=1,\\ j=1\\ i\neq j}}^{k} b_j x_i x_j + \sum_{i=1}^{k} b_{ii}\left(x_i^2 - \bar{x}_i^{\,2}\right) \qquad (3)$$

If the matrix is orthogonal, the coefficients of the regression equation will be determined by the relations:

$$b'_0 = \frac{\sum_{n=1}^{N} x_{0n} y_n}{\sum_{n=1}^{N} x_{0n}^2} \qquad (4)$$

$$b_i = \frac{\sum_{n=1}^{N} x_{in} y_n}{\sum_{n=1}^{N} x_{in}^2} \qquad (5)$$

$$b_{ij} = \frac{\sum_{n=1}^{N} x_{in} x_{jn} y_n}{\sum_{n=1}^{N} (x_{in} x_{jn})^2} \qquad (6)$$

$$b_{ii} = \frac{\sum_{n=1}^{N} x'_{in} y_n}{\sum_{n=1}^{N} (x'_{in})^2} \qquad (7)$$

The transition equation (1) at its usual form most commonly used, respectively of a polynomial of the second order:

$$\tilde{y} = b_o + \sum_{i=1}^{k} b_i x_i + \sum_{\substack{i=1\\ j=1\\ i\neq j}}^{k} b_{ij} x_i x_j + \sum_{i=1}^{k} b_{ii} x_i^2 \qquad (8)$$

It can be done by explaining the coefficient value b'_0:

$$b_0 = b'_0 - \sum_{i=1}^{k} b_{ii} \bar{x}_i^2 \qquad (9)$$

with dispersion: $S^2_{b_o} = S^2_{b'_o} + \sum_{i=1}^{k} (\bar{x}_i^2)^2 - S^2_{b_{ii}}$ (10)

Calculation dispersions of the regression equation coefficients;

$$S'_{b_o} = \frac{S_0^2}{\sum_{n=1}^{N} x_{0_n}^2} \qquad (11)$$

$$S^2_{b_i} = \frac{S_0^2}{\sum_{n=1}^{N} x_{i_n}^2} \qquad (12)$$

$$S^2_{b_{ij}} = \frac{S_0^2}{\sum_{n=1}^{N} (x_{i_n} y_{j_n})^2} \qquad (13)$$

$$S_{b_{ii}}^2 = \frac{S_0^2}{\sum_{n=1}^{N}\left(x_{i_n}'\right)^2} \quad (14)$$

where: (S_0^2) representing the dispersion of experiments reproducibility (experimental error).

S_0^2 was determined from the results of four experiments performed in identical conditions corresponding to the basic levels of the independent parameters (x_1=0.29%C; x_2=1025 °C; x_3=4h).

The results; $S_0^2 = \frac{\sum_{n=1}^{4}(y_n - \bar{y})^2}{\sigma_1} = \frac{1.29}{3} = 0.43$

Where $\sigma_1 = n - 1$ in which σ_1 = Number of free degrees and n = number of parallel experiments.

Calculate the confidence interval (Δbi, Δbij, Δbii) in which coefficients were estimated Δbi;

$$|\Delta b_1| = |\Delta b_2| = |\Delta b_3| = S_{b_i} \cdot t_{\alpha,N} \quad (15)$$

where: $$S_{b_i} = \pm\sqrt{S_{b_i}^2}; \quad (16)$$

$t_{\alpha,N}$ - Tabulated criterion value;

α – Level of Significance Student.

$$\Delta b_{ij} = \pm\sqrt{S_{b_{ij}}^2} \cdot t_{\alpha,N} \quad (17)$$

$$\Delta b_{ii} = \pm\sqrt{S_{b_{ii}}^2} \cdot t_{\alpha,N} \quad (18)$$

Statistical verification of coefficients:

A coefficient is considered statistically determined (so with significant statistical influence), if and only if its absolute value is greater than or equal to its calculated confidence interval.

Verifying the hypothesis consistency of the adopted model:

An adopted model is considered to be consistent, so it expresses with good approximation the process / phenomenon realized if the calculated value of the Fischer criterion is lower than the table, so the condition of concordance can be written:

$$F_{calc} = \frac{S_{conc}^2}{S_0^2} = \frac{1}{S_0^2} \cdot \frac{\sum_{n=1}^{N}\left(y_{n_{calc}} - y_{n_{exp}}\right)^2}{\sigma_1} < F_{tabel_{\alpha,\sigma_1,\sigma_2}} \quad (19)$$

Where $\sigma_1 = N - k$ in which:

S_0^2 - Dispersion of Experiment Reproducibility.

σ_1 - Number of free degrees.

N - number of experiments (N=15).

K - the number of determined statistical coefficients of the regression equation, including the free term.

α- the level of significance (α = 0.05) which indicates that the probability with which the equation expresses the influences taken in the analysis is 95.

Concretely, going through the algorithm steps led to the following results:

The coefficient values of regression are:

$b_0' = 7.514$, $b_1 = +4.91$, $b_2 = -0.56$, $b_3 = -1.49$, $b_{12} = +0.038$,, $b_{13} = -0.598$, $b_{23} = +0.038$, $b_{11} = -2.33$, $b_{22} = -0.196$, $b_{33} = +0.04$

The calculated values of the coefficients of the regression equation (for $S_0^2 = 0.43$) are:

$S_{b_i}^2 = 0.0396 \rightarrow S_{b_i} = \pm 0.198$

$S_{b_{ij}}^2 = 0.053 \rightarrow S_{b_{ij}} = \pm 0.23$

$S_{b_{ii}}^2 = 0.098 \rightarrow S_{b_{ii}} = \pm 0.39$

$S_{b_0'} = 0.0286 \rightarrow S_{b_0}^2 = S_{b_0'}^2 + (\bar{x}_1^2)^2 \cdot S_{b_n'}^2 = 0.0808$

$\rightarrow S_{b_0} = \pm 0.898$

The confidence intervals values for coefficients of regression equation:

$|\Delta b_i| \rightarrow |\Delta b_1| = |\Delta b_2| = |\Delta b_3| = 0.42$

Comparing the calculated values of coefficients b_1, b_2, b_3 with their confidence interval are found to be statistically significant.

$|\Delta b_{ij}| \rightarrow |\Delta b_{12}| = |\Delta b_{13}| = |\Delta b_{23}| = 0.42$

By comparing the calculated values of the coefficients b_{12}, b_{13}, b_{23} with their confidence interval it is found that only the coefficient b13 has a higher value than the confidence interval, so it is statistically significant.

$|\Delta b_{ii}| \rightarrow |\Delta b_{11}| = |\Delta b_{22}| = |\Delta b_{33}| = 0.66$

By comparing the calculated values of coefficients b_{12}, b_{13}, b_{23} with their confidence interval it is found that only the coefficient b11 fulfills the condition of statistical significance. Concerning the free term b_0 = 9.33, this value is higher than the confidence interval.

$|\Delta b_0| = S_{b_0} \cdot t_{\alpha,N} = 0.898 \cdot 2.131 = 1.995$, so, it is also statistically determinant.

Followed by the particular formation of equation (8) will be:

$$y = 9.33 + 4.9x_1 - 0.56x_2 - 1.49x_3 - 0.598x_1x_3 - 2.33x_1^2 \quad (20)$$

in which:

- x_1, x_2, x_3 are the encoded forms of interdependent variations (Table 6 discussed);
- y is the natural value of the dependent parameter (%carbides) in the steel.

Verification the conformity of the adopted model

Table 6. *Calculating the dispersion produced by the regression equation,* S_{conc}^2

No.	y_{exp}	y_{calc}	$(y_{exp} - y_{calc})^2$	$\sigma_1 = N - k'$
1	14	14.548	0.3	15-6=9
2	2.15	2.432	0.179	
3	1.8	1.768	0.001	
4	0.8	0.648	0.023	
5	10.1	10.372	0.074	
6	13	13.428	0.183	
7	9.1	9.252	0.023	
8	3.46	3.552	0.0084	

9	11.8	11.843	0.00185	
10	0.2	0	0.04	
11	8.4	8.649	0.062	
12	9.9	10.01	0.012	
13	7.2	7.519	0.101	
14	11.8	11.14	0.43	
15	9	9.33	0.109	
$\sum_{1}^{15}(y_{exp} - y_{calc})^2 = 1.447$				

$$S^2_{conc} = \frac{\sum_1^{15}(y_{exp} - y_{calc})^2}{\sigma_1 = N - k'} = \frac{1.447}{9} = 0.16$$

$F_{calc} = 0.37$

$F_{tab_{0.05,9,3}} = 8.8$ (table value)

Because $F_{calc} < F_{tab}$ hypothesis about the conformance of the model is checked and the regression equation (18) expresses with an extremely high probability of water influences that show the parameters independent of the analysis taken on the proportion of eutectic carbides remaining after applying the solution. Introducing the expression in the equation (20) between the coded or natural values of the independent parameters can obtain a regression equation in which the variables are in their natural form:

$$\%\mathbf{Carbide} = 4.85 - 64.54(\%C)^2 + 67.42(\%C) - 7.46 \cdot 10^{-3}T_{cal} - 0.19t_{m_{iz}} - 1.05(\%C)t_{m_{iz}} \quad (21)$$

6. Conclusions

The particular forms determined for the regression equations allow the choice of the thermal processing conditions so that the proportion of the remaining eutectic carbide is predictable. The equation analysis clearly shows the following:

- The influence of carbon concentration on the proportion of steel eutectic carbide is extremely strong both in casting state as well as after applying the heat treatment.

- The best effect to dissolve the carbide it is maintaining time of the temperature than increasing the temperature – the statement must be controlled within the range of variance chosen for the two parameters, $T \in [950°C \ldots 1100°C]$, $t \in [1 \ldots 7\ h]$.

Thus, if the varying of treatment temperature between 950-1100 °C obtain lower proportion of carbide around 10%, a variation of the isothermal maintenance time within the chosen range, between 1 and 7, causes a decrease in the proportion of eutectic carbide by approx. 30%, (calculated value for the solution inlet temperature of 1100 °C and the initial carbon concentration of 0.48%).

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