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## CONTRIBUTION TO MODELING OF DECARBURIZATION PROCESS IN ELECTRICAL STEELS

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Electrical steels, regarding the chemical composition, are decarburized mainly in  $N_2-H_2-H_2O$  mixture to provide combination of magnetic and mechanical properties. The control of the decarburization process is important step in steel processing where balancing act have to provide enough water vapor to remove the carbon content to non-aging level but not to react with alloy in the steel. A mathematical model of the decarburization process, based on the diffusion laws is proposed, for Si-steels. The decarburization kinetics is known to be very sensitive to thickness of the steel sheet, concentration of alloying elements, temperature, time, type and dew point of the atmosphere. The effect of above factors on the decarburization is considered in the proposed model.

*Key words:* electrical steels, kinetic of decarburization, oxidation.

As pointed in numerous scientific works [1, 4, 5, 9, 14], decarburization is performed for the development of optimal magnetic properties in steel. Decarburization is accomplished by annealing in wet gas. The water content of the gas is controlled by the gas dew point. At temperature, the water is dissociate forming hydrogen and oxygen [1]:



The free hydrogen will then react with carbon on the surface of the steel by the following scheme [2]:



However, the methane creation rate is controlled by reaction in surface layer. The methane creations rate decrease if other atoms or molecules are occupying some adsorption center. Furthermore, the adsorption temperatures of both  $O_2$  and  $CO$  are higher than for hydrogen. These facts mean that even at low water vapor content of gas mixture the creation of methane will be blocked after several minutes of decarburization [3].

The free oxygen reacts with carbon at the steel surface, forming  $CO$  and  $CO_2$  [1]:



The carbon monoxide creation rate increases with increasing of the temperature and dew point of gas mixture. The concentration of adsorbed oxygen proportional to  $H_2O/H_2$  ratio. Thus, the reaction rate of reaction (7) is limited by  $\frac{H_2O}{H_2}$  ratio [4].

As carbon is depleted from the steel surface, a concentration gradient is created which allows more carbon to diffuse from the center of lamination to the surface. The carbon content in steel is thus lowered in this way.

Electrical steel sheets, regardless production type are annealed in the temperature range of 780–900 °C, i.e.  $\alpha$  or  $\alpha+\gamma$  region.

Theory of decarburization kinetic in which phase transformation (i.e.  $\gamma \rightarrow \alpha$  or  $\alpha+\gamma \rightarrow \alpha$ ) is involved was developed by Swisher [6] and Pyyry and Kettunen [7]. Mentioned methods are independent from oxidation potential of decarburizing atmosphere.

In paper [9] authors present an equation for decarburization of GO steels. The main non-availability of this model connected with measuring of oxidation subscale i.e. critical silicon fraction in oxide subscale.

This work presents a mathematical model for decarburization of electrical steels. The model tested on both NO and GO steels decarburised in atmosphere of different composition and dew point. The Si content and thickness of investigated steels changed in wide range.

Fully processed non-oriented steel was used as experimental material. Table 1 presents chemical composition of investigated steels. Samples in the form of Epstein strips were taken from the industrial line after cold rolling. The thicknesses of the samples were 0.5 and 0.65 mm.

Table 1

Chemical composition of steels, in wt. %

steel	C	Mn	Si	P	S	Al	N	h, mm
A	0.043	0.28	1.39	0.08	0.009	0.139	0.007	0.5
B	0.031	0.38	1.01	0.134	0.008	0.157	0.007	0.65
C	0.052	0.36	1.02	0.09	0.01	0.133	0.009	0.65

Investigated samples were annealed in the  $N_2-H_2-H_2O$  decarburizing atmospheres of different vapour content. The dew point of atmosphere was changed in range of 20°C to +55°C. Annealing temperature range lies within 800–900 °C.

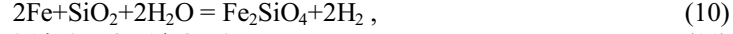
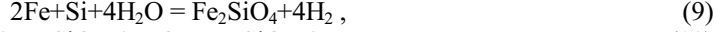
The residual carbon content after decarburization was determined by chemical analysis.

In the production of both non-oriented (NO) and grain-oriented (GO) steels the main alloying elements are Si and Al that added to decrease eddy current losses. The oxygen in water vapour will begin to react with element other than carbon. The next most easily oxidized elements in the steel are aluminium, silicon and manganese. An internal oxidation is often occurs during decarburization at sufficiently long-time and high oxygen potential.

Above-mentioned elements, primarily silicon, oxidize during the decarburization, forming small second phase oxide particles near the surface of sheet that impede grain growth, magnetisation and magnetic domain boundary motion. The control of the decar-

burization is thus a balancing act where one wants just enough water vapour to remove the carbon content to non-aging level but not to react with alloy in the steel.

The oxidation of silicon steels is carried out by the next reaction [14]:



Electrical steels, regarding the chemical composition, are decarburized mainly in  $\text{N}_2\text{-H}_2\text{-H}_2\text{O}$  mixture in the range of 780–900 °C. To achieve an effective decarburization, the dew point of above atmospheres is changing from +20 to +60°C [4, 5, 10, 11]. By the way presented in [5], the relation between dew point, temperature and silicon

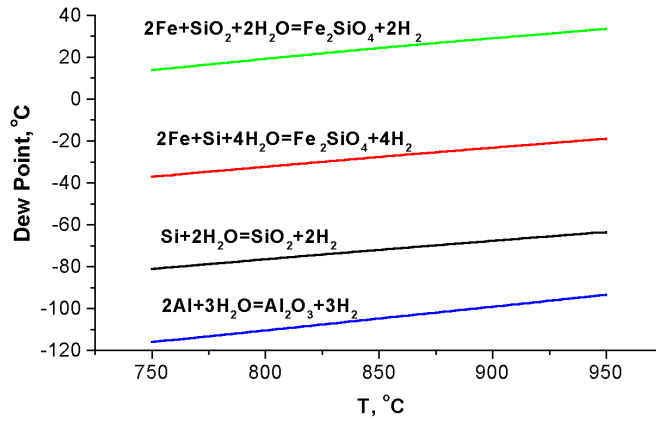


Fig. 1. Relation between oxides formation and dew point of  $\text{NH}_3$  atmosphere.

oxidation for electrical steel may be derived. The relation between formation of  $\text{SiO}_2$ ,  $\text{Fe}_2\text{SiO}_4$  and  $\text{Al}_2\text{O}_3$  and dew point of  $\text{NH}_3$  atmosphere is presented in fig.1. It can be seen that even at dew point of  $-80$  °C the oxidation process is occurs. As the dew point higher than  $-40$  °C, than fayalite formation take place. Beside these, lower annealing temperature corresponds to lower dew point of decarburizing atmosphere without oxidation.

Decarburization of electrical steel is a diffusion problem of carbon with phase transformation in steel from austenite to ferrite. A discontinuous concentration profile of carbon is observed during decarburization [6, 7, 17]. The last is caused by the continuity of chemical composition of carbon in ferrite and austenite [17].

The classical expression for carbon removing from sheet can be formulated as a function of carbon content, diffusion coefficient of one and thickness of plate. So, the decarburization process by reactions (6) and (7) are describing by equation:

$$\frac{dC}{dt} = f(C, D_f, l), \quad (13)$$

where  $C$  is extracted carbon;  $D_f$  is a diffusion coefficient of the carbon;  $l$  is the thickness of steel.

The decisive factor controlling the process is the gas-solid interface reaction. It is well known that ferrite decarburization occurs on the surface when the steel is kept at

around the temperature at which the microstructure of steel becomes ferrite and austenite duplex phase [17]. Thus, the carbon oxide creation is controlled by reaction in surface layer. Under the condition that carbon concentration at surface equals 0, the classical solution for carbon diffusion may be presented by Fourier series solution with period of  $l$  [5]:

$$C(x,t) = \sum_n a_n \exp\left(-D_f \left(\frac{\pi n}{l}\right)^2 t\right) \sin \frac{\pi n x}{l}. \quad (14)$$

For a square wave function:  $a_n = 4C_a/n\pi$ , where  $C_a$  is an amplitude of square wave function. Taking into account first (dominates) terms of equation (14), the average carbon concentration in steel after decarburization will be:

$$\bar{C} \approx C_i \exp\left(-\frac{\pi^2 D_f t}{l^2}\right), \quad (15)$$

where  $C_i$  – the initial carbon concentration (in wt. %);  $D_f$  is a diffusion coefficient, for Fe–Si steels  $D_f = 0.85 \cdot \exp(-113000/RT)$  [5];  $t$  – is the decarburization time (in s);  $l$  – is the thickness of sheet (in cm).

As mentioned above, the decarburization of silicon steels is controlled by oxidation process. As soon as silicon, aluminium and manganese react with wet decarburize atmosphere. As results, the external oxidation occurs and oxide subscale is created. Last one impede the decarburization process. With anneal temperature increasing the oxygen potential increase as well (fig.1).

The thermodynamics of segregation as well as for surface segregation and for grain boundary segregation are described by the Langmuir–McClellan equation [16]. The last was expressed in [5] for the occupancy of Fe–Si steel surface sites with the oxygen by reaction (1):

$$\Theta = \frac{k_0(p_{H_2O}/p_{H_2})}{1 + k_0(p_{H_2O}/p_{H_2})}, \quad (16)$$

where  $\Theta$  is the saturation coverage of steel surface with oxygen,  $k_0$  is constant for the given temperature.

The temperature dependence of  $k_0$  is [5]:

$$k_0 = 0.32 \cdot \exp\left(\frac{3000}{T}\right), \quad (17)$$

where  $T$  in K.

The formation of oxide subscale depends on Si, Mn and Al contents in steel and dew point of atmosphere (see eq. 16–19). For temperature range of 700–900 °C, the silicon concentration in subsurface region increase [16] and the intensive oxidation take place. But contrary to silicon oxidation, the Si presence increases the diffusion activity of carbon. Carbon activity depends on Si content by next way [5]:

$$a_C^{(Si)} = 0.122[Si]. \quad (18)$$

Taking into account the oxidation process and dependence of carbon activity upon Si content, the exponent in equation of average carbon concentration (15) has to be multiplied by the correlation factor  $z$ , that depend on  $\Theta$  and  $a_C^{Si}$  by following way:

$$z = (a \cdot a_C^{Si} + b \frac{\Theta}{1 + \Theta([Si] + 0.2 \cdot [Al] + 0.3 \cdot [Mn])} + c) , \quad (19)$$

where  $a$ ,  $b$ ,  $c$ , are constants. The relation between  $z$ ,  $\Theta$ ,  $a_C^{(Si)}$  and above coefficients is received from experimental data by interpolation.

For electrical steels of 1–3 wt.% Si these coefficients are as follows:  $a=0.165$ ,  $b=1.44$ ,  $c=-0.011$ .

Then

$$\bar{C} = C_i \exp\left(-\frac{\pi^2 D_f z t}{l^2}\right). \quad (20)$$

Presented model depends from:

- dew point of atmosphere through  $\Theta$ , that corresponds to oxidation process, i.e. creation of oxide layer and internal oxidation;
- carbon activity;
- content of oxidise alloying elements;
- oxide particle creation through coefficient  $z$  in eq. 20.

The decarburization process of studied steels will be discussed in terms of decar-

burization level ( $L.D. = \frac{C_{final}}{C_{initial}}$ ) and level of relative decarburization

$$(R.D. = \frac{C_{initial} - C_{final}}{C_{initial}}).$$

Fig. 2 presents well agreement between experimental and modelled data by (20) in sample B of medium Si content. As follows, the level of decarburization increases with temperature and time increasing. As shown, the level of relative decarburization increases with temperature increasing for all temperature range. The high intensity of decarburization corresponds to high annealing temperature.

It is widely known that the increasing of atmosphere's dew point lead to increasing of decarburization intensity. The effect of dew point on decarburization is detected in fig. 3 and 4. The kinetic of decarburization for atmospheres of three different dew points is presented in fig. 3. As shown, the experimental data well describes by presented model. The higher value of decarburization level ( $L.D.$ ) corresponds to higher value of dew point, in range of +20 to +40°C. It is obvious, that decarburization is retarded at temperatures above 875 °C. Whereat, the high dew point of atmosphere the slower intensity of decarburization (see fig. 3).

It is because of intensive oxidation take place at high temperature. Thus, the oxidation process is predominant at high temperature, and as a result the decarburization process is retarded. The similar phenomenon was observed during decarburization of the sample C in the same atmosphere (see fig. 4). Like previous case, the decarburization was retarded at temperatures about 900 °C, whereat the optimal decarburization corresponds to temperature of 875°C. The level of decarburization increase slowly above this temperature.

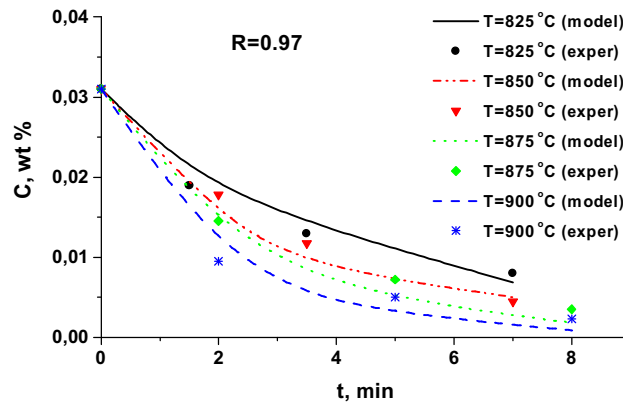


Fig. 2. The kinetic of decarburization process of sample B annealed in 75%(H<sub>2</sub>)+25%(N<sub>2</sub>) (d.p. +55°C).

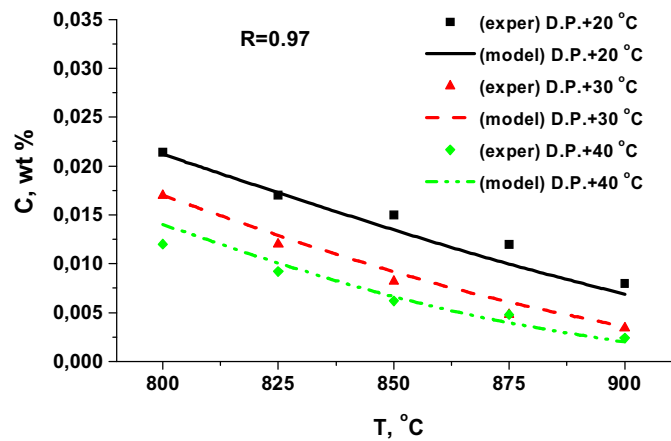


Fig. 3. The kinetic of decarburization process of sample A annealed in 35%(H<sub>2</sub>)+65%(N<sub>2</sub>) during 4 min.

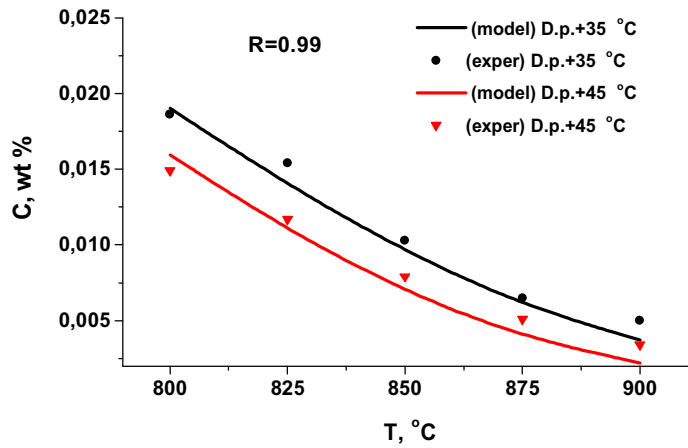


Fig. 4. The kinetic of decarburization process of sample C annealed in 35%(H<sub>2</sub>)+65%(N<sub>2</sub>) atmosphere of different dew point during 6 min.

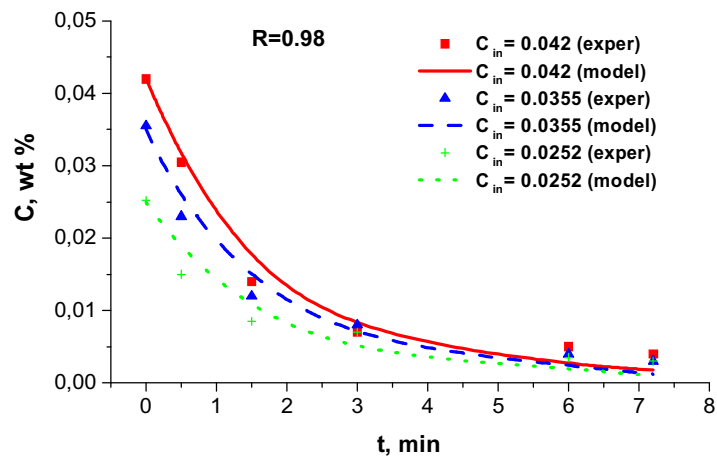


Fig. 5. The kinetic of decarburization process in Fe-3%Si steel [Zidek], annealed at 820 °C in 75%(H<sub>2</sub>)+25%(N<sub>2</sub>) atmosphere of d.p. +40°C.

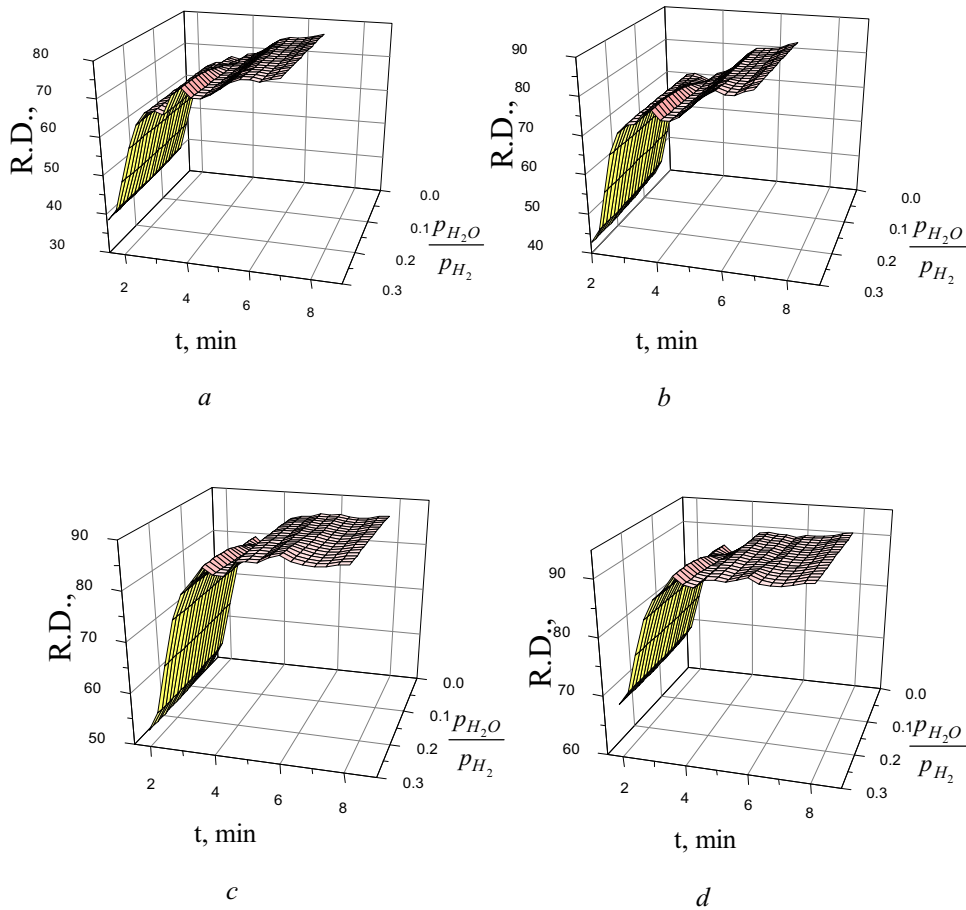


Fig. 6. The dependencies of relative decarburization level upon time and dew point of atmosphere for four temperatures: *a* – 825°C; *b* – 850°C; *c* – 875°C; *d* – 900°C.

The optimal condition of decarburization for non-oriented electrical steels could be chosen from dependencies of relative decarburization level upon the time and dew point of gas mixture for different temperature. The mentioned dependencies presented for sample A treated under different conditions. As shown in fig. 6, *a* and *b*, the relative decarburization level is not exceed the values of 80 and 85%, for  $T=825^{\circ}\text{C}$  and  $850^{\circ}\text{C}$  respectively. The increases in temperature cause the increasing of decarburization intensity. For temperature of  $875^{\circ}\text{C}$ , the level of decarburization approximates to value of 90% during 5 min. Treatment during next time invokes slight increasing in decarburization level. Following temperature increasing is not reasonable because the decarburization level increase very slightly (fig. 6, *d*). The influence of dew point is evidently clear from fig. 6, for next range of oxygen partial pressure: from 0.1 to 0.3 units. The higher



oxidation potential of atmosphere the higher level of decarburization. But the intensive decarburization occurs in next range of  $\frac{H_2O}{H_2}$  ratio: 0.2–0.3 units. Further increasing of dew point can lead to intensive oxidation, and the process of carbon removing will be retarded. As can be concluded, the optimal decarburization corresponds to temperature of 875 °C and time of about 5 min. As to the optimal partial pressure of oxygen, it thus lies in range of 0.2–0.3 units.

The model validity was confirmed by the substitution of the measured results presented in literature as well. In fig.5 the good agreement between experimental data [15] of Fe–3%Si steels of different initial carbon content is shown. As shown, the correlation coefficient  $R$  is exceeding the value of 0.98.

Proposed model well describes the decarburization process in electrical steels. The decarburization process of Fe–(1–3%)Si at different annealing conditions were modelled. The correlation coefficient between experimental and modelled data is exceeding the value of 0.97.

The level of decarburization increases with temperature and time increasing.

The higher value of decarburization level corresponds to higher value of dew point, in the investigated range of dew point.

The decarburization was retarded at temperatures about 900 °C, whereas the optimal decarburization corresponds to temperature of 875°C and time of about 5 min. Following temperature increasing is not reasonable because the decarburization level increases very slightly. As to the optimal partial pressure of oxygen, it thus lies in range of 0.2–0.3 units.

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1. Mannion F.J., Fruehan R.J. Metallurgical Transactions B. 1989. Vol. 20. P. 853.
  2. Grabke H.I., Müller E.M., Speck V., Konzas H.G. Steel Research. 1985. Vol. 56. P. 275.
  3. Münster P., Grabke H.I. Journal of Catalysis. 1981. Vol. 72. P. 279.
  4. Vaschenko A.I., Zenkovskiy A.G., Lifshits A.E. et al. Okislenie i obezугlerozhivanie stali. Moskva: Metallurgiya, 1972. P. 336.
  5. Mogutnov B. M., Emelyanenko L. P., Kononov A. A. et al. Fizicheskaya khimiya processov obrabotki elektrotehnicheskikh staley. M.: Metallurgiya, 1990. P. 167.
  6. Swisher J. H. Trans. Metall. Soc. AIME, 1968. P. 763.
  7. Pyry J., Kettunen P. Scand J. Met. 1973. Vol. 2. P. 265.
  8. Smith R. P. Trans. Metall. Soc. AIME, 1962. P. 105.
  9. Marini P., Abbruzzese G. JMMM, 26. 1982. P. 15–21.
  10. Lyudkovsky G., Prebah A.G., Shapiro J.M. J. Appl. Phys. 1982. Vol. 53. N 3. P. 2419.
  11. Lyudkovsky G. IEEE Transactions On Magnetics. MAG–22. 1986. N 5. P. 508.
  12. Geiger A.L. J. Appl. Phys. 1979. Vol. 50. N 3. P. 2366.
  13. Lyudkovsky G., Rastogy P.K. Metallurgical Transactions A. 1984. Vol. 15. P. 257.
  14. Yamazaki T. Transactions ISIJ. 1969. Vol. 9. P. 66–75.
  15. Zidek A., Lonsky B. Metallic materials. 1977. Vol. 3. P. 293.
  16. Grabke H. J. ISIJ International. 1989. Vol. 29. P. 529.
  17. Nomura M., Morimoto H., Toyama M. ISIJ International. 2000. Vol. 40. N 6. P. 619.

**ДО ПИТАННЯ МОДЕЛЮВАННЯ ПРОЦЕСІВ ДЕКАРБЮРИЗАЦІЇ В  
ЕЛЕКТРИЧНИХ СТАЛЯХ****Ю. Сідор\*, Ф. Ковац***Інститут дослідження матеріалів, Академія наук Республіки Словачії**вул. Ватсанова 47, 043 53 Косіце, Республіка Словачів**тел.: +421 556 3381 15, факс: +421 556 3371 08**\*Відповідальний автор, e-mail: [sidor@imrnov.saske.sk](mailto:sidor@imrnov.saske.sk)*

Електротехнічні сталі залежно від хімічного складу відпалюють переважно в атмосферах  $N_2-H_2-H_2O$  для забезпечення магнітних та механічних властивостей. Контролювання процесу декарбуризації є важливим моментом у процесі виготовлення сталей, де збалансована реакція з атмосферою, з одного боку, повинна давати достатню кількість вологи для видалення вуглецю до кількості, яка забезпечить нестаріння матеріалу, з іншого – не повинна відбуватися реакція окиснення летких компонентів сталі. Запропоновано математичну модель процесу декарбуризації, яка ґрунтується на законах дифузії вуглецю. Кінетика цього явища залежить від товщини сталі, концентрації легуючих елементів, температури, часу та точки роси середовища. Вплив цих факторів на процес декарбуризації розглянуто на підставі цієї моделі.

*Ключові слова:* електричні сталі, кінетика декарбуризації, окислення.

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