MODELING DESCARBURISATION PROCESS OF HEAT TREATMENT OF ELECTRICAL STEELS

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Abstract: *Non-oriented semi-processed electrical steels are used for the core of electrical motors. To avoid the magnetic aging phenomena, these materials are usually heat-treated under controlled atmospheres, usually* N_2-H_2-H_2O *or* N_2-H_2-H_2O-CO-CO_2*, to promote carbon removal. The kinetics of the decarburization process is function of these atmospheres as well as dew points. Another important decarburization variable is the initial carbon content. To evaluate the effect of these variables on the decarburization, a model was developed using the finite volume method (FVM). This model allows to studying the effect of technological parameters such as furnace atmosphere, treatment time and strip thickness on the final carbon content. The model indicated that the reaction control is not due to the carbon diffusion, but should be either attributed to the chemical reaction in the gas-solid interface or to the transport of products and reactants within the strips. If the carbon content is small, in such way the steel is ferritic, the carbon is almost uniformly distributed inside the sheet (small carbon gradient). However, if the carbon is high and austenite is present, the decarburization process will be slower (and with a strong carbon gradient).*

Keywords: *Electric steels, mathematical modeling, decarburization, numerical solutions*

1. INTRODUCTION

Rotating machines like electrical motors employ ideally isotropic Si steels (Campos et al, 2006) commercially called “Non-oriented electrical steels”, which are classified in two main types: totally processed and semi-processed. The last ones are supplied with a temper rolling6 - usually ~6% reduction - by the steel producers. In the usual industrial procedure, the first step is the punching of the steel sheets and the assembling of the stators of motors. Then, the assembled stators are submitted to a heat treatment named “final annealing” that will eliminate plastic deformation and provide stress relief. The final annealing has also as objectives: i)attain the optimum grain size (100-150 µm, depending on the resistivity of the alloy) to minimize the core losses ii) decarburizing and iii) obtain an insulating layer of oxide between the sheets.

The aim of the present paper is modeling the decarburization, which is fundamental to avoid the phenomenon known as “magnetic aging”,(Werner et al,1992). During the working-life of electrical steels, microstructural changes may happen: carbon and/or nitrogen in solid solution precipitate as iron carbides or nitrides, respectively, increasing the losses. Aluminum is usually added to form AlN, avoiding the formation of iron-nitrides, and thus preventing magnetic aging .

Although it has been pointed out that the carbon content should be equal or less than 30 ppm to avoid the magnetic aging, even with lower carbon content, as 10 ppm, deterioration of the magnetic properties has been observed. However, when the carbon content is reduced to less than 50 ppm, another phenomenon can take place(Standaert, 1996), the subsurfacial oxidation. This is a technological question of extreme interest: to estimate the necessary time to obtain 0.003 %C, (Campos et al, 2004) or any other desirable carbon content, avoiding long time of permanence inside the furnace that could result in subsurfacial oxidation.

Figure 1 shows an example of the “final annealing” heat treatment with 1st and 2nd stages. Until recently, the typical gas for industrial-scale decarburization was an atmosphere composed by water vapour (H_2O), nitrogen (N_2) and small amount of hydrogen (H_2), but with also CO and CO_2. To avoid the problem of subsurfacial oxidation, it is now recommended an atmosphere with only N_2, H_2 and H_2O.

The most important parameter regarding the atmosphere of the heat treatment is the ratio (PH_2O/PH_2), which is function of the dew point. A typical industrial procedure is to avoid the FeO region. For example, to a decarburization temperature T=760°C, a value of (PH_2O/PH_2) =0.35 could be chosen, assuring that the decarburisation is performed in the Fe region (see Fig. 2). At a second stage (see Fig. 1) a heat treatment aiming to oxidize the surface of the steel is carried out at the temperature around 550 °C. In this stage, its is usual to employ a very high water partial pressure (for example, PH_2O/PH_2 around 0.6) aiming to form an electric insulating phase Fe_3O_4, commonly referred to as Steam Blue Oxide, instead of FeO that does not provide good insulation between the sheets. It should be also mentioned that the alloying elements Al and Si can form other different oxides (fayalite Fe_2SiO_4, trydmite SiO_2 or hercynite $FeAl_2O_4$ besides those predicted in the Fe-O system, and that the exact type and composition of the oxides is function of the chemical composition of each specific steel. This paper deals with the first stage of the heat treatment, where the decarburization takes place. Therefore, from now, all the discussion will be focused on the decarburization process (1st stage in Fig. 1).

The Fe-H-O phase diagram, showed in Fig. 2, is an important tool to choose the better conditions for decarburisation. However, the peculiar nature of the material submitted to decarburization – packs of steel sheets – imply in an out-of-equilibrium situation that makes difficult the modeling of this process.

According to Stephenson,(Stephenson,1990) there are three possible factors controlling the decarburizing kinetics: i) the gas transport of reactants or products ii) the chemical reaction at gas-steel interface iii) the carbon diffusion.

Calculations have indicated(Stephenson,1990, Werner et al, 1992 and Marra,2004) that, if the diffusion of carbon were the control step, the decarburization (until 30 ppm) could be finished in less than 5 minutes. Thus, the transport of carbon inside the sheet can not be the dominant aspect for kinetics, since in practical industrial and experimental conditions is observed about 2 h, depending on the atmosphere and temperature conditions(Campos et al, 2006). The other possibilities are the chemical reaction at gas-steel interface and the gas transport of reactants or products. The space between the sheets is very limited to <6μm according Standaert et al.,(Standaert et al, 1996), thus Stephenson,(Stephenson, 1990) has concluded that the controlling step is the gas penetration in the space between the strips of the stators. The gas composition near the surface of the sheets can be locally affected, becoming richer in carbon, and slowing down the reaction.

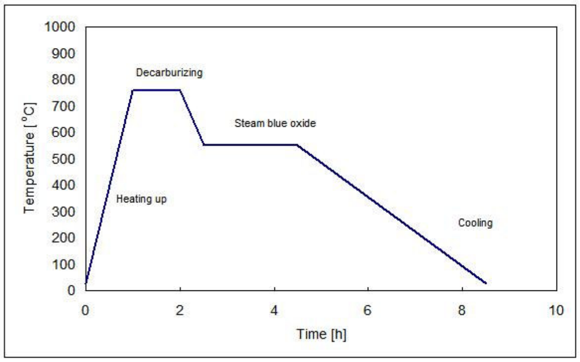

Figure 1 heat treatment procedure for electric steels

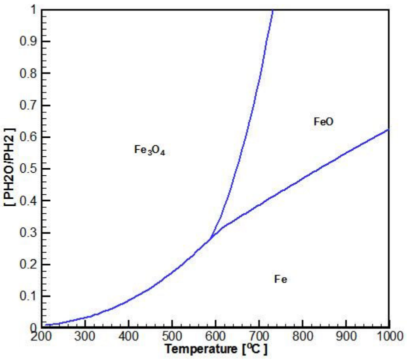

Figure 2 Phase diagram for oxidation of sheet surface under oxidizing conditions

However, an additional problem is the formation of an oxide on the surface of the sheets. According the Fe-H-O equilibrium phase diagram (Fig. 2), for T=760°C if Kp> 0.42 oxide formation occurs.

Thus, the kinetics can be controlled by either two different mechanisms: gas transport of reactants or products or the oxide layer. For technological purposes, there is no large importance the knowledge of the exact mechanism, but it is very important to be able to predict the necessary time for decarburization before subsurface oxidation may take place(Stephenson,1990 and Marra et al, 2004). In previous studies,(Marra et al,2004), precise knowledge of boundary and experimental conditions have limited the treatment of the major phenomena. However, the importance of the gas transport of reactants or products and possible oxidation layer formation was recognized, as well as the limitations of the prediction of decarburization kinetics due to such mechanisms. In the present work, a numerical simulation procedure based on the Finite Volume Method (FVM) is presented aiming to couple the carbon diffusion and kinetics of decarburization process. The numerical simulation has the advantage of taking into consideration detailed phenomena in the thin layer, where the reactions takes place and include important effects due to the iron oxide layer, local carbon concentration and atmosphere conditions. The model described below, can be used to investigate the parameters controlling the kinetics of decarburization and provide fundamental knowledge both for producers and users of this class of steel.

2. METHODOLOGY

2.1 Transport Equation coupled with chemical reaction

The decarburisation occurs combining the carbon diffusion within the matrix and the reaction near the surface of the material and oxidized layer. In order to model the phenomena, the transport equation of the carbon is proposed as follows:

$$\frac{\partial C}{\partial t} = div\left[D_C^{steel}\, grad(C)\right] - K_c \tag{1}$$

In Eq. (1), the fist term on the left side represents the local change of the carbon concentration along the time of treatment, and the first term on the right hand side accounts for the carbon diffusion within the steel strip and oxidized layers and the last term on the right side is the consumption of the carbon on the surface and oxidized layer by the chemical reaction, regarding as a sink term of carbon into.

The diffusion coefficient is modelled using the classical expression with a pre-exponential factor and an activation energy as shown in Eq. (2). Diffusion of carbon is quite different for ferritic (bcc) and austenitic (fcc) structures: it is faster for the bcc iron. Equation. 2a describes the diffusion coefficient into the austenitic structure and Eq. (2b) describes the diffusion coefficient within the ferritic structure.

$$D_C^{\gamma} = (0.07 + 0.06C)\exp\left(-\frac{32000}{1.987T}\right) \tag{2a}$$

$$D_C^{\alpha} = 0.256\exp\left(-\frac{24200}{1.987T}\right) \tag{2b}$$

In order to determine the interface between the austenitic and ferritic region a linear profile was determined based on the equilibrium diagram as given by Eq. (3).

$$C_{\alpha}^{\gamma} = 0.1295 - 1.099 \times 10^{-4}\,T \tag{3}$$

The main chemical reactions of decarburization, which occur in the steel strip, are modeled as reversible reactions

$$C + H_2O \leftrightarrow CO + H_2 \tag{4a}$$

$$C + CO_2 \leftrightarrow 2\,CO \tag{4b}$$

$$C + 2H_2 \leftrightarrow CH_4 \tag{4c}$$

$$C + \frac{1}{2}O_2 \leftrightarrow CO \tag{4d}$$

The relevance of Eqs (4c) and (4d) can be considered negligible if the PH_2O/PH_2 ratios are high (>0.1), case of typical atmospheres for decarburization.

The rate equation for the reactions $C + H_2O \leftrightarrow CO + H_2$ and $C + CO_2 \leftrightarrow 2\,CO$ depends on the local carbon activity of the steel, the partial pressure of water vapour and carbon dioxide, temperature and the thickness of the oxide layer formed on the surface. Discussions regarding the kinetics of these reactions are found elsewhere. Equation (5) presents the rate equation for the decarburization reaction, where a time dependent parameter was introduced to take into account the additional resistance due to the oxidation of the surface and subsurface of the steel strip.

$$K_c = F(t)\left\{k_{4a}\left(\frac{P_{H_2O}}{P_{H_2}}\right) + k_{4b}\left(\frac{P_{CO_2}}{P_{CO}}\right)\right\}\left[a_C\right] \tag{5}$$

Where the rate constants are given by the Arhenius type equations, determined by Eqs. (6a) and (6b):

$$k_{4a} = 84 \times T^{0.15} \times EXP\left[-\frac{8200}{RT}\right] \tag{6a}$$

$$k_{4b} = 56 \times T^{0.13} \times \mathrm{EXP}\left[-\frac{8400}{RT}\right] \tag{6b}$$

And the time dependent parameter was modeled by the following equation:

$$F(t) = A_0 + A_1 \mathrm{EXP}\left[-\frac{t}{B}\right] \tag{7}$$

The carbon content of the semi-processed steel is usually very low, therefore the carbon activity can be approximated by its carbon content. The time dependent function, F(t), takes into consideration the controlling steps mentioned by Stephenson,(Stephenson, 1990), and the oxide layer thickness evolution. Thus, the particular aspects of each heat treatment process can be modeled. The parameters values, A0, A1 and B can be obtained by experimental data and used to model the industrial process.

2.2 Numerical method

The solution of Eq. (1) was obtained numerically with help of the Finite Volume Method (FVM) for discretizing the partial differential equation. The time derivative was formulated based on the fully implicit method. The boundary conditions for Eq. (1) were assumed to be of a symmetry type where no carbon gradient is imposed on the surface. The reaction of carbon with the water vapor of the atmosphere is allowed within a narrow layer on the surface where the iron oxide is formed. The numerical mesh used for all the simulations is composed of 8000 finite volumes with 20 divisions on the length direction, 10 divisions on the width direction and 80 divisions on the thickness direction. Therefore, the numerical grid was refined in the thickness direction in order to capture details of the carbon concentration near the surface of the steel strip. Details of the discretization and solution for Eq. (1) can be found elsewhere,(Maliska et al, 2000 and Maliska et al, 1984). A Fortran 90/95 program was developed and adapted in this work to calculate the decarburization process of semi-processed electrical steels.

2.3 Analytical Solutions

To date, analytical model applied to describe decarburisation process is limited to very simple boundary conditions. The authors that have assessed this problem presented solutions only for the case of carbon diffusion control mechanism with uniform carbon distribution as follows, (Crank, 1975):

$$\overline{C}(t) = \sum_{n=0}^{\infty} \frac{8C_0}{(2n+1)^2 \pi^2} \exp\left\{-D_C^{\mathrm{steel}}\left[\left(\frac{2n+1}{e}\right)\pi\right]^2 t\right\} \tag{8}$$

For such conditions, a solution based on the Fourier series expansion can be obtained under the assumption of one dimensional transient distribution along the thickness, resulting in the following expression:

$$C(x,t) = \sum_{n=0}^{\infty} \frac{4C_0}{(2n+1)\pi} \exp\left[-\left(\frac{(2n+1) D_C^{steel} \pi}{\rho e}\right)^2 t\right] \sin\left(\frac{(2n+1)\pi x}{e}\right) \tag{9}$$

Equation (9) stands for the time evolution of the carbon distribution at the thickness direction of the steel strip, with the assumption of uniform initial distribution C0 and the carbon diffusion within the strip controlling the decarburisation mechanism, which is equivalent to impose C(0,t)=0 at the steel surface.

There are obvious advantages for using a computer code, as implemented in this work, since it allows considering non linear boundary conditions imposed by the chemical reactions. Finally, it should be mentioned that analytical solutions considering the highly non-linear boundary conditions introduced by the kinetics of the chemical reactions that take place at the surface and subsurface of the steel strip are virtually impossible to obtain, which limits their application for modeling industrial heat treatment

Table 1 Symbol and units used in the mathematical formulation

a_C : Carbon activity	[-]
C_0 : Initial carbon content	[ppm]
C : Carbon concentration	[ppm]
D_C^{γ} : Carbon diffusion coefficient in austenite phase	[m^2s^{-1}]
D_C^{α} : Carbon diffusion coefficient in ferrite phase	[m^2s^{-1}]
D_C^{steel} : Carbon diffusion coefficient into steel strip	[m^2s^{-1}]
e : Steel strip thickness	[m]
F(t) : Time dependent function accounting for the mass transfer resistance	[-]
$\left(\frac{PH_2O}{PH_2}\right)$: Ratio of partial pressure for H_2O to H_2	[-]
$\left(\frac{P_{CO_2}}{P_{CO}}\right)$: Ratio of partial pressure for CO_2 to CO	[-]
R: Gas constant	($Jmol^{-1}. K^{-1}$)
K_C: Reaction rate of carbon, used in Eq. (1)	(ppm s^{-1})
T – Soaking temperature	[K]
t : Heat treatment time	[s]
ρ : Steel density	[kg m^{-3}]

3. RESULTS AND DISCUSSIONS

3.1 Calculation conditions and comparison

The model assumes that the carbon is dissolved in the steel strip uniformly at the beginning of the calculation. Therefore, the initial condition for the calculation was set as the carbon content of the strip. The atmosphere is selected for each calculation and the temperature of the steel strip is assumed constant and equal to the furnace temperature.

3.2 Comparison with experimental data

One of the objectives is providing a comparison of the old industrial method (Stephenson,1990) with a new method(Marra,2004). According to the recent procedure, the starting material should be steel with low initial carbon, and the atmosphere should have only N_2, H_2 and H_2O to prevent subsurfacial oxidation. The former method makes use of an exothermic atmosphere and performs the decarburization in steels with high carbon content.

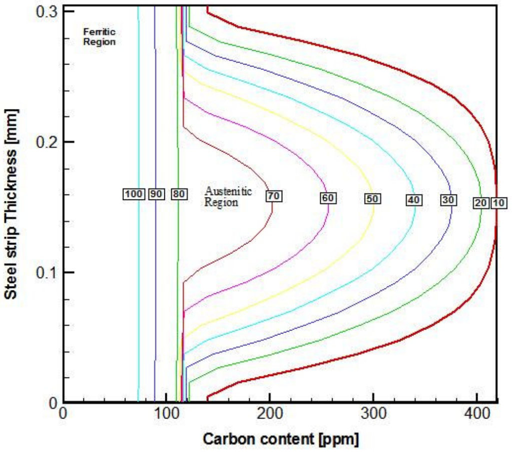

Figure 3a Carbon distribution at the thickness direction along the decarburization process (0,10,20,30,40,50,60,70,80,90 and 100 minutes)- old industrial method of heat treatment – Stephenson data(Stephenson,1990)- treatment in the austenitic region

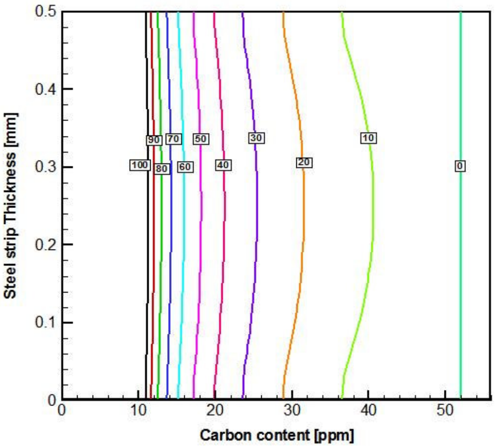

Figure 3b Carbon distribution at the thickness direction along the decarburization process (0,10,20,30,40,50,60,70,80,90 and 100 minutes)- recent industrial method of heat treatment – Marra et al. data,(Marra et al,2004) – treatment in ferritic region and hydrogen atmosphere

Figures 3a and 3b shows the transient calculated results for the carbon distribution along the steel strip thickness for both methodologies. In case of the old method (see Fig. 3a) the decarburization starts at the austenitic region where the carbon diffusion is lower, with austenite transforming into ferrite at the end of the treatment. Thus, the region near the surface transforms into ferrite before the central one. Therefore, associated with the presence of austenite, a strong carbon concentration gradient is developed at the beginning (for the case analyzed, the austenite remains until approximately 1.5 h, slowing down the entire decarburization process). This is relevant information, because if the decarburization time is long, subsurfacial oxidation is likely to occur in a large extent. Fig (3b) shows the same results for the new methodology,(Marra et al, 2004), where all the treatment is performed at the ferrite region and hydrogen atmosphere. The carbon concentration developed a very smooth concentration gradient along the treatment time and became uniform at the final stage.

The result of Fig. 3b shows that, at the first instants of treatment, the carbon distribution is almost (but not completely) uniform, and the carbon will be uniformly distributed at the end of the treatment when adequate treatment time is used. If one compares, the two procedures. Figures 3a and 3b the clear advantage is for the new procedure that allows decarburization in a shorter time of treatment, avoiding subsurfacial oxidation and providing uniform carbon distribution. The model can help to predict the necessary treatment time to get a given carbon content, and this is important information for both the steel producers and users.

Figures 4a and 4b compares the model prediction and measured results for both the old, (Stephenson, 1990) and new methods of treatment, (Marra et al, 2004). The analytical prediction of the carbon content by using eq (9), which is based on the carbon diffusion controlling mechanism, are also shown for both cases. As can be observed from these results, the carbon diffusion control mechanism only, is not sufficient to explain the decarburisation process, since the solution predicted a final carbon content much lower than the measured results, specially, at the end of decarburization process, while for high initial carbon content the diffusion mechanism plays important role, since strong carbon concentration gradient is often observed.

In addition, the analytical solution obtained by eq. 9, indicated that the whole decarburisation process could be completed before 10 minutes, which is not confirmed in industrial practice. In this work, the calculations were performed until 200 minutes, which is a typical industrial treatment. Although the treatment conditions are quite different, the model predicted carbon content evolution very close to the experimental measurement, thus validating the numerical procedure proposed in this work. Figure 4a shows the results for the old method of treatment using initial carbon of 420 ppm and exothermic gas ($CO_2/CO=1.6$) atmosphere. In the case showed in Fig. 4a, the decarburization took place in the region of austenite, resulting in a slow condition for decarburization because the carbon diffusion in this region is lower than in the ferrite region.

Figure 4b shows the calculated results for carbon content evolution of a semi-processed electric steel with initial carbon content of 52 ppm measured by Marra et al, (Marra et al, 2004). The effect of water vapor pressure is evidenced when one compares the results for ($PH_2O/PH_2 = 0.12$ and $PH_2O/PH_2 = 0.24$). When the water vapor was increased, the kinetics of decarburization went faster. In these cases, the effect of surface oxidation is probably not relevant because the atmosphere is located in the iron stability region, as seen in Fig. 2.

Some researchers have pointed out that even 17 ppm of carbon may result in magnetic aging,(Campos et al, 2006, Campos et al, 2004, Standaert, 1996), and it is worthy of mention that, for the same period of time (200 minutes), the model indicates (see Fig. 4a and 4b) that a value of less than 15 ppm of carbon can be obtained for the conditions chosen by Marra et al,(Marra et al, 2004) while for the conditions tested by Stephenson,(Stephenson, 1990) the carbon is always above 15 ppm.

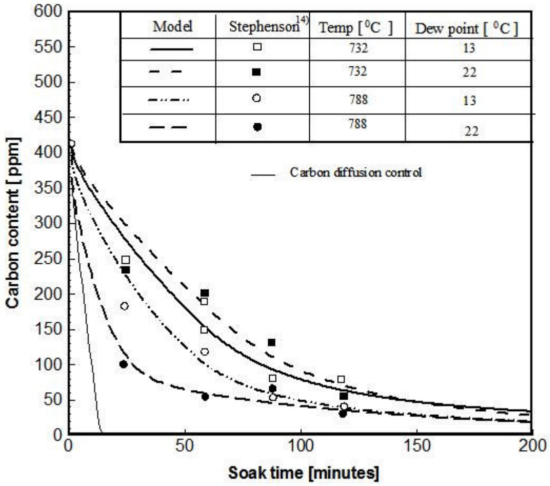

Figure 4a Measured14 and calculated average carbon content for CO-CO2-H2O-H2-N2 atmosphere under temperatures of 732 and 788 oC. The calculated results took into account the $\gamma \rightarrow \alpha$ transformation.

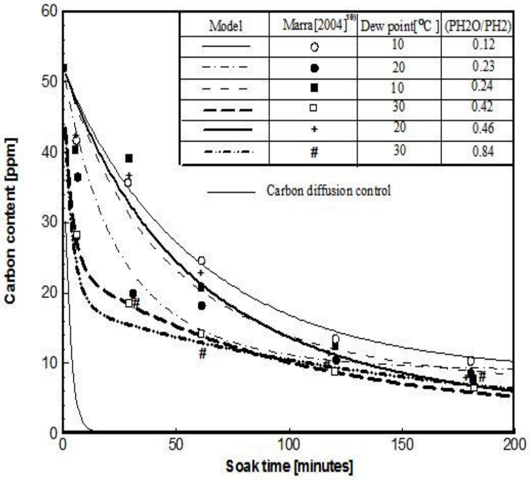

Figure 4b Measured[19] and calculated average carbon content for H_2O-H_2-N_2 atmosphere and 760 °C.

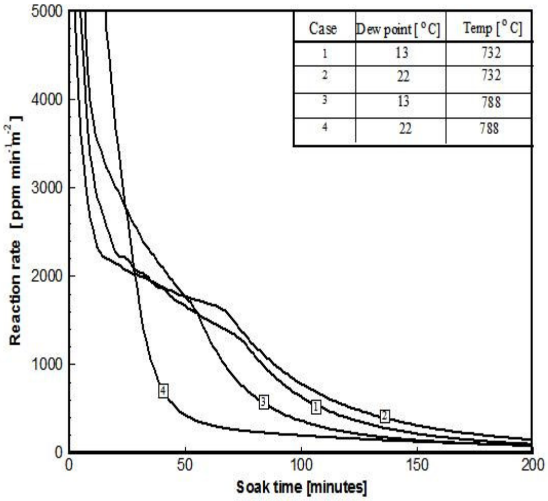

Figure 5a Calculated reaction rates for CO-CO_2-H_2O-H_2-N_2 atmosphere and temperature of 732 and 788 °C, respectively

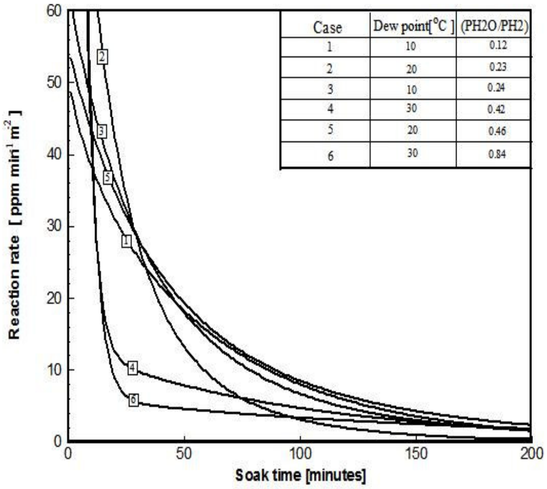

Figure 5b Calculated reaction rates for H_2O-H_2-N_2 atmosphere and temperature of °C

In Figs. 5a and 5b the calculated reaction rate, the parameter k_c defined in Eq. (5), is presented for both cases. As we infer comparing Fig. 5a with Fig. 5b, at the beginning of the decarburization the reaction rate kc is almost two orders of magnitude higher for the Stephenson data,(Stephenson, 1990) shown in Fig. 5a, but the k_c becomes very slow with the time and a lower carbon content can not be reached. On the other hand, for the new methodology, see Fig. 5b, the reaction rate is not that fast in the beginning of decarburization as for the old methodology, however the reaction keeps occurring in a given extent, allowing lower levels of final carbon content at the end of the process, as showed in Figs. 4a and 4b.

4. CONCLUDING REMARKS

A mathematical model was developed to evaluate the decarburization process of semi-processed electric steel sheets. The modeling was based on the transport equation of carbon and the oxidation kinetics at the surface. The model was confronted with experimental results of decarburisation and has allowed a prediction of the carbon content of the steel strip during the heat treatment. The model was used to investigate the effect of furnace atmosphere, initial carbon content, and strip thickness on the technological parameters of treatment time and final carbon content. The parameters reaction rate, k_c and a time dependent function, F(t), are proposed to take into account the kinetics of the whole process. The model indicates that the control of the reaction is not due to the carbon diffusion, but steps controlling are the gas transport of reactants or products as well as the chemical reaction at gas-steel interface. If the steel is ferritic, the carbon is uniformly distributed inside the sheet (small carbon gradient) but, if the carbon is high and austenite is present, this will slow down the decarburization process, with formation of a strong carbon gradient. The calculated results pointed out the importance of controlling the furnace atmosphere in order to accelerate the reactions and at the same time avoid deleterious effects such as oxide formation.

5. ACKNOWLEDGEMENTS

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