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CARBON DIFFUSION COEFFICIENT IN ALLOYED FERRITE

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Abstract. A novel expression of carbon diffusivity in pure ferrite has been derived with parameters fitted to known empirical equations and additional experimental data obtained by the tracer atoms method. The expression is then refined by allowance for the alloying effect on the activation energy revealed with available experimental data on Fe-X binary alloys (X = Cr, Mo, Ni, Si) and our investigation of strain aging kinetics in low-carbon automotive BH−steels with various contents of Mn and P.

Keywords: alloy, carbon, diffusion, ferrite, steel

1. Introduction

Many processes of structure formation in steels are controlled by the diffusion of carbon atoms in ferrite (bcc structure) and martensite (tetragonal structure). In particular, the strain aging of the low-carbon automotive bake-hardening (BH) steels [1-6] can be quoted, as well as phenomena taking place in tempering martensite supersaturated with carbon [7, 8]. The effect of alloying by the substitution elements on the carbon diffusion in ferrite [9, 10] and austenite (fcc structure) [11] has not still investigated properly. As shown in Ref. [9], Si, Ni, Mo, and Cr reduce the diffusion mobility of carbon in ferrite increasing the corresponding activation energy. Thus, at 0.93 wt.% of chromium the energy grows from ~ 80 to ~ 140 kJ/mol. A significant retarding effect of chromium is also confirmed by the results of the strain aging kinetics investigation in the steel alloyed with this element [4].

There are many empirical equations in literature [12-18] to calculate the carbon diffusion coefficient (CDC) in pure ferrite. At the same time, despite practical importance, there are no similar expressions for the ferrite alloyed with substitution elements. The present work based on relevant experimental data is aimed to obtain such an equation applicable to complexly alloyed ferritic steels.

2. Analytical expression for carbon diffusion coefficient in alloyed ferrite

Let's obtain the analytical expression for the effective CDC in ternary ferrite solid solution Fe-C-X in the presence of a carbon concentration gradient. The carbon and substitution alloying element (SAE) atoms are considered to be randomly distributed over the corresponding sub-lattices, and their concentrations are quantitatively characterized by the occupied site fractions y_C and y_X. Taking carbon atoms interaction into account, we consider only the pair interaction between the nearest neighbors. By u_{CC} we designate the interaction energy between carbon atoms located at the nearest octahedral interstitial positions (at a distance of *a/2*, where *a* is the lattice parameter), and by u_{CC}^{*} the interaction energy of a carbon atom, located in the saddle point P, with a carbon atom in the nearest interstitial position (at a

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distance of *a/4*) (Fig. 1). Using the statistical average energy method, for the CDC in binary Fe-C alloy one may obtain [17]:

$$D_C(T;y_C) = D_{C0}\left(1+\frac{5u_{CC}}{RT}y_C(1-y_C)\right)\exp\left(-\frac{\Delta U_C+\alpha_C y_C}{RT}\right), \tag{1}$$

where D_{C0} is a constant factor, ΔU_C is the activation barrier for carbon migration in pure ferrite ($\alpha-$iron); $\alpha_C = 4u^*_{CC} - 3u_{CC}$ determines the concentration dependence of the activation energy; R and T have their usual meaning.

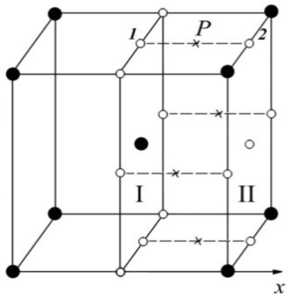

Fig. 1. Carbon atoms migrate in the *x* direction between planes I and II along a concentration gradient. The dashed lines are ways of possible migration. ● – Fe atoms; ○ – interstitials

Taking into account a very low equilibrium carbon concentration in ferrite ($y_C \to 0$), we rewrite (1) in the simplified form:

$$D_C(T) = D_{C0}\exp\left(-\frac{\Delta U_C}{RT}\right). \tag{2}$$

This equation may be refined by accounting for the entropy change. For this purpose, the potential barrier for migration, ΔU_C, should be replaced by the corresponding change in the free Gibbs energy, $\Delta G_C = \Delta U_C - T\Delta S_C$, where ΔS_C is the activation entropy described by the following formula [13,14]:

$$\Delta S_C = \theta\Delta U_C \approx (-d\ln\mu/dT)\Delta U_C, \tag{3}$$

where μ is the shear modulus of $\alpha-$iron. As a result we have:

$$D_C(T) = D_{C0}\exp\left(\frac{\theta\Delta U_C}{R}\right)\exp\left(-\frac{\Delta U_C}{RT}\right). \tag{4}$$

Equation (4) may be easily generalized for the case of carbon diffusion in the binary ferrite solid solution Fe-X containing X atoms (y_X<<1). Taking into account changing the diffusion energy, we should carry out the following replacement: $\Delta U_C \Rightarrow \Delta U_C(y_X) = \Delta U_C + \alpha_X y_X$, where α_X is an empirical parameter. Therefore:

$$D_C(T;y_X) = D_{C0}\exp\left(\frac{\theta(\Delta U_C+\alpha_X y_X)}{R}\right)\exp\left(-\frac{\Delta U_C+\alpha_X y_X}{RT}\right). \tag{5}$$

Assuming the additivity of SAE effects on the activation energy of carbon diffusion, equation (5) for CDC in binary Fe-X alloys may be generalized for a multi-component alloy Fe-X-…-Z, containing a number (X,…,Z) of SAE. In this case the CDC may be calculated as follows:

$$D_C(T;y_X;...;y_Z) = D_{C0}\exp\left(\frac{\theta\left(\Delta U_C + \sum_{S=X}^{Z}\alpha_S y_S\right)}{R}\right)\exp\left(-\frac{\Delta U_C + \sum_{S=X}^{Z}\alpha_S y_S}{RT}\right), \tag{6}$$

where $\alpha_X, ..., \alpha_Z$ are the empirical parameters determining CDC dependence on SAE concentrations.

3. Determination of carbon diffusion coefficient and discussion of the results

Ferrite Fe-X (X = Si, Ni, Mo, Cr). Equation (4) for CDC in pure ferrite contains three empirical parameters: $D_{C0}, \Delta U_C, \theta$. Equation (6) for ferrite Fe-X- ... -Z contains an additional set of such parameters: α_X ..., α_Z. The values of these parameters are determined in two steps.

First, the values of parameters $D_{C0}, \Delta U_C, \theta$ are obtained. Forming the required experimental data set for the CDC in ferrite, we proceed as follows. At present there are several empirical equations for calculating the considered diffusion coefficient [12 - 18]. The most commonly used is the equation proposed by Wert [14]:

$$D_C^{Wert}(T) = 0.02\exp\left(-\frac{84160}{RT}\right)\ (\mathrm{cm^2s^{-1}}). \tag{7}$$

In addition, McLellan equation [16] is known, which has the form:

$$D_C^{McLellan}(T) = 10^{-6}\exp\left(-2.087 - 1.197\frac{10^4}{T} + 3.7\frac{10^5}{T^2}\right)(\mathrm{cm^2s^{-1}}). \tag{8}$$

Despite the fact that the experimental data sets, used to obtain the indicated equations, are practically coincide, the CDC values predicted with their help differ (Fig. 2). The effective diffusion activation energy calculated using (8) (in the temperature range of 350÷850°C) is ~ 89.1 kJ/mol. It is noticeably higher than the corresponding activation energy in equation (7).

It should be noted that the experimental data set used in deriving equations (7) and (8) does not contain reliable data obtained in Ref. [15] by the tracer atoms method in the temperature range of 200÷750°C. Taking it into account, the data base for determining the parameters of equation (4) is formed as a set of 24 values for the considered coefficient, calculated using equations (7) and (8) (12 values for each equation) in the temperature range of 200÷750ºC with a step of 50°C. This data is supplemented with the most reliable data of the CDC measurements obtained in Ref. [15] for the temperature interval of 350÷700°C (Fig. 2).

Thus the created data set includes 31 CDC values. It should be noted that 'mixing' of the actual experimental data [15] with the calculation results obtained using equations (7) and (8) is inevitable, since all the experimental data used for deriving these equations can't be accurately extracted from published sources. At the same time, equations (7) and (8) were obtained on the basis of reliable experimental data and, consequently, the CDC-s calculated with their help are trustworthy.

The parameters $D_{C0}, \Delta U_C, \theta$ are determined using the procedure for minimizing the mean absolute value of the relative deviation of CDC calculated from the experimental data. The values of the specified parameters are respectively equal to: 0.013 $\mathrm{cm^2s^{-1}}$, 84.38 kJ/mol, and $2.6\times10^{-4}\,\mathrm{K^{-1}}$. The results obtained on the basis of equation (4) with the found parameters are very close to those provided by equation (7) which is most often used (Fig. 2). The corresponding activation energies differ by the value less than 0.22 kJ/mol. The parameter

θ (2.6×10^{-4} K^{-1}), at the accuracy level considered, coincides with its value given in [14]. This justifies relevance of our approach to determining CDC parameters for pure ferrite.

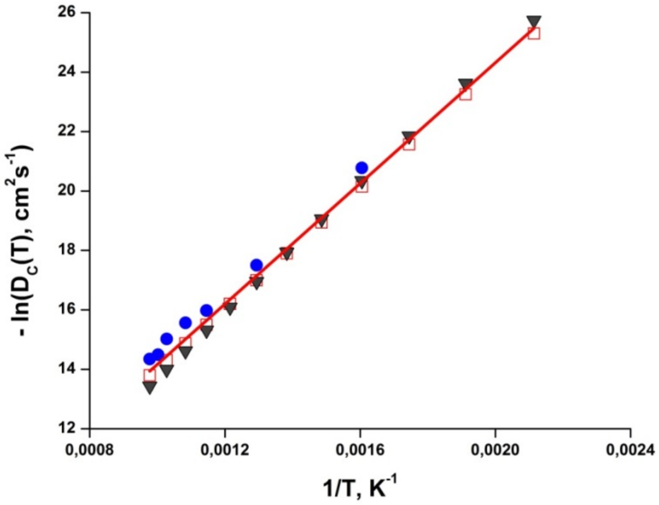

Fig. 2. Illustration to the procedure of determining the CDC parameters for pure ferrite. Symbols (□) and (▼) indicate the calculation results using equations (7) and (8); and (●) correspond to experimental data [15]. The line presents calculation results using equation (4) with the found values of empirical parameters

At the next step, we find the values of parameters determining the CDC dependence in the alloyed ferrite on SAE contents. The values of these parameters for such elements as Si, Ni, Mo, and Cr are obtained from the experimental results on carbon diffusion investigation in binary Fe-X alloys performed by the tracer atoms method [9]. This investigation was carried out not only for alloys containing the listed SAE, but also for a comparatively pure ferrite. However, the exact composition of the burden used in smelting the 'pure' ferrite, as well as the corresponding alloys, is not given in Ref. [9]. In addition to a certain amount of Mn and Si, the burden also contained undefined amounts of S and P, which may appreciably affect the carbon mobility (a significant phosphorus effect is demonstrated below). Taking into account the indicated issues, the data on CDC in the 'pure' ferrite [9] are not used in the present study when determining parameters of equation (4). The calculation of the effective activation energy of carbon diffusion, performed for the material under discussion (Fig. 3a), confirms the correctness of such a solution. Indeed, for this 'pure' ferrite the activation energy obtained is about 103 kJ/mol (Table 1). It significantly exceeds the corresponding value (84.38 kJ/mol) for the actual pure ferrite considered above.

Let's determine the dependences of activation energy of carbon diffusion on the SAE contents. First, using the available experimental data for ferrite alloyed by Si, Ni, Mo, and Cr, we perform standard calculations of the corresponding effective activation energies (Fig. 3), the results of which are given in Table 1. Further, for each alloy we define the differences $\Delta Q_C(y_X) = Q_C(y_X) - Q_C$, the set of which, in combination with the assumption of their linear dependence on the atomic SAE concentrations, allows calculating α_X parameter (Table 2).

The results presented in Fig. 4 clearly show that the assumption of a linear dependence of the activation energy increment on the SAE concentration is fully justified. In particular, in the case of Si, this linearity is observed up to the concentration reaching 5 at. %.

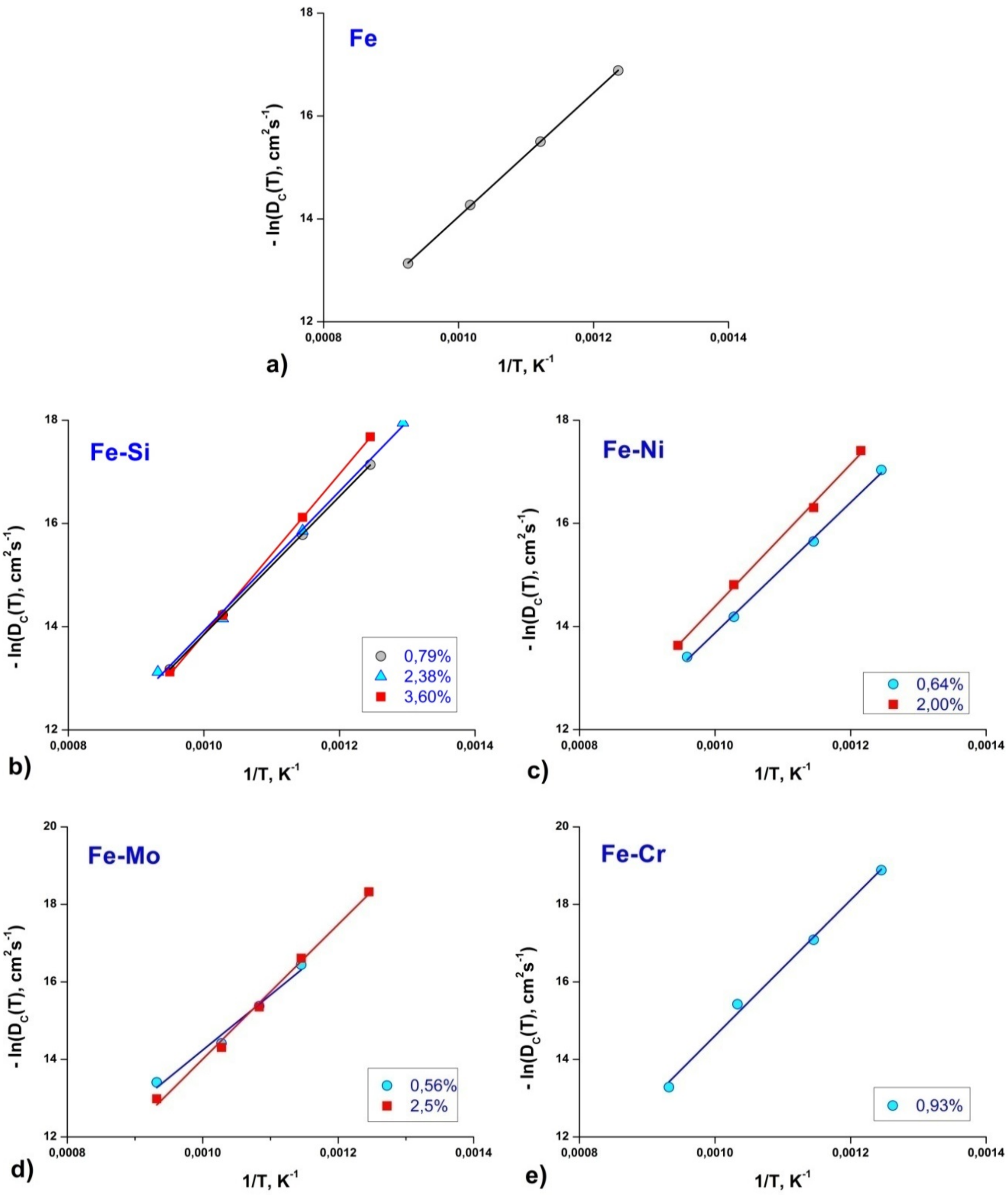

Fig. 3. Data used for calculating activation energies for carbon diffusion in 'pure' (a) and alloyed ferrite (Fe-X) (b–e) on the basis of experimental data [9]

Table 1. Activation energy of carbon diffusion in the 'pure' ferrite and Fe-wt.%X alloys (X = Si, Ni, Mo, Cr)

Alloy	'Pure' ferrite	Si 0.79	Si 2.38	Si 3.60	Ni 0.64	Ni 2.00	Mo 0.56	Mo 2.58	Cr 0.93
Q_C, kJ/mol	103.0	108.0	117.8	125.2	110.5	126.5	107.8	125.5	148.5

Table 2. α_X parameter and α_X / α_{Si} ratios for different SAE

Parameter	Si	Ni	Mo	Cr	Mn*	P*
α_X , kJ/mol	321.5	1236.8	1486.7	4563.2	3770.0	-38035,3
α_X / α_{Si}	1.0	3.8	4.6	14.2	11.7	-118.3

*The procedure for determining α_{Mn} and α_P is described below.

The alloying of ferrite with the elements under consideration leads to a significant decrease in the carbon diffusion mobility, wherein chromium provides the most significant effect. With 1 at.% of this element, the activation energy increases by about 46 kJ/mol (approximately 55% of the activation energy in pure ferrite), making the activation energy of carbon diffusion close to that of austenite [11].

It is interesting to note that the slowing down effect on the carbon diffusion is exerted not only by the carbide-forming elements (Mn, Mo, Cr), which decrease the thermodynamic activity of carbon in ferrite, but also by such elements as Si and Ni that increase this activity. Thus unlike austenite [11], in the case of ferrite there is no correlation between the SAE ability to influence the carbon activity in the solid solution and the effect on its diffusion mobility.

In Table 2 Si, Ni, Mo, Cr are arranged according to their increasing efficiency (at content of 1 at.%) of reducing the carbon diffusion mobility. The efficiency of Mn is also high, but lower than that of Cr (Fig. 4). Analysis of the physical reasons of different influence of SAE on the carbon diffusion in ferrite is also of interest, but beyond the scope of this paper.

Figure 5 enables comparison of the measured and calculated CDC values for 'pure' ferrite and Fe-X alloys. The calculations are carried out according to equation (6), where ΔU_C is substituted by Q_C = 103 kJ/mol (the activation energy in 'pure' ferrite). This approach allows take into account the 'background' effect of additional SAE, which content was not determined in Ref. [9]. Fig. 5 shows that calculation results are in good agreement with the experimental data.

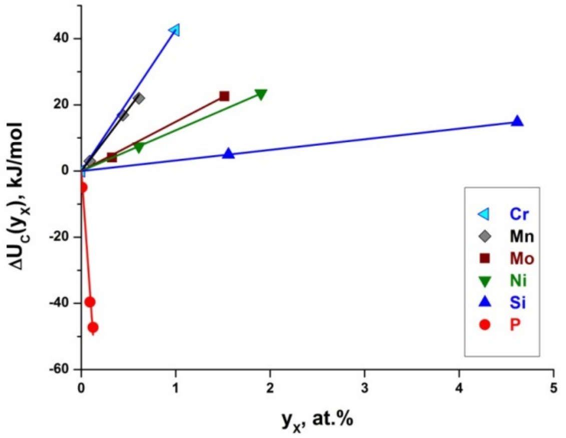

Fig. 4. Increment of carbon diffusion activation energy in Fe-X (X = Cr, Mn, Mo, Ni, Si, P) alloys as a function of the SAE concentration

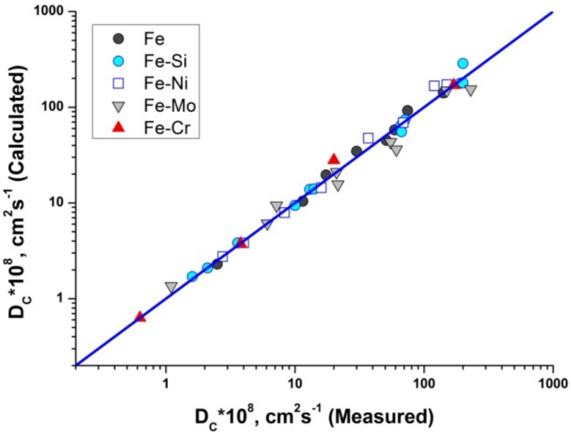

Fig. 5. Comparison of the measured [9] and calculated CDC values for the 'pure' ferrite and Fe-X alloys (X = Si, Ni, Mo, Cr)

Ferrite Fe-X (X = Mn, P). The values of α_X for Mn and P given in Table 2 are determined by means of quantitative analysis of the experimental data on the strain aging kinetics in low-carbon automotive bake-hardening (BH) steels. The investigated samples were cut out from the sheets of appropriate industrial steels produced by POSCO. Their chemical composition is presented in Table 3. The strain aging kinetics at the initial (quick) stage of the process (formation of Cottrell atmospheres) is investigated by measuring the accompanying changes of dynamic Young's modulus using the acoustic method described previously in details [5,6]. The procedure of calculating the activation energy of carbon diffusion is based on the Cottrell equation and is also presented in Ref. [5, 6].

The obtained activation energy for steels 1, 2, and 3 is equal to 55.0, 68.3 and 96.9 kJ/mol, respectively. These values are notably differing from the corresponding value for the pure ferrite (84.38 kJ/mol). For steels 1 and 2 this value is significantly lower, but for steel 3 it is much higher. A rather close activation energy for steel 1 (~ 57 kJ/mol) is obtained by a simpler method that uses processing the experimental data on the Cottrell atmospheres formation time at three temperatures: 60, 80, and 100 °C (Fig. 6). The correctness of the employed experimental methods and of processing the obtained data [5, 6] excludes the influence of experimental errors on the activation energy obtained. Therefore, it can be assumed that the distinction is due to different chemical compositions of investigated steels.

Table 3. Chemical compositions of the investigated steels (wt.%)*.

Steel	C	Mn	P	Ti	Nb
1	0.003	0.45	0.07	0.012	–
2	0.002	0.60	0.052	0.002	0.008
3	0.003	0.44	0.005	0.012	–

*Only SAE influencing the carbon diffusivity are listed.

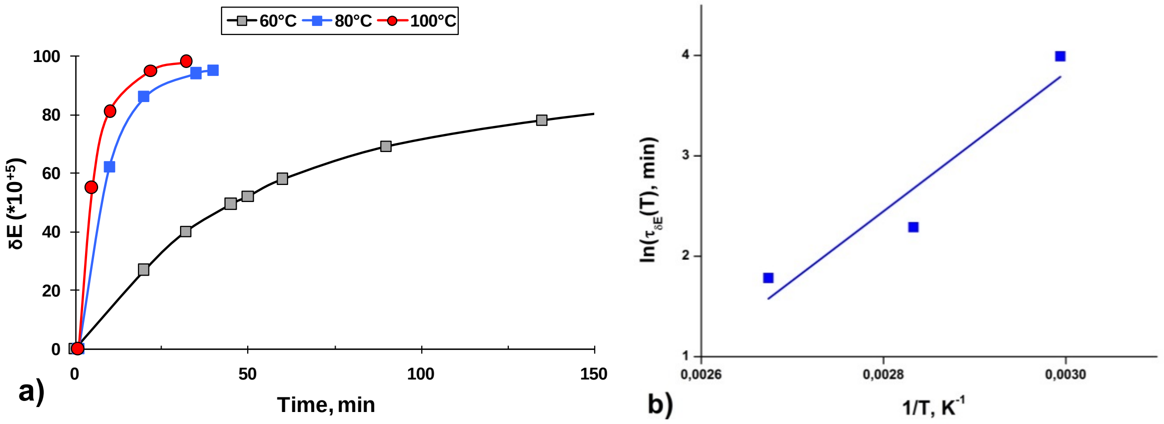

Fig. 6. Experimental data on relative change of the Young's modulus for steel 1 during formation of the Cottrell atmospheres, and their approximation with the Avrami equation (a), and the data for deriving the activation energy of carbon diffusion based on the process duration, $\tau_{\delta E}(T)$, at different temperatures (b)

Note, that the activation energy for steel 3 is almost 1.8 times higher than for steel 1. Thus, the effect of alloying of the solid solution of ferrite in this case is very large. From the chemical composition of the considered steels it follows that the most affecting the activation energy of carbon diffusion are Mn and P. The least activation energy is obtained for steel 1 with the most content of P (0.07 wt.%), whereas steel 3 containing a minimum amount of

P (0.005 wt.%), has the maximum energy. Therefore phosphorus exerts a strong accelerating effect on the carbon diffusion in the ferrite solid solution.

In accordance with this assumption, the linear approximation for the activation energy is suggested:

$$\Delta U_C(w_{Mn}; w_P) = \Delta U_C + \alpha^*_{Mn} w_{Mn} + \alpha^*_P w_P, \qquad (9)$$

where w_{Mn} and w_P are the quantities of Mn and P in wt.%. Using the data on the activation energy of carbon diffusion for three steels, a simple optimization problem is solved, and the parameters α^*_{Mn} and α^*_P are obtained. The values of α_{Mn} and α_P, corresponding to the atomic fractions of the elements (Table 2), are obtained using the parameters α^*_{Mn} and α^*_P found. According to these results, the activation energy of carbon diffusion diminishes linearly with increasing P content (Fig. 7). The relative intensity of the effect exerted by P is more than an order of magnitude higher than the corresponding intensity for Mn, which, similar to all previously studied SAE, increases the activation energy (Table 2). This result complies with the fact that P, introducing large local distortions (stretching) in the ferrite crystal lattice, has the highest solid-solution hardening among all SAE [19]. Accordingly, it may be assumed that an extremely strong P effect, exerted on the activation energy of carbon diffusion, is due to carbon atoms interaction with elastic distortions generated by P atoms in the ferrite lattice.

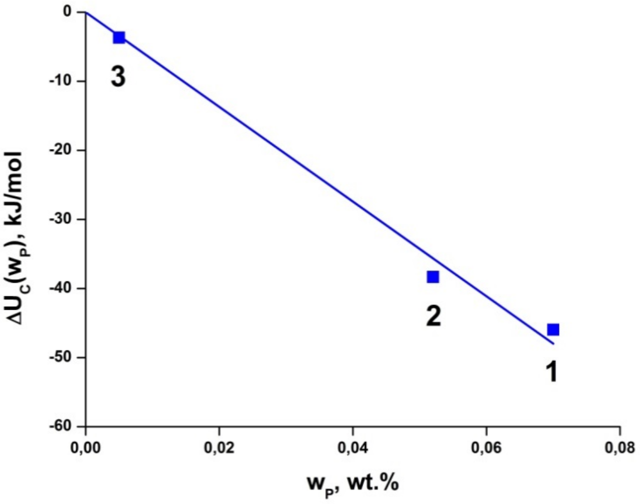

Fig. 7. Dependence of increment in the activation energy of carbon diffusion in steels 1−3 on the phosphorus content. ■ − experimental data; —— − trend line

4. Conclusions

Based on the known empirical equations and the data obtained by the tracer atoms method, the expression for carbon diffusivity in pure ferrite ($\alpha -$iron) has been refined. With the presumed linear response of activation energy of carbon diffusion to concentrations of substitution alloying elements, this expression is extended to complex alloyed ferrite. Involved empirical parameters are determined by treating the data obtained by the tracer atoms method for binary alloys Fe-X (X = Cr, Mo, Ni, Si) and our investigations of Mn and P effects on the kinetics of strain aging in the low-carbon automotive BH−steels. Trial calculations comply well with experimental results.

The retarding effect of alloying elements on the carbon diffusivity in ferrite solid solutions have been evaluated at their contents of 1 at.%. In these terms elements Si, Ni, Mo, Mn, Cr are arranged in order of increasing influence. At the same time an extremely strong accelerating effect of P has been first established that is seemingly due to the highest elastic distortions of the ferrite lattice by P atoms.

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