

## THE FORMATION OF CARBON ATOM PAIRS IN ALPHA IRON AFTER QUENCHING FROM HIGH TEMPERATURES\*

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(Received June 16, 1976)

A simple formula describing the formation of C–C pairs in  $\alpha$  Fe after quenching from high temperature was deduced. The formula was verified experimentally by isothermal magnetic permeability disaccommodation measurements, made for one sample of iron containing carbon in solid solution. On the grounds of these measurements the binding energy  $B$  of C–C pairs was estimated to be 1500 cal/mol.

### 1. Introduction

In spite of the small carbon and nitrogen solubility in alpha iron, a great part of the atoms of these elements forms C–C and N–N pairs in solid solution. The pair formation is related to the existence of a binding energy between the atoms of the pair. The formed pairs introduce locally in the matrix a shape deformation and some changes in the electronic structure, which could interact with external stresses and with the spontaneous magnetization. As a result of these interactions, directional ordering of pairs occurs, which causes mechanical and magnetic migrational after effects.

Pairs of carbon atoms in  $\alpha$ Fe were observed for the first time in 1960 by means of magnetic permeability disaccommodation (MPD) [1]. Three years later Keefer and Wert corroborated this result [2]. By the method of stress relaxation at constant strain, in the case of one sample containing 0.08 at % C investigated at  $-24.3^{\circ}\text{C}$ , they obtained 1900 cal/mol for the interaction energy and 22000–23000 cal/mol for the activation energy of directional ordering.

On the other hand, in many papers, and especially in those devoted to the influence of substitutional atoms on the migration of carbon in  $\alpha$ Fe there was no need for C–C pairs in analyses and interpretations of internal friction (IF) curves measured in the region of the Snoek relaxation (e.g. [3], and also [4]). Recently, however, the existence of pairs

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\* Work supported by the Polish Academy of Sciences.

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was confirmed by means of isothermal and isochronal MPD measurements made on  $\alpha\text{Fe—Al—C}$  [5] and  $\alpha\text{Fe—V—C}$  [6] alloys, with a small content of aluminium or vanadium in solid solution, and on  $\alpha\text{Fe—C}$  [5, 7]. In [8] pairs of carbon atoms were observed indirectly by comparing internal friction and electrical resistance results.

In this work, using the generally accepted theory of Damask et al. concerning the precipitation of carbon in  $\alpha\text{Fe}$  [9, 10], a formula was obtained, which describes the formation of C—C pairs after quenching from high temperatures. The formula was used in the analysis of results obtained by means of MPD measurements.

## 2. Kinetics of C—C pair formation in $\alpha\text{Fe}$

When the formation and dissociation of trios and greater clusters of interstitial atoms can be neglected, the equation of the kinetics of pair formation has the form

$$\frac{dn_2}{dt} = k_{21}n_1^2 - k_{12}n_2. \quad (1)$$

In this formula  $n_1, n_2$  are atomic fractions of singlets and pairs of interstitial atoms, respectively, relative to the number of iron atoms.  $n_1$  and  $n_2$  satisfy the equation

$$n_1 + 2n_2 = \text{const} = n_0, \quad (2)$$

where  $n_0$  stands for the total amount of carbon in solid solution.

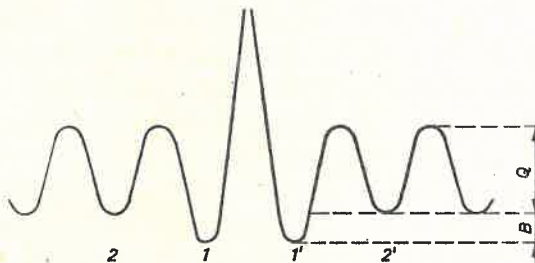


Fig. 1. The energy of a carbon atom occupying an interstitial site in the neighbourhood of another carbon atom; jump  $1 \rightarrow 2$  and  $1' \rightarrow 2'$  correspond to pair dissociation

For the dependence of the interstitial atom energy on position in the lattice, presented in Fig. 1, the probabilities of pair formation and dissociation per unit time are given by

$$k_{21} = g_2 v_2 \exp\left(\frac{\Delta S}{R}\right) \exp\left(-\frac{Q}{RT}\right) \quad (3a)$$

$$k_{12} = g_1 v_1 \exp\left(\frac{\Delta S'}{R}\right) \exp\left(-\frac{Q+B}{RT}\right). \quad (3b)$$

$Q, \Delta S$  are the activation energy and entropy of the Snoek relaxation,  $B$  is the binding energy of the pair and  $\Delta S'$  is the change of entropy originating from pair dissociation;

$\nu_2, g_2$  and  $\nu_1, g_1$  are vibrational frequencies and configurational factors of single and paired carbon atoms; for  $\nu_1, \nu_2$  the Debye's frequency of the matrix is usually taken.

In the equilibrium state

$$k_{21}\bar{n}_1^2 - k_{12}\bar{n}_2 = 0 \quad (4)$$

$$k_{21}\bar{n}_1^2 - \frac{1}{2} k_{12}(n_0 - \bar{n}_1) = 0, \quad (4a)$$

where  $\bar{n}_1, \bar{n}_2$  are atomic fractions corresponding to that state, hence

$$\bar{n}_2 = K\bar{n}_1^2, \quad (5)$$

where

$$K = \frac{k_{21}}{k_{12}}.$$

Integration of equation (1) with the initial condition  $n_2(0) = \alpha_0$  gives

$$n_2(t) = \alpha_2 \frac{1 - \frac{\alpha_1}{\alpha_2} \frac{\alpha_0 - \alpha_2}{\alpha_0 - \alpha_1} \exp[-4k_{21}(\alpha_1 - \alpha_2)t]}{1 - \frac{\alpha_0 - \alpha_2}{\alpha_0 - \alpha_1} \exp[-4k_{21}(\alpha_1 - \alpha_2)t]}. \quad (6)$$

in this formula  $\alpha_1, \alpha_2$  are solutions of equation (4a);  $\alpha_2$  is the atomic fraction of pairs for  $t \rightarrow \infty$ ,  $\alpha_1$  has no physical meaning. Assuming that  $\alpha_0 \ll \bar{n}_2$  (6) may be expressed in the form

$$n_2(t) = n_0^2 \exp\left(\frac{B}{RT}\right) \left[1 - \exp\left(-\frac{t}{\theta_p}\right)\right] = \alpha_2 \left[1 - \exp\left(-\frac{t}{\theta_p}\right)\right], \quad (7)$$

where

$$\theta_p = \frac{1}{k_{12}(1 + 8Kn_0)^{1/2}} \quad (8)$$

is the relaxation time of pair formation.

### 3. Procedure and results

Measurements testing formula (7) were made on a toroidal sample of electrolytic iron containing no more than 0.01% substitutional impurities; the sample was prepared in the Institute of Iron Metallurgy, Gliwice. Analysis of preliminary results obtained by means of isochronal MPD measurements showed that the nitrogen content in solid solution was very small (disaccommodation of 15% and of 1% originated from C and N, respectively).

The sample was heat-treated in a vacuum furnace at 950°C for 10h, whereafter it was carbonized in an atmosphere produced by the decomposition of isohexane at 850°C for 2h. After these treatments the isochronal measurements did not show any nitrogen

relaxation at all, whereas the carbon relaxation rose to 25%. Two hundred turns of coil wire in ceramic insulation were wound on the sample, which was subsequently heated in an argon atmosphere at 700°C for 1h and quenched in liquid nitrogen, this quenching prevented the carbon atoms from forming pairs.

The kinetics of pair formation was investigated at  $-18.9^{\circ}\text{C}$  by means of isothermal MPD measurements performed on a Maxwell-Wien bridge, described in detail elsewhere [11]. The magnetizing field frequency and field intensity amounted to 520 Hz and 1 mOe. The time  $t$  of pair formation was counted from the instant the sample attained the measuring temperature.

Before the measurements the sample was demagnetized by a 50 Hz field, of which the amplitude dropped from 14 Oe to zero during 7 seconds. After demagnetization the bridge was balanced continuously. Five isothermal MPD curves were obtained for  $t = 1, 2, 5, 7$  and 10 h; each curve was measured during 60 minutes.

For isothermal MPD curves the following formula is valid [12]

$$\frac{1}{\chi(\tau)} = \frac{1}{\chi(\infty)} - \sum_{i=1}^n \frac{1}{\chi_i} \exp\left(-\frac{\tau}{\theta_i}\right), \quad (9)$$

$\frac{1}{\chi(\tau)}$  is the reciprocal magnetic susceptibility at time  $\tau$  after demagnetization,  $\theta_i$ ,  $\frac{1}{\chi_i}$  are the time constant and intensity of the  $i$ -th relaxation. The last parameter is given by the expression [12]

$$\frac{1}{\chi_i} = \frac{rw_i^2 l}{kTdI_s^2} c_i = a_i n_i \quad (10)$$

In this formula  $r, l, d$  are parameters corresponding to the ferromagnetic domain structure ( $r$  is a numerical coefficient dependent on the kind and position of the Bloch wall,  $d$  — the wall thickness,  $l$  — the domain width),  $I_s$  is the spontaneous magnetization,  $w_i$  — Néel's interaction energy, and  $k$  — the Boltzmann constant;  $c_i$  is the number of  $i$ -th relaxators in volume unit,  $n_i$  is the corresponding atomic fraction.

In the investigated problem the disaccommodation was originated from two relaxation processes, only ( $n = 2$ ): the Snoek carbon relaxation (intensity  $\frac{1}{\chi_s}$ ) and the C—C pair relaxation (intensity  $\frac{1}{\chi_p}$ ). To obtain the parameters  $\frac{1}{\chi_s}$  and  $\frac{1}{\chi_p}$  five isothermal MPD curves, measured after different ageing times at  $-18.9^{\circ}\text{C}$ , were decomposed on the computer ODRA 1204 by means of the minimum  $\chi^2$  test. For the time constants of directional ordering of pairs and of single carbon atoms the values obtained in [7] were used. The theoretical disaccommodation curves evidently well fitted the experimental points (about 60 for each curve): the relative differences between the calculated and experimental values never exceeded  $\pm 1\%$ .

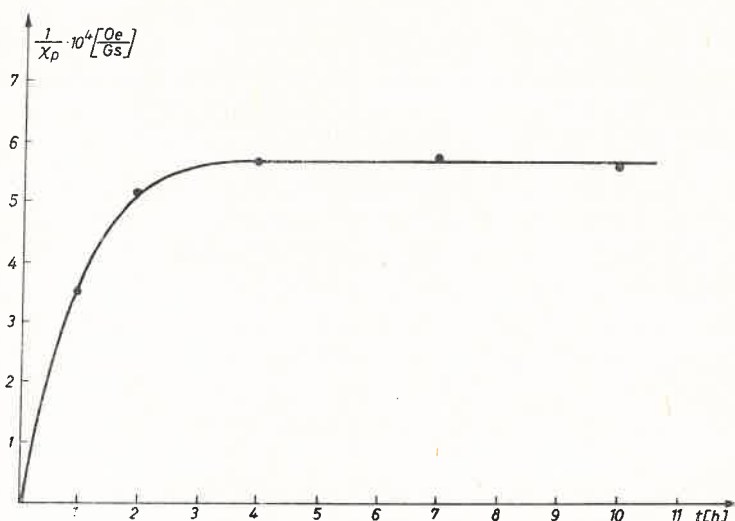


Fig. 2. The dependence of C-C pair relaxation intensity in  $\alpha$ Fe-C on ageing time at  $-18.9^\circ\text{C}$  after quenching from  $700^\circ\text{C}$ . The full line is the theoretical curve calculated from (7)

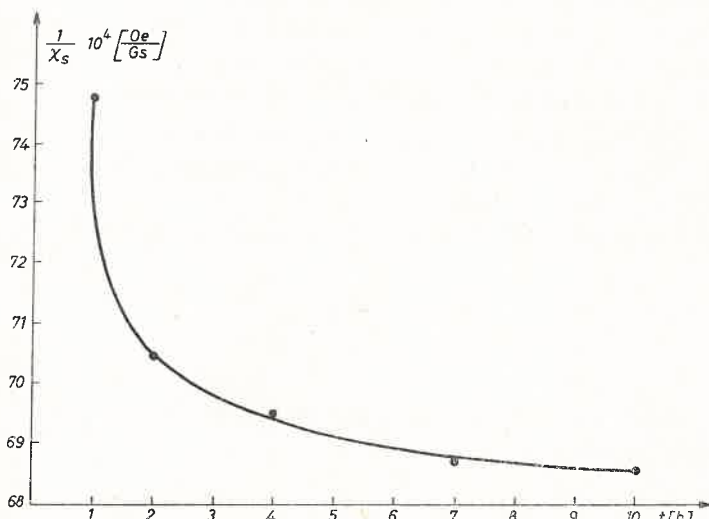


Fig. 3. The dependence of Snoek relaxation intensity in  $\alpha$ Fe-C on ageing time at  $-18.9^\circ\text{C}$ , after quenching from  $700^\circ\text{C}$

Fig. 2 and 3 present the dependences of intensities  $\frac{1}{\chi_s}$  and  $\frac{1}{\chi_p}$  on time  $t$  of pair formation. The curve of Fig. 2 is the theoretical curve calculated from formulae (7) and (10) by means of the minimum  $\chi^2$  test. The greatest relative differences between the values calculated from formulae (7) and (10) and the values obtained from disaccommodation curves decomposition amounted to 3.5% (the average difference amounted to 1.4%, only). For the relaxation time of pair formation at  $-18.9^\circ\text{C}$   $\theta_p = 61$  min was obtained.



## 4. Discussion

Fig. 2 shows that the theoretical curve (7) fits well the experimental points. It is worthwhile to emphasize that for  $t = 0$  the computer gave  $\frac{1}{\chi_p} = 0$ .

Thus it has been shown that after quenching from high temperature pairs of carbon atoms form in  $\alpha\text{Fe}-\text{C}$ . The process can be described by an exponential law, which time constant, as can be seen from formula (8), depends mainly on the sum of the Snoek activation energy and of the binding energy of pairs.

The results of this work also permit one to estimate  $B$ . In this estimation, formula (8), in which the binding energy occurs in  $k_{12}$  and  $K$ , and the value of  $\theta_p$  at  $-18.9^\circ\text{C}$  were used. Because the result of this calculation depends essentially on  $k_{12}$ , and the square root expression influences it only weakly, great care was taken to properly choose the parameters occurring in  $k_{12}$ .

Apart from  $(Q+B)$  the jump probability  $k_{12}$  contains three further parameters: the vibration frequency  $\nu_1$ , the configurational factor  $g_1$  and the entropy of dissociations  $\Delta S'$ . As  $\nu_1$  the Debye frequency of iron was assumed, which for room temperature amounts to  $10^{13} \text{ sec}^{-1}$  [13]. For  $g_1$ , however, 4 was taken; this value corresponds to the four jumping ways of dissociating atoms, which are possible in the configuration "a" of Johnson et al. [14] (the C—C pair, for which theoretically the highest binding energy was obtained).

The entropy of dissociation  $\Delta S'$  was estimated on the ground of Zener's semi-empirical formula of activation entropy of interstitial atoms migration in BCC metals, which was published in 1951 [15]; until now this formula has been generally accepted in literature devoted to diffusional processes, e.g. [16, 17].

At present, in agreement with Fig. 1, the Zener relation could be expressed in the form

$$\frac{\Delta S'}{R} = \left(\frac{\Delta S'}{R}\right)_1 + \left(\frac{\Delta S'}{R}\right)_2 = \frac{sQ}{RT_m} + \frac{sB}{RT_m}, \quad (11)$$

where  $T_m$  is the melting temperature of the matrix (for iron  $-1809^\circ\text{K}$ ),  $Q = 19500 \text{ cal/mol}$  [5], and  $s$  is given by the formula

$$s = - \frac{d\left(\frac{\mu}{\mu_0}\right)}{d\left(\frac{T}{T_m}\right)}. \quad (11a)$$

$\mu$ ,  $\mu_0$  are the rigidity moduli of the matrix at  $T$  and 0 K, respectively; for iron  $s = 0.43$  [16].

The first part of (11) gives  $\exp\left(\frac{\Delta S'}{R}\right)_1 = 10.4$ , the second part, however,  $\exp\left(\frac{\Delta S'}{R}\right)_2 = 1.2$  (for  $B = 1900 \text{ cal/mol}$  [2]).

In the expression under the square root (8), for  $n_0$  two extreme values were taken: 0 and the maximum content, which amounts to  $n_0 = 0.0008$  [18]. In the second case, as formula (5) is identical with expression (11.4-6) given in the monograph [19], for  $K$

$$K = \frac{4}{9} \exp\left(\frac{sB}{RT_m}\right) \exp\left(\frac{B}{RT}\right)$$

was taken.

Finally, using (8), (3a), (3b) and (11) the binding energy was calculated by means of formula

$$B = \frac{-\ln\left[g_1 v_1 \theta_p \left(1 + \frac{3^2}{9} \exp\left(-\frac{sB}{RT_m}\right)\right)^{1/2} \exp\left(\frac{B}{RT}\right)\right]}{s/RT_m - 1/RT} - Q. \quad (12)$$

After two iterations the following values were obtained: for  $n_0 = 0$  —  $B = 1400$  cal/mol, for  $n_0 = 0.0008$  —  $B = 1500$  cal/mol.

The value of  $B$ , estimated in this work, seems to be almost equal to the result of Keefer and Wert — 1900 cal/mol [2]. It differs, however, distinctly from the binding

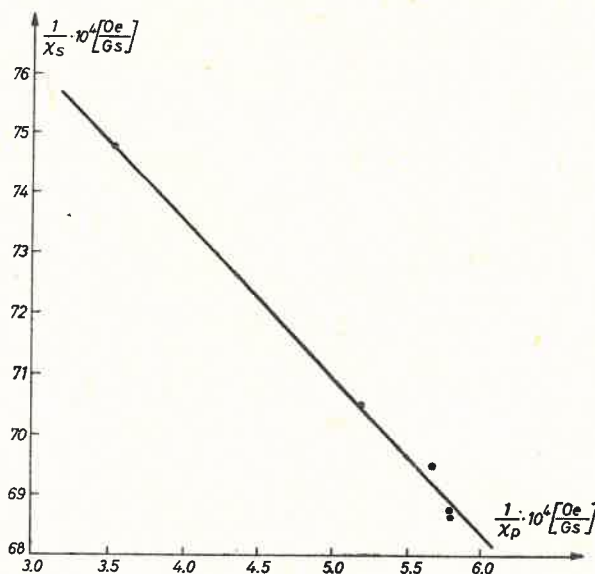


Fig. 4. The dependence of the pair relaxation intensity in  $\alpha\text{Fe-C}$  on the Snoek relaxation intensity at  $-18.9^\circ\text{C}$

energy calculated theoretically by Johnson et al. [14], and also from the value obtained experimentally (through IF measurements) by Mathé et al. [8] — 3200 cal/mol.

The results of this work, shown in Fig. 2 and 3, can also be presented in another form. Since the total number of carbon atoms remains constant during pair formation, from

(2) and (10) the following formula can be obtained

$$\frac{1}{\chi_s} = \frac{1}{\chi_{s0}} - \frac{2a_s}{a_p} \frac{1}{\chi_p}, \quad (13)$$

where  $\frac{1}{\chi_{s0}}$  is the intensity of the Snoek process at  $t = 0$ , and  $a_s$ ,  $a_p$  are values of  $a$  (formula 10) corresponding to the Snoek and the pair relaxations.

Fig. 4 shows the  $\frac{1}{\chi_p}$  versus  $\frac{1}{\chi_s}$  dependence. It can be seen, that in accordance with formula (13) a straight line was obtained. The slope of this line enables one to calculate the ratio of Néel's interaction energies of pairs ( $w_p$ ) and of single atoms ( $w_s$ ). The value  $w_p/w_s = 0.86$  was obtained.

#### REFERENCES

- [1] A. J. Bosman, P. E. Brommer, L. C. H. Eykelenboom, C. J. Schinkel, G. W. Rathenau, *Acta Metall.* **8**, 728 (1960).
- [2] D. Keefer, C. Wert, *J. Phys. Soc. Japan* **18**, Suppl. III, 110 (1963).
- [3] W. Jäniche, J. Brauner, W. Heller, *Archiv Eisenhüttenw.* **37**, 719 (1966).
- [4] J. Garigue, P. Astie, J. P. Peyrade, *Ser. Metall.* **7**, 145 (1973).
- [5] L. Kozłowski, J. W. Moroń, J. Rasek, *Phys. Status Solidi* (a) **13**, 691 (1972).
- [6] G. Haneczok, J. Ilczuk, R. Kuśka, J. W. Moroń, *Phys. Status Solidi* (a) **33**, 313 (1976).
- [7] J. Rasek, J. Przybyła, *Fizyka i Chemia Metali* **1** 43 (1976), Prace Naukowe Uniwersytetu Śląskiego w Katowicach (in Polish).
- [8] E. L. Máthé, J. Parisot, J. Santrot, J. Grilhé, *Acta Metall.* **22**, 1529 (1974).
- [9] A. C. Damask, G. C. Danielson, G. J. Dienes, *Acta Metall.* **13**, 973 (1965).
- [10] M. Koiwa, *Phil. Mag.* **30**, 877 (1974).
- [11] J. Ilczuk, *Physics Papers* **II**, 57 (75), Silesian University, Katowice.
- [12] J. Rasek, *Acta Phys. Pol.* **A44**, 85 (1973).
- [13] International Tables for X-Ray Crystallography Vol. III, Ed. C. H. Macgillavry, G. D. Rieck, Kynoch Press, Birmigham 1967, p. 235.
- [14] R. A. Johnson, G. J. Dienes, A. C. Damask, *Acta Metall.* **12**, 1215 (1964).
- [15] C. Zener, In *Imperfections in Nearly Perfect Crystals*, Ed. by Shockley, Hollomon, Mawrer, Seitz, J. Wiley, New York 1952, p. 280.
- [16] Y. Adda, J. Philibert, *La diffusion dans les solides*, Tome I, Institut National des Sciences et Techniques Nucléaires, Saclay 1966, p. 486.
- [17] B. S. Bokshtein, S. Z. Bokshtein, A. A. Zhukhovitskij, *Termodinamika i kinetika diffuzji w tverdykh telakh*, Metallurgija, Moskva 1974, p. 74 (in Russian).
- [18] H. Schuman, *Metallographie*, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1969, p. 317.
- [19] A. S. Nowick, B. S. Berry, *Anelastic Relaxation in Crystalline Solids*, Academic Press, New York 1972, p. 314.