THE MIGRATION OF CARBON IN αFe—Al (ABOUT 25 at. %) ALLOY. PART I*

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The magnetic permeability disaccommodation was investigated in an αFe–Al (13.4 wt. %)–C alloy, by means of isochronal and isothermal measurements. Four elementary processes (I–IV) were observed for samples slowly cooled or quenched in water after heat treatment at 400°C, but five (I–V) for a sample quenched from 700°C. Ageing at 400°C allowed us to describe some features of the relaxations.

1. Introduction

Alpha iron, containing carbon in solid solution displays internal friction (IF) with a peak at 40°C for 1 Hz frequency. The peak originates from the directional ordering of single interstitial C atoms. Measurements made for αFe—Al—C samples, with small aluminium contents, showed that the carbon maximum shifts to higher temperatures and the whole IF — curve becomes distinctly broader [1, 2]. In alloys with about 25 at. % Al, after heat treatments introducing DO_3 long range order, the carbon maximum appears again as a sharp peak at about 130°C for 1 Hz [3]. In samples without Fe_3Al type order, however, the $Q^{-1} = f(T)$ curves are very broad and only after ageing at temperatures lower than the order-disorder transition temperature of the DO_3 superstructure (T_k = 550°C) does the sharp carbon peak occur gradually with time.

Magnetic permeability disaccommodation (MPD) was also used in investigations concerning the migration of carbon in alpha iron with high aluminium content [4]. In αFe—Al—C with 12.4, 14.0 and 16.0 wt. % aluminium, after Fe_3Al ordering treatment, a distinct peak appeared at about 50°C in the isochronal MPD curves. The peak temperature, the activation energy and the influence of different heatings on the shape of the curves indicated, that the observed relaxation corresponds with Tanaka's IF maximum.

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The analysis of IF and MPD curves, performed in [3, 4], showed that the after-effect band observed in αFe—Al (about 25at.%)—C is much broader than for a single relaxation process. Unfortunately, until now it has not been possible to ascertain univocally by what kind of time constant spectrum — linear or continuous — the experimental curves could be described. This problem, however, has to be solved before any effort can be made to find correlations between the migrational properties of interstitial atoms and the atomic microstructure of the substitutional solid solution.

In connexion with this problem, the investigations described in [4] have been continued for one alloy containing 13.4 wt.% Al (24.3 at.%) prepared from high purity iron and aluminium.

2. *Investigated alloy*

The alloy was prepared in the Institute of Iron Metallurgy, Gliwice, and the materials used were electrolytic iron and aluminium, containing no more than 0.01 wt.% substitutional additions. The alloy was remelted several times in an induction vacuum furnace and great care was taken to insure good homogeneity of the Fe—Al solution.

The samples, consisting of several rings (0.3 mm thick, inner and outer diameters — 31 and 45 mm, respectively) and containing 0.005 wt.% C and 0.003 wt.% N, were heated in a vacuum furnace at 950°C for 20 hours and then slowly cooled in the furnace. After such heating all the nitrogen precipitates as AlN [5], which was corroborated by chemical analysis.

The average grain size was $6 \cdot 10^4$ μm^2. Microbeam analysis showed that the solution homogeneity of aluminium was better than (13.4±0.2) wt.%.

Three samples were investigated: 1 — slowly cooled after heating at 400°C (sample W), 2 — quenched in water after heating at 400°C (sample H1), 3 — quenched in water after heating at 700°C (sample H2); before cooling or quenching the samples were heated for 1 hour at 400°C or 700°C, respectively.

3. *Procedure*

The MPD measurements were performed on a Maxwell-Wien bridge, described in details in [6]. Before measurement the sample was demagnetized by a 50 Hz field, in which the amplitude decreased from 13 Oe to zero in 5 seconds. The bridge was balanced continuously and the frequency and intensity of the magnetizing field amounted to 500 Hz and 2 mOe.

Isochronal and isothermal MPD curves were measured. For an isotherm having a linear spectrum of time constants the following formula is valid [7]

$$\frac{1}{\chi(t)} = \frac{1}{\chi_\infty} - \sum_{i=1}^{n} \frac{1}{\chi_i} \exp\left(-\frac{t}{\theta_i}\right) \tag{1}$$

in which $\frac{1}{\chi(t)}$ is the reciprocal magnetic susceptibility at time t after demagnetization, and $\frac{1}{\chi_i}$, θ_i are the intensity and time constant of the i-th elementary relaxation process; $\frac{1}{\chi_\infty}$ corresponds to $t \to \infty$. The time constants θ_i obey the Arrhenius law

$$\theta_i = \theta_{0i} \exp\left[\frac{Q_i}{RT}\right] \tag{2}$$

where θ_{0i} is the preexponential factor and Q_i the activation energy of migration of the i-th relaxator.

From (1) for isochrons one gets

$$\Delta\left(\frac{1}{\chi}\right) = \frac{1}{\chi(t_2)} - \frac{1}{\chi(t_1)} = \sum_{i=1}^{n} \frac{1}{\chi_i}\left[\exp\left(-\frac{t_1}{\theta_i}\right) - \exp\left(-\frac{t_2}{\theta_i}\right)\right]. \tag{3}$$

Because $\frac{1}{\chi_i}$ changes slowly with temperature in comparison with the difference between exponentials, the time constant at the temperature of the maximum of the i-th process (T_{pi}) is given by the expression [8]

$$\theta_i(T_{pi}) = \frac{t_2 - t_1}{\ln \frac{t_2}{t_1}}. \tag{4}$$

And hence, for the peak temperature and peak height (A_i) one gets

$$T_{pi} = \frac{Q_i}{R\left[\ln \frac{t_2 - t_1}{\ln \frac{t_2}{t_1}} - \ln \theta_{0i}\right]}, \tag{5}$$

$$A_i = \frac{1}{\chi_i}\left[\exp\left(\frac{-t_1 \ln \frac{t_2}{t_1}}{t_2 - t_1}\right) - \exp\left(\frac{-t_2 \ln \frac{t_2}{t_1}}{t_2 - t_1}\right)\right]. \tag{6}$$

Isochronal MPD curves were measured for all samples; in further calculations the susceptibilities at $t_1 = 25$ s and $t_2 = 295$ s were used. The curves were decomposed on an ODRA 1204 computer by means of the minimum χ^2 test. In these calculations it was supposed that elementary relaxations obey the Wert–Marx law [9, 10]: for θ_{0i}-s of all processes 3.2×10^{-15} s was assumed [10]. This value is very close to the result of Stephenson's calculations, in which the data obtained by many authors for the Snoek relaxation in BCC metals were compiled ($\theta_0 = 3.26 \cdot 10^{-15}$ s) [12].

Isothermal curves were measured for sample W, only. In this case the isochrons could be decomposed into four elementary relaxations (see Sec. 4).

As the time of measurement of an isotherm, $t = 5\,\theta$ was accepted, where θ was the time constant of the longest component relaxation process; the values of θ at the measurement temperatures were calculated by means of isochronal results. After $t = 5\theta$ the longest process was practically finished.

In analysing isothermal curves, as the start data in a searching programme θ_i and $1/\chi_i$ values of relaxations I–IV, calculated by means of isochronal results, were used; $\frac{1}{\chi_\infty}$ was estimated by extrapolation to $t \to \infty$. All parameters — θ_i, $\frac{1}{\chi_i}$, $\frac{1}{\chi_\infty}$ were allowed to change simultaneously.

4. Results

Fig. 1 presents the $\Delta/(1/\chi)$ vs. T curves obtained after treatments 1, 2 and 3. As one can see, apart from the investigated disaccommodation, an additional MPD band of great intensity occurs at higher temperatures in the sample quenched in water after heating at 700°C.

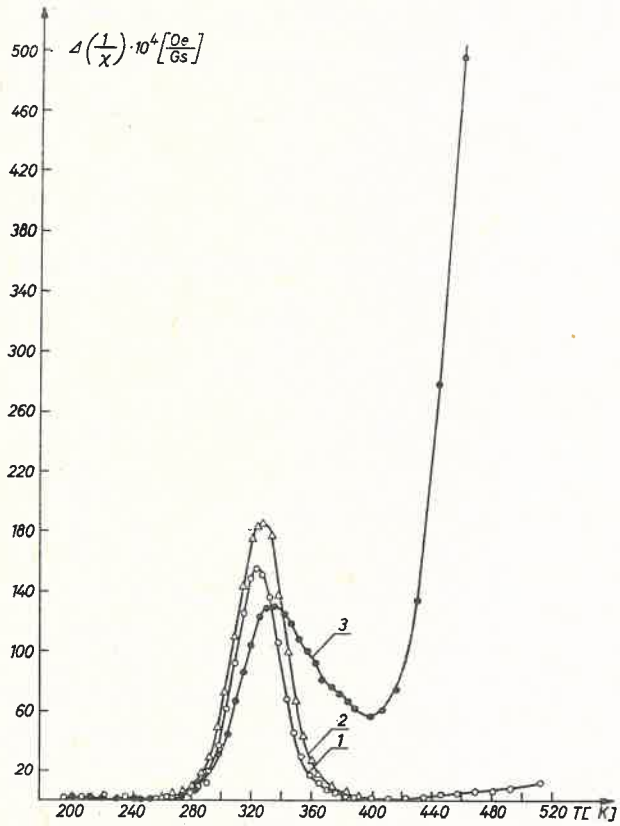

Fig. 1. Isochronal MPD curves in αFe–Al (13.4 wt. %)—C. Sample heated: *1* — at 400°C and slowly cooled (W), *2* — at 400°C and quenched (H1), *3* — at 700°C and quenched (H2)

Fig. 2 shows the curves from Fig. 1 normalized to the maximum values of $\Delta/(1/\chi)$; before normalization the MPD background was subtracted linearly. It may be seen that in the region of the investigated MPD band a broadening at higher temperatures occurs after treatment 3.

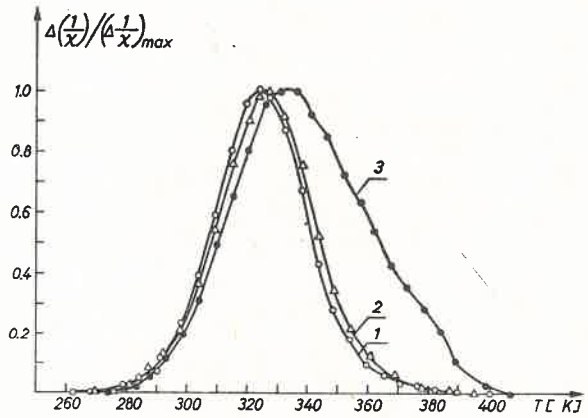

Fig. 2. Isochronal MPD curves normalized after linear background subtraction

In the case of treatments 1 and 2 the computer decomposed the experimental curves without background into four relaxations, in the case of curve 3, however, into five processes. Figs 3, 4 present the theoretical curves of the elementary processes and the resultant theoretical curve. The last curve coincides very well with the experimental points.

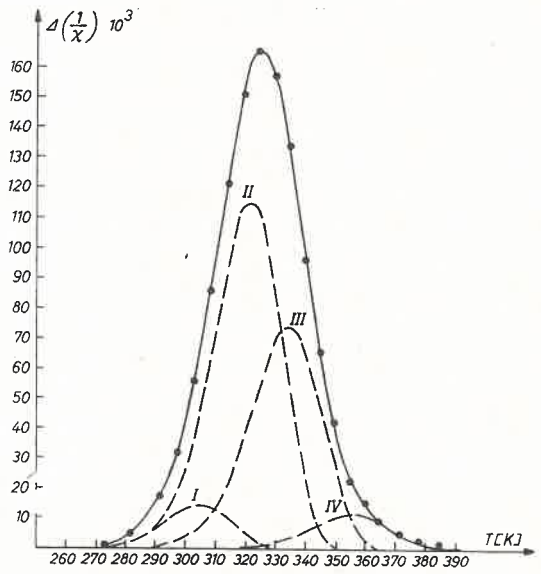

Fig. 3. Theoretical isochronal MPD curves calculated for sample W; – – – elementary process curves, ——— the resultant theoretical curve

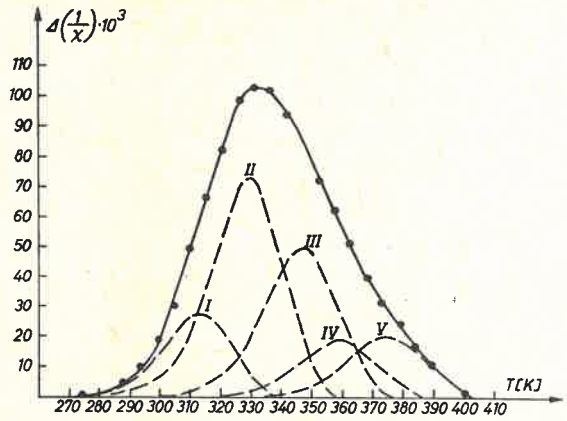

Fig. 4. Theoretical isochronal MPD curves calculated for sample H2; – – – curves of elementary processes, ——— the resultant theoretical curve

The measurements were repeated several times for sample W, after ageing at 400°C (until 24 h).

Table I contains activation energies obtained by means of computer analysis. In the case of sample W, the average values for Q were taken from eight isochrons corresponding to succesive ageing treatments; the error was estimated by taking into account the average absolute deviations $|\Delta T_{pi}|$ from the average values of T_{pi} and the $|\Delta\theta_{0i}|$ determined in [11].

TABLE I

Activation energies and peak temperatures of elementary processes obtained by means of isochronal curves

Process	Treatment 1		Treatment 2		Treatment 3	
	Q [cal/mole]	T_p[K]	Q [cal/mole]	T_p[K]	Q [cal/mole]	T_p[K]
I	23150±630	306.2	23000	304.2	23700	313.5
II	24430±540	323.1	24400	322.7	24900	329.3
III	25640±790	339.1	25600	338.6	26200	346.5
IV	27340±770	361.6	27200	359.7	27200	359.7
V					28400	375.6

Fig. 5 depicts the theoretical isothermal $1/(\chi t)$ curve, obtained for sample W at 45.6°C. The curve fits the experimental points wery well. Fig. 6 presents the $\left(\ln\theta_i, \frac{1}{T}\right)$ points given by the computer. It can be seen that the points group evidently well in four straight lines. From the equations describing the lines the Arrhenius law parameters were calculated (Table II).

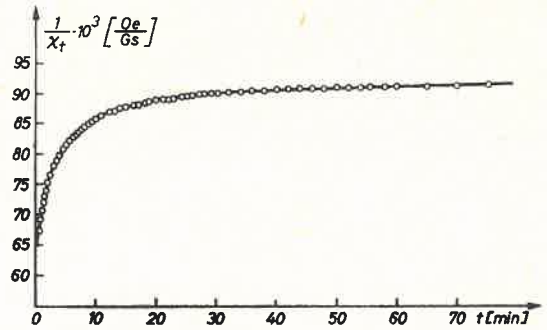

Fig. 5. The theoretical isothermal MPD curve obtained for sample W at 45.6°C

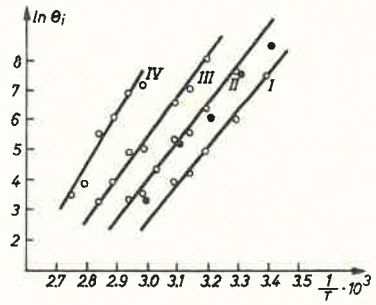

Fig. 6. ln θ_i vs $1/T$ obtained from decomposition of isothermal curves; ○ — points obtained in this paper, ● — points obtained in [4] for the relaxation of greatest intensity

TABLE II

Arrhenius law parameters of elementary processes obtained by means of isothermal curves for sample W

Process	Q [cal/mole]	$\theta_0 \times 10^{15}$ [s]
I	24000 ± 1400	$1.9\ ^{+15}_{-1.7}$
II	25000 ± 1400	$2.2\ ^{+17.2}_{-2.1}$
III	26000 ± 1300	$2.6\ ^{+16.3}_{-2.2}$
IV	29000 ± 2500	$0.2\ ^{+5.5}_{-0.15}$

5. *Discussion*

The results of the analysis of MPD curves, in which a linear spectrum of time constants was assumed, gave the same values for parameters of carbon migration in αFe–Al (24.3%) for three kinds of samples, heat treated differently, and for two types of experimental curves. And so the activation energies of elementary processes, obtained for samples

W, H1, H2 by means of isochronal MPD curve measurements, are equal within the limits of error (Table I).

In Table III the isochronal and isothermal results are compared. As one can see there is a good agreement between the values yielded by both methods:

1. They give the same number of relaxations (in the case of isotherms a bad fit was obtained for three relaxations).

TABLE III

Arrhenius law parameters of the relaxations originated from carbon in αFe–Al (13.4 or 8 wt. %)

This work				Ref. [2]	
α FeAl (13.4 wt. %)–C (0.005 wt. %)				αFe–Al (8 wt. %)–C (0.008 wt. %)	
Relaxation	*MPD* isochrons	*MPD* isotherms		Relaxation	Internal friction
	Q [cal/mole] $\left(\theta_0 = \left(3.2^{+1.7}_{-1.1}\right) \times 10^{-15}\text{[s]}\right)$	Q [cal/mole]	$\theta_0 \times 10^{15}$ [s]		Q [cal/mole] ($\theta_0 = 1.14 \times \times 10^{-15}$ [s])
1	2	3	4	5	6
I	23150 ± 630	24000 ± 1400	$1.9^{+15}_{-1.7}$	5	23200
II	24430 ± 540	25000 ± 1400	$2.2^{+17.2}_{-2.1}$	6	24600
III	25640 ± 790	26000 ± 1300	$2.6^{+16}_{-5.5}$	7	25800
IV	27340 ± 770	29000 ± 2500	$0.2^{+5.5}_{-0.15}$	8	27500
V	28400			9	29700

2. The activation energies are equal within the limits of error.

3. As can be seen from columm 4, within the error limits the θ_0-s of all relaxations are equal.

The last remark means that the Wert-Marx law is valid and can be used in the analysis of MPD curves.

The results of this work are in good agreement with the results of papers [3, 4]. In Fig. 6 points are also shown, obtained in [4] for the process of the highest intensity (black points). They were obtained by the method of successive subtractions of elementary processes, described in [13]. The Arrhenius law parameters amounted to $Q = (24500 \pm 1000)$ cal/mole, $\theta_0 = 3.2 \cdot 10^{-(15 \pm 1)}$ s and are equal to the values obtained in this work for relaxation II, though the sample was highly contaminated and the intensity of MPD was small.

Tanaka compared his results with a curve of one elementary process [3]. There was no fit between the curve and the experimental points (Fig. 7 in [3]). In spite of that fact

the peak of this relaxation corresponds with maximum II of this investigation: assuming the data of [3] the MPD isochron maximum should amount to 50°C (323 K), whereas $T_{pII} = 49.9$°C (322.9 K).

Table III also contains the results of Jäniche et al. [2], obtained by means of IF measurements for a sample with 8% Al (relaxations 5–9). The sample was quenched from

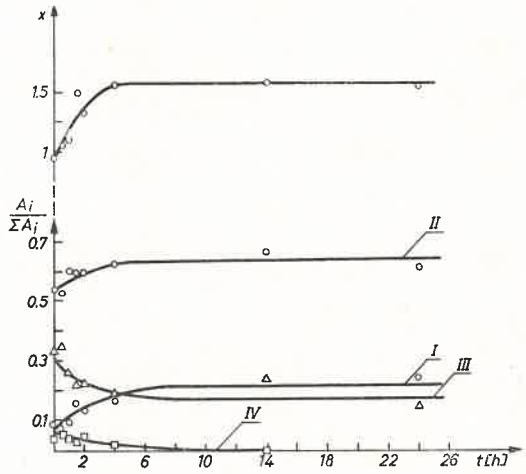

Fig. 7. The dependence of long range order parameter x and of the relative heights of the peaks $A_i/\Sigma A_i$ on ageing time at 400°C

$T = 693$°C and 727°C and $\theta_0 = 1.14 \cdot 10^{-15}$ s was assumed. Though the aluminium content was much smaller, the IF — measurements gave very similar results.

Some additional investigations have also been taken up [14] with the purpose finding correlations between the heights of peaks A_i of particular relaxations and the long range order parameters x and y of the DO_3 and B2 superstructure [15]. Fig. 7 depicts the dependence of relative heights $A_i/\sum A_i$ on ageing time at 400°C. If one assumes that the Néel interaction energies w_i are approximately equal [16], the relative heights $A_i/\sum A_i$ give the contribution of particular relaxators in the MPD effect.

It is seen that the relaxation of greatest intensity (II) and relaxation I grow with time and after certain period become constant, whereas III and IV diminish; after 14 hours III is just constant, and IV vanishes completely. The long range order parameter x of the DO_3 superstructure changes in the same way as I and II: grows and becomes constant with time (Fig. 7).

The results discussed above seem to show that the relaxation observed in this work originate from directional ordering of carbon atoms in different regions of atomic structure. Further details concerning this problem will be discussed in the next paper [14].

In this paper a second MPD band at higher temperatures was observed, too. The band occurs in quenched samples only. Preliminary results show that its intensity grows distinctly with the quenching temperature.

6. Conclusions

1. By means of isochronal and isothermal MPD curves it was shown that in αFe–Al (13.4%)–C a disaccommodation band occurs in the range from −10°C to +130°C (263–403 K).

2. In samples slowly cooled or quenched from temperatures lower than the DO_3 superstructure phase transition temperature (T_k), the band could be decomposed into four (I–IV) or three (I–III) elementary relaxations.

3. In samples quenched from $T > T_k$ the band could be decomposed into five (I–V) processes; all processes could be described by single time constants.

4. Ageing at 400°C shows that relaxations I and II behaves like the long range order parameter x of the DO_3 superstructure — grow and become constant with time, whereas III and IV diminish.

The results of this work show univocally that the IF and MPD band in αFe–Al (about 25 at. %)–C is related to 3–5 relaxation processes, described by single time con stants.

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