

MIGRATION OF CARBON IN Fe-Al (ABOUT 25% at.) ALLOY. PART II*

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A sample of an iron 25% at. aluminium alloy containing carbon was furnace cooled after annealing at 1230 K for 20 h, and aged at 673 K. For each ageing time the magnetic permeability disaccommodation was measured. The curves obtained were decomposed into 3 or 4 elementary relaxations (I-IV). Besides disaccommodation, the long-range order parameters x and y were measured by means of X rays. The results of this investigation and of a previous paper published in *Acta Phys. Pol.* A51, 407 (1977) were related to particular relaxations depending on the migration of carbon atoms in different regions of atomic structure: the regions with less Al than the DO_3 phase (I), regions of DO_3 phase (II) and of $B2$ phase (III), regions containing more Al than 50% at. (IV, V).

1. Introduction

In paper [1] it was demonstrated that in alpha iron, containing about 25% at. aluminium, the magnetic after-effect, originating from carbon atoms migration in solid solution, is composed of 3 to 5 elementary relaxations, each described by a single time constant. Relaxations I to IV were found in samples slowly cooled after annealing at 1230 K, whereas relaxations I to V were found in samples quenched from temperatures higher than the order-disorder transition temperature of superstructure DO_3 ($T_k \cong 823$ K). The alloy, investigated in [1], was made from very pure electrolytic iron and the solid substitutional solution was highly homogeneous. The Arrhenius-law parameters of the relaxations were determined by means of isochronal and isothermal magnetic permeability disaccommodation curves; both methods gave the same results.

The results of paper [1] are in principle consistent with those of Tanaka obtained by means of internal friction measurements [2]. In [2], however, the damping curves were not analysed with elementary relaxation processes in mind.

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The purpose of the present work was to find the dependences of the migrational relaxations of carbon in Fe-Al (~25% at.), obtained in [1], on atomic structure of the substitutional solution.

2. Method

The investigation was performed on the same alloy as before. A series of isochronal curves was measured on a sample furnace cooled after annealing at 1230 K for 20 h and ageing at 673 K. The measuring procedure was described in [1].

The phase diagram of Fe-Al alloys shows (Fig. 1, [3]) that in the samples investigated the following ferromagnetic phases can be present; 1. disordered substitutional

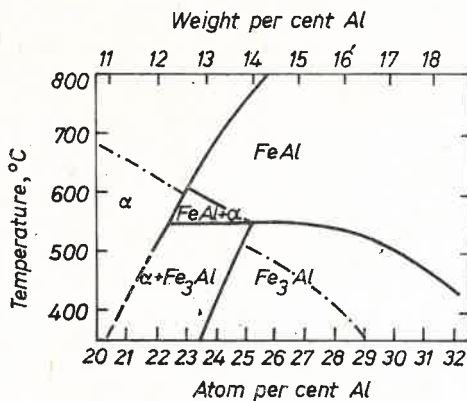


Fig. 1. Phase diagram of Fe-Al alloys; according to [4]. The diagram contains all essential features, found in many diagrams published lately for these alloys; - - - - - ferromagnetic phase transition line

alloy, 2. ordered phase Fe₃Al of the DO₃ structure, 3. ordered phase FeAl of the B2 structure. Therefore, besides the disaccommodation measurements, the long range order parameters x and y of the DO₃ and B2 structures were determined by X-rays diffraction.

For the Fe_{3-ε}Al_{1+ε} alloy the following diffraction reflections can be found [4]:

1. Reflections for odd h, k, l originating from regions of the DO₃ superstructure; the structure factor is given by the formula

$$F_{hkl} = \pm 2i(f_{\text{Fe}} - f_{\text{Al}})x, \quad (1)$$

in which $f_{\text{Fe}}, f_{\text{Al}}$ are atomic scattering factors of Fe and Al, respectively.

2. Reflections for even h, k, l and odd $(h+k+l)/2$ originating from the B2 regions; for the structure factor one gets:

$$F_{hkl} = 4(f_{\text{Fe}} - f_{\text{Al}})y. \quad (2)$$

3. The reflections for even h, k, l and $(h+k+l)/2$ are identical with the fundamental ones; the structure factor is given by

$$F_{hkl} = 4\{(3-\varepsilon)f_{\text{Fe}} - (1+\varepsilon)f_{\text{Al}}\}. \quad (3)$$

The following reflections were used: for DO_3 — 111, $B2$ — 200, as fundamental — 220.

The values of the long range order parameters x and y were calculated from integrated intensities of superstructure and of fundamental reflections; thus, for the DO_3 regions the following formula was used

$$\frac{I_{111}}{I_{220}} = \frac{P_{111}L_{111}}{P_{220}L_{220}} \frac{|F_{111}|^2}{|F_{220}|^2}, \quad (4)$$

where P_{111} , P_{220} are the multiplicities of the reflecting planes and L_{111} , L_{220} are the Lorentz-polarization factors of the DO_3 and fundamental reflections, respectively.

The X-ray measurements were performed by means of the Philips diffractometer. The sample rotated at 60 rpm. To obtain sharp superstructure lines the shift of the counter was slow (as a function of 2θ — $0.125^\circ/\text{min}$).

3. Results

Fig. 2 presents the peak height A of the experimental isochronal curves vs ageing time t at 673 K. After linear background subtraction, the computer analysis [1] gave the peak heights A_i of particular elementary relaxations; Fig. 3 shows the dependences of A_i

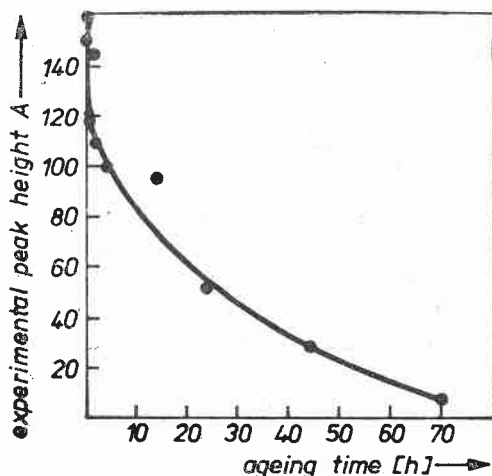


Fig. 2. The experimental peak height A vs ageing time (t) at 673 K

and of the sum $\sum A_i$ on time. All heights — A , A_i , $\sum A_i$ — diminish with ageing time; A_{IV} vanishes completely after 4 hours. The slopes of the $A_i(t)$ curves are different for particular relaxations.

Fig. 4 presents the parameters x and y vs ageing time at 673 K. At this temperature y seems to be constant, whereas x grows at first and then becomes constant.

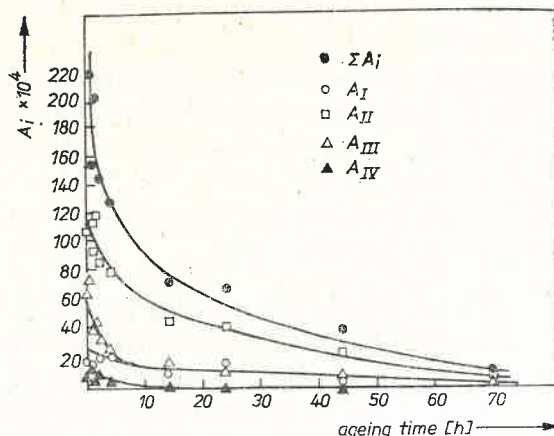


Fig. 3. The A_i and $\sum A_i$ dependences on ageing time at 673 K

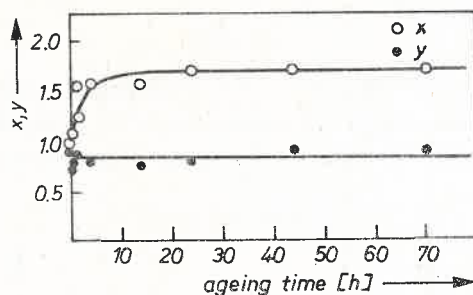


Fig. 4. The parameters of long-range order x and y vs ageing time at 673 K

4. Discussion

In [1] it was shown that the magnetic permeability disaccommodation band found in the Fe-Al (about 25% at.)-C alloys in the temperature range from 263 K to 403 K can be described by a superposition of 3 to 5 elementary migrational relaxation processes, preexponential factors θ_{oi} which are of the order of 10^{-15} s. The good agreement between the results of the disaccommodation curve analyses and atomic structure measurements, discussed below, supports these suggestions. The values of θ_{oi} show that the relaxators are directionally ordering point defects [5].

In investigations devoted to migrational after-effect in interstitial solid solutions of the Fe-Me-C type one looks usually for relations between the peak heights of particular relaxations; such relations can make it possible to obtain conclusion concerning structural configurations of relaxators (e. g. [6, 7]).

Fig. 5 presents the dependence of A_I , A_{III} and A_{IV} on the peak height of the relaxation of the greatest intensity (A_{II}). The range in which the parameter x is practically constant was also marked in the figure. In this range A_I and A_{III} are proportional to A_{II} ; for lower x values the curves have completely different shapes.

The theory of migrational magnetic after-effects, originating from directional ordering of point relaxators, gives — within the approximation of one Bloch wall — the following relation between the intensity of the i -th process and the concentration of the i -th relaxator (c_i) [8]:

$$\frac{1}{\chi_i} = \frac{rw_i^2 l}{kTdI_s^2} c_i. \quad (5)$$

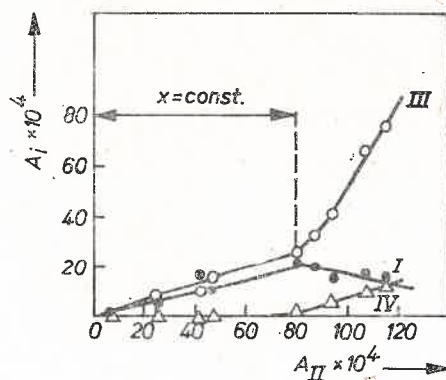


Fig. 5. Peak heights A_I , A_{III} and A_{IV} as a function of A_{II}

In this formula r , l , d are parameters corresponding to ferromagnetic domain structure (r is a numerical coefficient depending on the kind and position of a 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. For a certain domain structure, it follows from (5) and from the relation $A_i = \text{const} / \chi_i$ [1] that

$$A_i = \text{const}' c_i. \quad (6)$$

If, therefore, we accept the simplest assumption that relaxators II are single carbon atoms, it follows from Fig. 5 and formula (6) that relaxators I and III contain, or more simply are, single carbon atoms, too.

The shape of the curves presented in Fig. 3, and Tanaka's results showing that during decarburization the whole internal friction band lowers in a continuous manner [2], prove that relaxators IV and V also contain carbon atoms.

Because for $x \neq \text{const}$ the dependences of A_I , A_{III} , A_{IV} on A_{II} behave differently, we can assume that relaxators I–IV and perhaps also V are carbon atoms migrating in different atomic regions of the matrix.

The values of Néel's energy w reported in the literature for carbon and nitrogen in αFe do not differ much from each other [9–11]. It was also proved recently that the quotient w_C^2/w_{C-C}^2 determined for single and pairs of carbon atoms amounted to 1.34 [12]. Therefore, in subsequent discussions the interaction energies w_i of particular relaxators were assumed to be approximately equal and, hence, $A_i/\sum A_i$ are simply atomic fractions of carbon atoms contributing to particular relaxations.

Fig. 6 shows $A_i/\sum A_i$ and x vs ageing time t . Relaxations I, II, III behave as the long range order parameter x : at first, during 4 to 6 hours, I and II grow and III diminishes, and then, for longer times, all these relaxations become constant. With reference to process IV, its relative height also diminishes with ageing time, but after a time longer than 4 hours $A_{IV}/\sum A_i$ certainly equals zero.

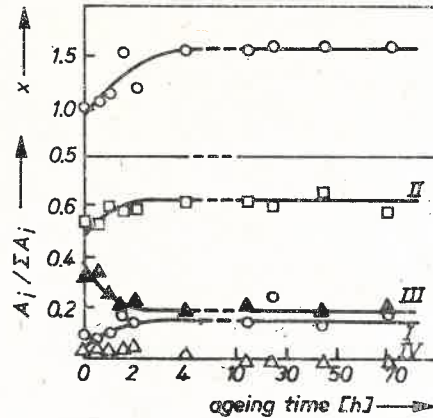


Fig. 6. The relative heights $A_i/\sum A_i$ and parameter x vs ageing time at 673 K

5. Model

The simplest hypothesis, consistent with the results of the above discussion, is formulated as follows: relaxations I, II and III originate from directional ordering of single carbon atoms in three kinds of different atomic regions — in DO_3 and $B2$ domains, as well as in regions of poorer Al content than in the Fe_3Al phase.

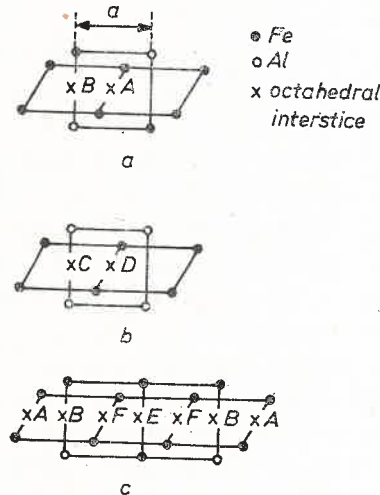


Fig. 7. Octahedral interstices in Fe-Al (about 25% at.)-C; a. region of the DO_3 structure, b. region of the $B2$ structure, c. region of poorer Al contents than Fe_3Al (perhaps the $Fe_{13}Al_3$ structure)

Fig. 7a shows two neighbouring octahedral interstices in DO_3 domains. Site A is surrounded by 2Fe atoms at a distance of $a/2$ and 2Fe and 2Al atoms at $a\sqrt{2}/2$. Site B , however, is surrounded by 1Fe and 1Al atom at $a/2$ and 4Fe atoms at $a\sqrt{2}/2$.

According to Tanaka [2] $A \leftrightarrow B$ jumps correspond to a single relaxation process, with time constants obeying the formula:

$$\theta = \frac{1}{3\nu_0} \left\{ \exp\left(\frac{F_A}{kT}\right) + \exp\left(\frac{F_B}{kT}\right) \right\}, \quad (7)$$

where ν_0 is the frequency of carbon atom vibrations, and F_A, F_B are the free energy barriers separating sites A and B . For $(F_A - F_B) \gg RT$ and $(F_A - F_B) \ll RT$ formula (7) reduces to the Arrhenius law

$$\theta = \theta_0 \exp\left(\frac{F}{RT}\right), \quad (8)$$

where $F = F_A$ or F_B for the first and the second condition, respectively.

The results obtained in [1] show that the Arrhenius law is valid for the elementary relaxations in Fe-Al (about 25% at.)-C occurring in the temperature range from 263 K to 403 K. Hence, it can be assumed that one of the above-mentioned conditions is approximately fulfilled.

In domains B2 there is a different pair of octahedral sites at a distance of $a/2$ -C and D (Fig. 7b). Carbon atoms jumping between these sites produce a second relaxation (jump $C \leftrightarrow D$). A third process may be expected from carbon atoms migrating in regions of lower aluminium content than in Fe_3Al . Such regions of the matrix could have a superstructure of the $Fe_{13}Al_3$ type, the existence of which was postulated by some authors [13]. Interstices in that structure are shown in Fig. 7c; they enable jumps $B \leftrightarrow F$ and $E \leftrightarrow F$ to occur.

Recently, it was shown [14] that in Fe-Al-C alloys aluminium and carbon atoms interact. For Al-C pairs the interaction energy $E_{Al-C} = -0.07$ eV was obtained. For such value of E_{Al-C} the carbon atoms ought to occupy sites A, B and F with a much higher probability than sites E , so that jumps $E \leftrightarrow F$ can be neglected.

The result discussed in Section 4 and the above considerations show clearly that relaxation II originates from directional ordering of single carbon atoms in DO_3 domains. It increases monotonically with the parameter x (Fig. 6), the growth of which is indicative of the volume increase of the DO_3 phase. Process II has also the greatest intensity. Relaxations III and I, however, correspond to carbon atoms ordering in B2 and in regions of lower Al content, respectively. The suggested sequence is corroborated by the fact that the disaccommodation and the internal friction band in Fe-Al (0.003-8% wt.)-C alloys shifts to higher temperatures as the Al content increases [6, 15]. The same could be assumed for $Fe_{13}Al_3, Fe_3Al, FeAl$; relaxations associated with these regions have to occur at even higher temperatures. The last remark suggests also that processes IV and probably V originate from carbon atom migrations in regions containing more than 50% at. Al.

Before we continue our considerations devoted to the model of the investigated relaxations two further facts, discussed in [1], should be mentioned. 1. A good agreement

was found between Arrhenius law parameters obtained for two kinds of alloys: (a) atomically long-range ordered alloy Fe-Al (13.4% wt.)-C (disaccommodation data in Ref. [1]), (b) atomically disordered alloys Fe-Al (0.049-8% wt.)-C (internal friction data in Ref. [15]) and Fe-Al (0.9% wt.)-C (disaccommodation data in Ref. [6]) (Table I). According to the phase diagram (Fig. 1), in the latter case only the disordered alpha phase should occur. 2. For samples cooled quickly from temperatures higher than T_c , relaxation II, and also I were observed, although the parameter x was zero.

TABLE I
Activation energies of carbon migrational relaxations in Fe-Al-C alloys

Ordered alloy		Disordered alloys		
Relaxation	13.4% wt. Al [1]	Relaxation	0.9% wt. Al [6]	0.049-8% wt. Al [15]
	Q [eV]		Q [eV]	Q [eV]
I	1.00 ± 0.03	5	0.99 ± 0.03	1.00
II	1.06 ± 0.02	6	1.10 ± 0.03	1.07
III	1.11 ± 0.03	7	—	1.12
IV	1.19 ± 0.03	8	—	1.19
V	1.23	9	—	1.29

In order to explain all the facts found in [1] and in this paper, the relaxation model should be completed as follows. Because relaxations I to V were also found in samples containing only 0.049-8% wt. Al (Table I), in which no long-range order was observed, we can assume that they occur always when several Fe and Al atoms form short-range ordered clusters of the $Fe_{13}Al_3$, DO_3 , $B2$ etc. types, containing $A-F$ interstices. Hence, processes I and II were also discovered in samples quenched from high temperatures, for which x was equal zero.

During ageing at 673 K of the slowly cooled sample the DO_3 domains and the regions depleted in Al grow in a continuous manner, because they are equilibrium phases. The volume of the $B2$ phase, however, diminishes, mostly at the cost of the small clusters not revealed by X rays. Hence, ageing at 673 K causes the parameters x and also the atomic fractions $A_{II}/\sum A_i$ to grow and the fraction $A_{III}/\sum A_i$ to diminish, whereas the parameter y is practically constant.

During ageing of a slowly cooled sample, regions of more than 50% at. Al vanish completely. Hence, in such samples relaxation V could not be found at all [1] and relaxation IV was only small and decreased to zero within four hours (Fig. 6).

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