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MAGNETIC MIGRATIONAL RELAXATIONS IN αFe—Ti—N IN THE TEMPERATURE RANGE FROM —60°C TO +200°C*

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The magnetic permeability disaccommodation (MPD) in α Fe–Ti (0.22–0.60 wt pct) alloys saturated with nitrogen was investigated. A broad MPD of high intensity was observed above room temperature. Computer analysis decomposed the isochronal curves into five elementary relaxations, described by single time constants.

1. *Introduction*

Until now, abnormal relaxations above the temperature range of the Snoek process observed in iron samples with small amounts of titanium, originating from jumps of carbon [1] or nitrogen [2] in solid solutions, were reported in only two papers. Recently magnetic permeability disaccommodation (MPD) measurements displayed, however, that in α Fe–Ti (0.22 wt pct) containing very small additions of C and N, as a result of heat treatment at high temperatures, there is no maximum in the isochronal curves, neither in the Snoek region, nor above room temperature [3]. This means that there is no carbon and nitrogen in solid solution form.

Similar results were obtained before by internal friction (IF) methods in samples containing 0.15 [4,5], 0.04 [6] or 0.33 wt pct Ti [7] and small amounts of interstitials (C, N, O, B in [4,5], C, N in [6, 7]). In [8] only the nitrogen Snoek peak appeared in samples saturated with N at 950°C; in the region of this relaxation disaccommodation was also discovered in an α Fe–Ti (0.16 wt pct)–N alloy [9].

Szabó-Miszenti measured internal friction curves in Fe–Ti–N alloys with 0.04–0.6 wt pct Ti [2]. Besides the Snoek maximum, occuring in samples with small amounts of Ti, two IF-peaks were observed at 1 Hz frequency; the first appeared at 111°–166°C, the

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second, however, at 221° - 242°C. The peak temperatures changed with nitrogen and titanium concentrations.

In [1] MPD curves were measured in carbonized α Fe–Ti (0.10 and 0.22 wt pct). The isochronal measurements displayed one relaxation peak in the region of the carbon Snoek process, for which the activation energy amounted to $Q = 0.85$ eV and the peak temperature to $T_p = -16$°C. A broad MPD band was also found above room temperature, which could be decomposed into three elementary processes; their peaks occured at 41.4°C, 70.2°C and 97.8°C (for $t_1 = 23$ sec and $t_2 = 293$ sec).

2. *Experimental procedure and results*

The measurements were performed on a Maxwell-Wien bridge, described in detail elsewhere [10]. The magnetizing field frequency and intensity amounted to 1030 Hz and 2 mOe. The samples were demagnetized by a 50 Hz field, in which the amplitude dropped from 7 Oe to zero during 7 seconds.

Isochronal MPD curves — $\Delta\left(\frac{1}{\chi}\right) = \frac{1}{\chi_2} - \frac{1}{\chi_1} = f(T)$ — were measured, $\frac{1}{\chi_1}$ and $\frac{1}{\chi_2}$ are the reciprocal magnetic susceptibilities at times t_1 and t_2 after demagnetization. The experimental procedure was described in other papers [1, 3].

The Fe-Ti alloys were prepared in the Institute of Iron Metallurgy, Gliwice. The iron used contained only 0.01 wt pct substitutional impurities. In Table I the results of chemical analysis are shown.

TABLE I

Chemical composition of the investigated Fe–Ti samples

Sample	Ti [wt pct]	N [wt pct]	C [wt pct]
A	0.22	0.002	0.006
B	0.46	0.002	0.004
C	0.60	0.006	0.004

The samples, rolled in the shape of toroids from strips 0.1 mm thick, were submitted to different heat treatments: stress-relieving heating, nitriding treatment, ageing. Table II describes the particular heatings.

All samples were submitted to treatment 1. For alloys containing 0.22 and 0.46 wt pct Ti treatment 2 (A_1, B_1) or 3 (A_2, B_2) were applied. Alloys with 0.60 wt pct were subjected to heatings 2, 5, 6, 7 (C_1) or 3, 4, 5, 6, 7 (C_2). After charging with nitrogen sample C_1 contained 0.11 and sample C_2 0.45 wt pct nitrogen.

Fig. 1 presents $\Delta(1/\chi)/[\Delta(1/\chi)]_{max} = f(T)$ curves, normalized to the maximum value of experimental isochrons, measured immediately after saturation with N (treatment 2 or 3);

TABLE II

Heat treatments applied to samples Fe-Ti

Number	Heat treatment
1	950°C — 10h — vacuum furnace 820°C — 45 min. vacuum furnace slowly cooling in the furnace to room temperature
2	400°C — 10 min. nitriding 400°C — 2h vacuum furnace slowly cooling in the furnace to room temperature
3	400°C — 30 min. nitriding 400°C — 2h vacuum furnace slowly cooling in the furnace to room temperature
4	196°C — 4h ageing in furnace slowly cooling in the furnace to room temperature
5	300°C — 2h vacuum furnace, slowly cooling in the furnace to room temperature
6	500°C — 2h vacuum furnace slowly cooling in the furnace to room temperature
7	850°C — 1h vacuum furnace slowly cooling in the furnace to room temperature

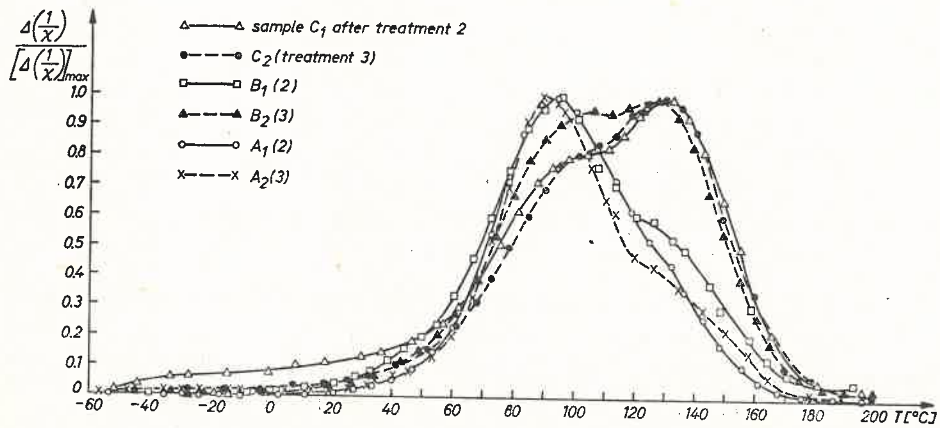

Fig. 1. The $\Delta(1/\chi)/[\Delta(1/\chi)]_{max} = f(T)$ curves for samples A, B, C measured immediately after nitriding

the disaccommodation background was not greater than 4 pct of the maximum. Fig. 2 shows isochronal MPD curves obtained for sample C_1 after heatings *1, 2, 5, 6, 7*.

The high temperature parts of the disaccommodation were decomposed into elementary processes under the following assumptions:

1. The experimental curves are superpositions of elementary processes, which can be described by single time constants.

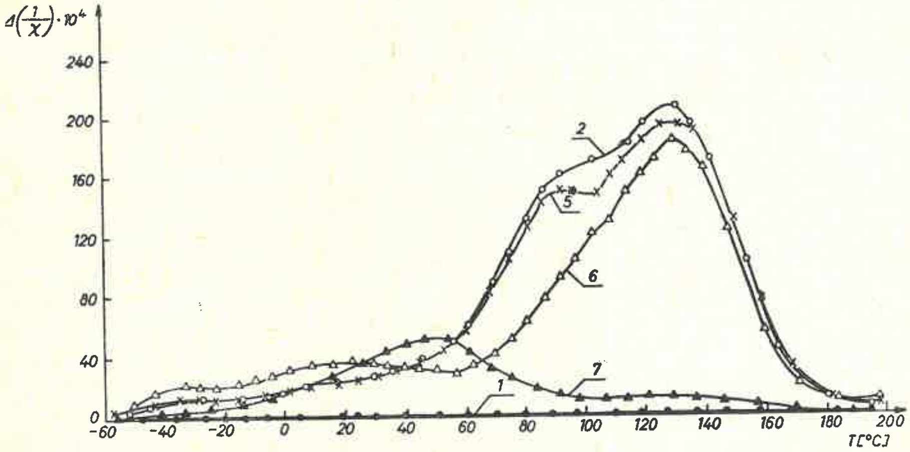

Fig. 2. The $\Delta(1/\chi) = f(T)$ curves obtained for sample C_1; curves *1, 2, 5, 6, 7* correspond with treatments 1, 2, 5, 6, 7 respectielyv

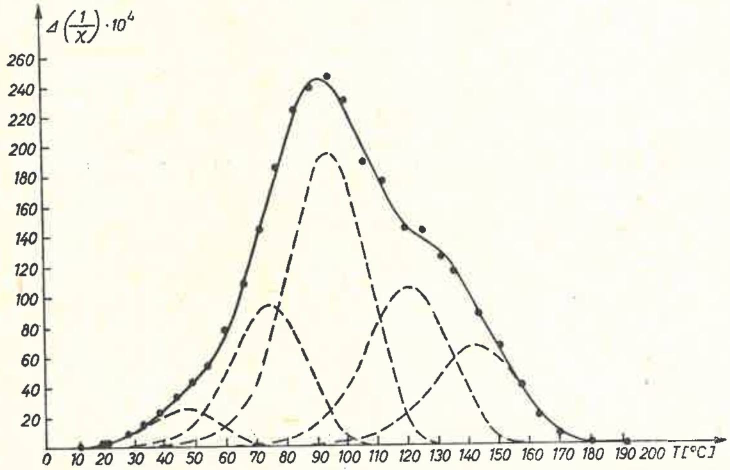

Fig. 3. Results of analysis of the high temperature part of the MPD curve obtained for sample B_1 after treatment 2; – – – theoretical curves of the elementary processes, ——— the sum of these curves

2. The elementary processes obey the Wert-Marx law with $\theta_0 = 4.5 \times 10^{-15}$ s; this value was obtained for the nitrogen Snoek relaxation [11].

Fig. 3 presents e. g. the results of analysis obtained for αFe-Ti (0.46%) after treatment 2; the background was subtracted linearly. The full line is the sum of single time constant theoretical curves.

For alloys A and B five relaxations were found (I–V), for C the computer calculations gave one process more, occuring at temperatures lower than I–V. The peak height of this relaxation, however, was very small and therefore, it was considered to be part of the background.

In Table III the peak temperatures and activation energies, obtained for all samples after saturation with nitrogen, are given.

TABLE III

The activation energies and peak temperatures of elementary processes obtained for particular samples

Sample	Titanium content [wt pct]	I		II		III		IV		V	
		T_p [°C]	Q [eV]	T_p [°C]	Q [eV]	T_p [°C]	Q [eV]	T_p [°C]	Q [eV]	T_p [°C]	Q [eV]
A_1	0.22	51.6	1.053	80.6	1.148	97.9	1.204	120.6	1.277	141.4	1.345
A_2	0.22	54.6	1.063	85.2	1.162	96.3	1.199	113.3	1.254	138.8	1.337
B_1	0.46	47.1	1.039	74.9	1.129	94.5	1.193	121.0	1.279	143.2	1.351
B_2	0.46	44.6	1.031	72.9	1.122	94.4	1.192	121.1	1.279	143.1	1.350
C_1	0.60	45.1	1.032	76.4	1.134	98.3	1.205	127.8	1.301	148.3	1.367
C_2	0.60	49.6	1.047	76.3	1.133	98.8	1.206	127.9	1.300	151.7	1.378
Average values		49±3	1.04 ±0.01	77±3	1.14 ±0.01	97±2	1.20 ±0.01	122±4	1.28 ±0.01	144±4	1.36 ±0.01

3. *Discussion*

In this paper, like in previous ones [1,3–7], it was shown that after high temperature heating, in αFe–Ti samples containing sufficient amounts of titanium there is no carbon and nitrogen in solid solution: curve *1* on Fig. 2 displays no maximum, neither in the Snoek region, nor above room temperature.

After nitrogen charge, in the case of five samples no Snoek disaccommodation was observed. A small peak appeared in the region of that process only in sample C_1 (Fig. 1). In samples C_1 and C_2 the Snoek peak occured once more, after ageing at 500°C (curve *6* in Fig. 2); heating at 850°C caused it to disappear (curve *7* in Fig. 2).

Saturation with nitrogen introduces a broad reproducible MPD band (Fig. 1), with peak heights ranging from 20 to 40 pct $\left(\text{relative permeability changes } \frac{\mu(t_1)-\mu(t_2)}{\mu(t_1)} \text{ from } t_1 = 23\,\text{s to } t_2 = 293\,\text{s}\right)$. In αFe–N(C), αFe–Al–C and αFe–Ti–C similar maxima occured, but they were not higher than 1.5% [3], 0.3% [12] and 4% [1], respectively.

The MPD band in αFe–Ti–N alloys seems to be composed of two nearby bands of smaller width and displays a tail occuring at lower temperatures (Fig. 1 and 3).

The decomposition of the high temperature part of the band gave five elementary processes (Table III). Among the results obtained for particular alloys there seems to be, however, some systematical differences concerning values of activation energies and peak temperatures; for instance, in the case of samples B and C the difference in T_p grows from 1.5°C for relaxation I to 6.8°C for relaxation IV and V.

The results of this work, obtained by means of magnetic permeability measurements, corroborate that there is a band of migrational relaxations in Fe–Ti–N alloys, occuring at temperatures higher than the temperature region of the Snoek process. The band was discovered by Szabó-Miszenti, who performed internal friction measurements. For $\theta_0 = 4.5 \times 10^{-15}$ sec his IF-band corresponds with disaccommodation in the range from +45° to +146°C, whereas isochronal MPD, obtained in this work occurs between +49°C and +143°C. Thus, it is seen that the agreement is rather good.

Results of MPD and IF measurements are compared in Table IV; the internal friction values of Szabó-Miszenti were recalculated to disaccommodation by means of the Arhenius law. For internal friction the temperature ranges given in the Table IV are related to changing peak temperatures. It seems that S_1 corresponds to relaxations I, II and III, S_2, however, with relaxations IV and V.

TABLE IV

Comparison of MPD and IF results

This work		G. Szabó–Miszenti [2]	
Relaxation	T_p [°C]	Relaxation	T_p [°C]
I II III	49 77 97	S_1	45 — 86
IV V	122 144	S_2	121 — 146

TABLE V

Peak heights of elementary processes for sample C_1 after treatment 2 and for sample C_2 after treatment 3

	Peaks number				
	I	II	III	IV	V
$A_i(C_1)$	21	69	119	160	69
$A_i(C_2)$	24	78	181	257	103
$\frac{A_i(C_2)}{A_i(C_1)}$	1.1	1.1	1.5	1.6	1.5

The above discussion shows that the great differences, observed by Szabó-Miszenti in peak temperatures, could have originated from changes in peak height ratios of component relaxations. The results of this work seem to indicate that the peak temperatures of elementary processes do not change by more than ±4°C.

The peak heights obtained for samples C_1 and C_2 after nitriding for 10 and 30 minuts — $A_i(C_1)$, $A_i(C_2)$ — are shown in Table V. The ratios of the heights are also given in this table. It is well seen that A_I and A_{II} do not depend too much on N content, whereas A_{III}, A_{IV} and A_V grow distinctly with time of nitrogen charge.

Fig. 4 nad 5 present the dependences of $\frac{A_i}{\sum A_i} \cdot 100\,\%$ on ageing temperature for sample C_1. Similar results were obtained for C_2. If one assumes that Néel's interaction energies w_i are approximately equal [13], the relative heights correspond to the relative numbers

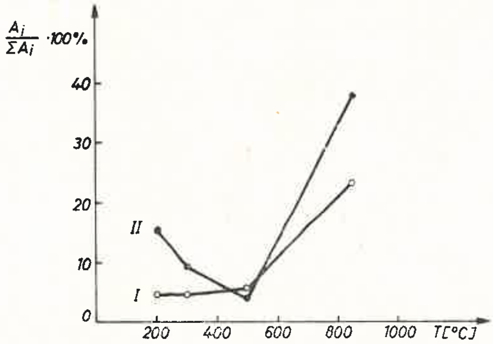

Fig. 4. The dependence of the relative heights $A_i/\Sigma A_i \cdot 100\,\%$ of relaxations *I* and *II* on ageing temperature; sample C_1

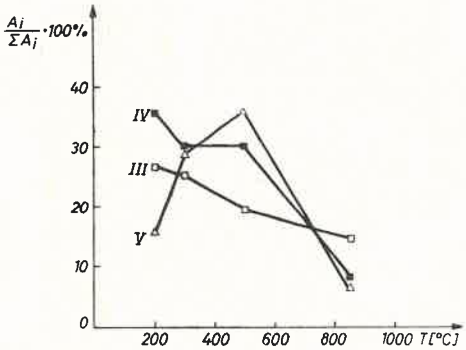

Fig. 5. The dependence of the relative heights $A_i/\Sigma A_i \cdot 100\,\%$ of relaxations *III*, *IV* and *V* on ageing temperature; sample C_1

of particular relaxators contributing to the MPD effect. It is well seen that ageing at 850°C causes A_{III}, A_{IV} and A_V to drop, whereas the contributions of A_I and A_{II} grow distinctly at this temperature.

Fig. 6–8 show the influence of titanium content on each process. Apart from peak V, other dependences, obtained after 10 and 30 min. of nitriding, are similar. The contribution of A_I in the sum is the smallest one and does not depend on Ti content.

It is known from literature that in Fe–Ti–N alloys nitrogen precipitates as titanium nitride during heating at 850°C [14]. The results presented in Table V and in Fig. 5 suggest,

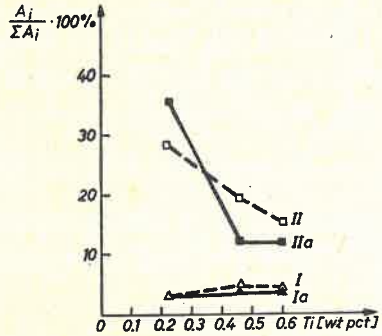

Fig. 6. Relative heights $A_i/\Sigma A_i \cdot 100\%$ of relaxations *I* and *II* vs titanium content; curves *I* and *II* — 10 min. nitriding, curves *Ia* and *IIa* — 30 min. nitriding

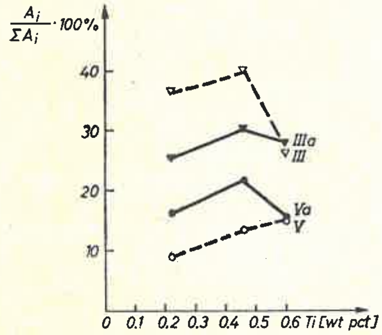

Fig. 7. Relative heights $A_i/\Sigma A_i \cdot 100\%$ of relaxations *III* and *V* vs titanium content; curves *III* and *V* — 10 min. nitriding, curves *IIIa* and *Va* 30 min. nitriding

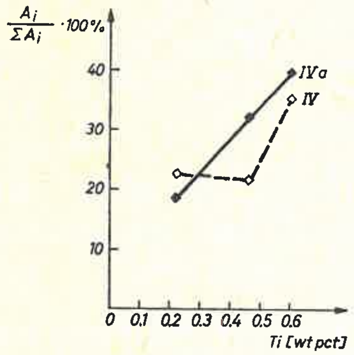

Fig. 8. Relative height $A_i/\Sigma A_i \cdot 100\%$ of relaxation *IV* vs titanium content; curve *IV* — 10 min. nitriding, curve *IVa* — 30 min. nitriding

therefore, that processes III, IV and V originate from relaxators containing N atoms in solid solution.

For the time being it is difficult to explain the behaviour of I and II during heating at high temperature. However, it is worth while to emphasize the following two points:

1. Castagna et al. observed that the height of the IF-peak occuring in the Snoek region grew during ageing at 720°C [6]. The authors suggested, therefore, that carbides and nitrides of titanium could have already decomposed at this temperature. However, it is well known, that TiN is stable until 1500°C [15], so the effect observed in [6] seems to indicate that a certain amount of TiC decomposes at 720°C. 2. The temperature range of MPD originated from I, and II corresponds with the range of disaccommodation of relaxations I and II, observed recently in αFe–Ti–C samples [16]. In samples saturated with nitrogen — T_{pI} = 49°C, T_{pII} = 77°C, in carbonized samples T_{pI} = 47°C, T_{pII} = 76°C.

Rather good agreement between the values of activation energies and peak temperatures, obtained for many samples assuming $\theta_0 = 4.5\times10^{-15}$ sec., seems to indicate that

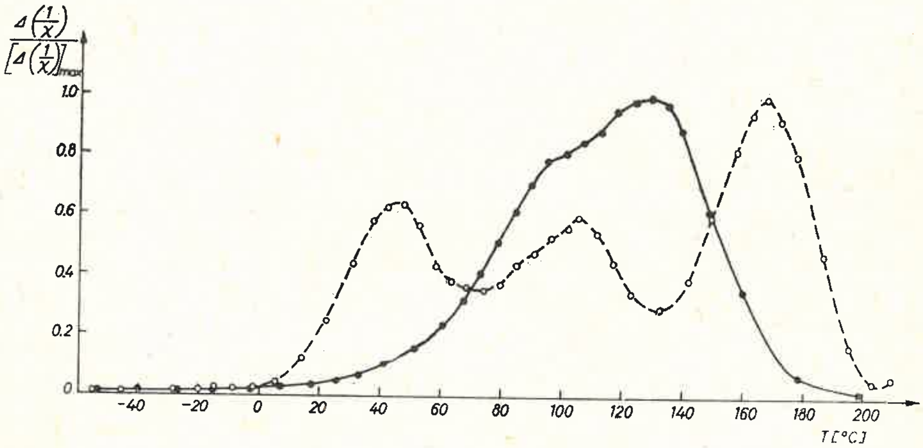

Fig. 9. Normalized $\Delta(1/\chi)/[\Delta(1/\chi)]_{max}$ vs temperature curves, obtained for αFe-Ti (0.60 wt pct); ——— sample saturated with nitrogen, – – – carbonized sample

the investigated MPD originates from directional ordering of point relaxators containing probably N or C atoms [17].

Last of all, the $\Delta(1/\chi)/[\Delta(1/\chi)]_{max} = f(T)$ curves, depicted for two alloys — αFe–Ti (0.60%)–N and αFe–Ti(0.60%)–C [16], are shown for comparison in Fig. 9.

4. Conclusions

1. In αFe–Ti (0.22–0.60 wt pct) samples saturated with nitrogen there is a magnetic permeability disaccommodation band of high intensity, above room temperature; the band corresponds with the internal friction band discovered by Szabó-Miszenti [2].

2. Computer analysis of the band, made by assuming a linear time constant spectrum and the Wert–Marx law, gives five elementary migrational relaxations.

3. For samples containing 0.60% Ti peak heights of relaxations I and II do not depend too much on the time of nitriding, whereas peak heights of III, IV and V grow distinctly with nitrogen content.

4. Peaks III–V drop during ageing at 850°C, whereas peaks I and II grow at the same time.

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REFERENCES

[1] W. Ciurzyńska, J. W. Moroń, B. Zielińska, *Acta Phys. Pol.* **A49**, 409 (1976).
[2] G. Szabó-Miszenti, *Acta Metall.* **18**, 477 (1970).
[3] B. Zielińska, W. Ciurzyńska, J. W. Moroń, *Acta Phys. Pol.* **A46**, 731 (1974).
[4] W. C. Leslie, R. J. Sober, *Trans. ASME Qtrly* **60**, 99 (1967).
[5] H. D. Solomon, J. Mc Mahon, W. C. Leslie, *Trans. ASME Qtrly* **62**, 886 (1969).
[6] M. Castagna, A. Ferro, F. S. Rossi, J. Sebille, G. Szabó-Miszenti, *Mém. Sci. Rev. Metall.* **63**, 555 (1966).
[7] G. A. Beresnev, V. I. Sarrak, R. I. Entin, *Dokl. Akad. Nauk SSSR* **167**, 322 (1961).
[8] J. D. Fast, *Mét. Corr. Ind.* **36**, 431 (1961).
[9] R. H. Graham, M. Wuttig, *Scr. Metall.* **3**, 9 (1969).
[10] J. Moroń, *Acta Phys. Pol.* **26**, 1117 (1964).
[11] L. Kozłowski, J. W. Moroń, J. Rasek, *Phys. Status Solidi* (a) **13**, 891 (1972).
[12] J. W. Moroń, H. Wencek, B. Zielińska, *Phys. Status Solidi* (a) **6**, K13 (1971).
[13] G. Haneczok, J. Ilczuk, R. Kuśka, J. W. Moroń, *Phys. Status Solidi* (a) **33**, 313 (1976).
[14] B. H. Kirkwood, O. E. Atasoy, S. R. Keown, *Met. Sci.* **8**, 49 (1974).
[15] L. I. Levi, *Azot v chugunie dla otlivok. Izd. Mashinostrojenije* Moskva 1964, p. 42.
[16] B. Zielińska, W. Ciurzyńska, J. W. Moroń, to be published.
[17] R. De Batist, *Internal Friction of Structural Defects in Crystalline Solids*, North-Holland Publishing Company, Amsterdam 1972, p. 74.