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THE KINETICS OF PRECIPITATION OF NITROGEN ATOMS FROM SUPERSATURATED αFe-N SOLID SOLUTIONS

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The kinetics of nitrogen precipitation from a supersaturated solid αFe–0.012%N solution was investigated using electrical resistivity measurements in liquid nitrogen. The samples were aged in a temperature range of 353–453 K. Using a computer program eight models which describe the phenomenon of precipitation from solid solution were fitted. Based on the distance between the set of experimental values obtained from isothermal curves and the set of values calculated from the models, and on the basis of model parameters dependence on temperature and ageing time, it was ascertained that the precipitation kinetics, in a wide time interval, is best described by the Damask, Danielson and Dienes models. The isothermal precipitation curves for longer ageing times are described by a first-order kinetic equation. A deviation in initial ageing times is related to the nucleation period. For the growth period the activation energy of precipitation, Q_W, is smaller than the activation energy of nitrogen bulk diffusion in a perfect αFe lattice Q_P: $Q_W = (0.46 \pm 0.03)$ eV, $Q_P = (0.769 \pm 0.004)$ eV.

1. *Introduction*

The kinetics of precipitation processes from supersaturated αFe-N(C) solid solutions is usually investigated using internal friction, electrical resistivity measurements at low temperature, initial magnetic permeability relaxation and by transmission electron microscopy.

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One of the simplest models used to describe these phenomena is based on the chemical reaction rate equation. The change of concentration, c, of a system in time, t, is described [1, 2] by the formula:

$$\frac{dc}{dt} = -c^{\gamma} K_0 \exp\left(-\frac{Q}{kT}\right), \tag{1}$$

where γ is the chemical reaction order, Q — the activation energy of the phenomenon, k — the Boltzmann constant and T — the absolute temperature, K_0 is the so-called pre-exponential factor.

Model (1) disregards the nucleation period. Nevertheless, the foregoing treatment is very demonstrative and useful in describing the growth period. For $\gamma = 1$ the solution of equation (1) is of the exponential function type

$$\frac{c}{c_0} = \exp(-Kt), \tag{2}$$

where c_0 is the initial concentration of the solid solution immediately after solution heat treatment.

For the description of the precipitation process the so-called Johnson–Mehl or Avrami [3] formula is also generally used:

$$\frac{c}{c_0} = \exp\left[-\left(\frac{t}{\tau}\right)^n\right] \tag{3}$$

in which the time constant τ, depends on the temperature and activation energy of the solute atoms diffusing in the matrix of the solvent (Q_p) according to the Arrhenius law. Formula (3) was derived from basic laws of diffusion by Ham [4], under the asumption that nuclei are already present in solid solution from the very beginning. The power index depends then on the shape of the precipitated particles.

The first kinetic theory of N and C precipitation from αFe, taking into account the nucleation period, was elaborated by Fujita in 1964 [5]. However, in Koiwa's opinion [6–8], solutions obtained by Fujita are not correct from a mathematical point of view because the author assumed additional equations, describing the growth of nuclei. The solution obtained by Koiwa [6], of equations given by Fujita, is in the form:

$$\frac{c}{c_0} = \frac{1}{\cosh^2\left(\sqrt{\tfrac{1}{2} KK't}\right)}, \tag{4}$$

where K and K' are constants of precipitates and condensation points growth rates, respectively. For long time periods equation (4) transforms to the solution of the first-order kinetic equation.

Further development of the precipitation theory, including nucleation and precipitation growth, was done by Damask et al. [9]. These authors describe the precipitation phenomenon as a succession of elementary chemical reactions of growth and decomposition.

If in the sample there are no nuclei formed immediately after heat treatment of the solution, the concentration of the solution depends on time according to:

$$\frac{c}{c_0} = \left[\frac{1}{\cos(\beta t)}\right]^{\frac{2}{p}}. \tag{5}$$

In (5) the value of β depends on the initial concentration of the solution, stable cluster size, p, and constants of growth and decomposition reaction rates.

If in a sample there are nuclei immediately after solution heat treatment, Damask et al. [9] give an equation in a complicated form which was simplified first by Parisot and Fouquet [10], and later by Mathé, Riviére and Grilhé [11] to the following form:

$$\frac{c}{c_0} = \left[\frac{\cosh\varphi}{\cosh\left(\frac{1}{2}\delta t+\varphi\right)}\right]^{\frac{2}{p}}. \tag{6}$$

Quantities φ, δ depend on the number of nuclei, the initial concentration of the solid solution and the rate constants for growth and decomposition.

Koiwa [6–8] considers some further models differing in the behaviour of the reaction rate constants. For the reaction rate constants of growth independent on the size of clusters ($K_i = K$) and the decomposition rate constants equal to zero ($K_i' = 0$), the following equation is obtained:

$$\frac{c}{c_0} = (1-q)\cdot\exp(-q), \tag{7}$$

where the variable q is related to ageing time.

For the growth rate constants proportional to the number of atoms in the cluster ($K_i = nK$) and the decomposition rate constants equal to zero ($K_i' = 0$), the change in the solution concentration with time is described by:

$$\frac{c}{c_0} = \frac{1}{2\cdot\exp(c_0Kt)-1}. \tag{8}$$

Koiwa [8] also investigated two additional models in which interstitial atom pairs are the nuclei, but their formation is impeded. In order to express this, the author introduced a coefficient α, variable within the range of $0 < \alpha < 1$. If $K_1 = \alpha K$ and $K_i = K$ for $i \geqslant 2$ and $K_i' = 0$, then the concentration of the solid solution, as a function of time, is described by:

$$\frac{c}{c_0} = (1-\alpha)\exp(-\alpha q')\cdot\cos\left[\sqrt{\alpha-\alpha^2}+\arctan\frac{\alpha}{\sqrt{\alpha-\alpha^2}}\right], \tag{9}$$

where parameter q' is also connected with time.

For $K_1 = \alpha K$, further growth rate constants proportional to the size of the clusters ($K_i = nK$) and $K_i' = 0$, the solution of rate equations is the following:

$$\frac{c}{c_0} = \{1-2\alpha \cdot \exp[(1-2\alpha)q''] \cdot (1-2\alpha)^{-1}\}, \tag{10}$$

where parameter q'' is another function of time [6–8].

Because of the narrowness of the place in this review only those theoretical models were discussed which were subsequently used in the analysis of experimental curves.

3. *Investigated samples*

The measurements of the precipitation process were made on samples derived from electrolytic iron, containing 0.012 wt % of nitrogen as the main precipitating element. From the analysis of isothermal curves of the initial magnetic permeability dependence on time, determined in the Snoek relaxation region, it followed that the content of carbon in solid solution was a hundred times less than the nitrogen content [12, 13]. The electrolytic iron was produced at the Institute of Iron Metallurgy, Gliwice and contained, besides interstitial atoms, about 0.01 wt % substitutional atoms. The samples for electrical resistivity measurements were in the form of strips with dimensions of 0.2 × 5 × 140 mm.

Before measurements, the samples were annealed in a vacuum furnace at 1123 K for 5 hrs and then slowly cooled with the furnace to room temperature. The solutions of αFe-N were made by fast cooling of the sample in liquid nitrogen after previous annealing at 873 K or 623 K for 1 h in a vertical furnace with the atmosphere of pure argon.

4. *Experimental*

In order to determine isothermal precipitation curves the samples after solutioning were aged at a temperature range of 353 to 453 K. The ageing of samples was carried out in an ultrathermostat filled with water or silicon oil. The temperature was kept constant within an accuracy of ±0.1 K. The phenomenon of nitrogen precipitation from a supersaturated solid solution was studied by means of electrical resistivity measurements made at the temperature of liquid nitrogen. This method enables one to determine the changes of solid solution concentrations based on measurements of electrical resistivity changes. This method is convenient because measurements are made at a sufficiently low temperature at which precipitation processes practically do not occur. According to the Matthiessen rule, the total resistivity, ϱ_c, is a sum of the thermal resistivity, ϱ_T, and additional resistivity originating from the scattering of conduction electrons on nitrogen atoms existing in the solid solution of concentration, c, and in precipitates of concentration, c_w:

$$\varrho_c = \varrho_T + ac + bc_w, \tag{11}$$

where a and b are the proportionality coefficient. It is evident from the dependence (11) that the relative variations of the nitrogen atoms concentration in the solid solution in relation to the initial concentration, c_0, are given by the formula:

$$\frac{c}{c_0} = \frac{\varrho_t - \varrho_\infty}{\varrho_0 - \varrho_\infty}, \tag{12}$$

where ϱ_0, ϱ_t and ϱ_∞ are the resistivities measured immediately after solutioning at any moment, t, and after a very long time of ageing, when the value of resistivity is already steady, respectively.

In order to determine the resistivity value, the sample was transfered very quickly for the time of measurement to a cryostat. The total resistance was calculated from the voltage drop between the voltage electrodes on the sample connected to a compensating circuit in a two-point probe system. The drop of voltage was measured by a Diesselhorst compensator, made by Tettex. A more detailed description of the system was given earlier [14].

As the result of the experiment a set of values of points $(c/c_0, t)$ was obtained for a given ageing temperature, T. From a theoretical model with parameters $b_1, b_2, b_3 \ldots$ one derives a set of values

$$y_i = f(t_i, b_1, b_2, b_3 \ldots), \quad i = 1 \ldots n, \tag{13}$$

where n is equal to the number of experimental points and the number of fitting parameters, b_k, is considerably less than the number of measurement points. A fit of the given model to the experimental results was obtained by a choice of parameters b_k so that the difference, χ^2, between the experimental and the model values:

$$\chi^2 = \frac{1}{n} \sum_{i=1}^{n} \left[\frac{c}{c_0} - f(t_i, b_1, b_2, b_3 \ldots)\right] \tag{14}$$

was the least. The Euclidean distance, χ, is simultaneously the error estimator. For finding the optimum values of b_k, the program MARQ for minimizing multi-variable function was elaborated based on the algorithm given by Marquardt [15]. This algorithm is characterized by high precision with a relatively short time of calculation as well as by the elimination of the divergence danger and slow convergence of iterations. The calculations were carried out on an ODRA 1204 computer.

5. *Results of measurements and calculations*

With the aim of investigating precipitation phenomena, the isochronal and isothermal curves are usually determined. The isothermal curves are the best for the verification of which models give the most complete description of the phenomenon. However, the analysis of the isochronal curves, realized with some particular heating rate and with the application of a specified type of heating, requires the knowledge of the model which may not be acquired before the isothermal curves are investiged.

In this paper the effect of the solutioning temperature on the kinetics of nitrogen atoms precipitation from the supersaturated αFe-N solid solution at constant temperature

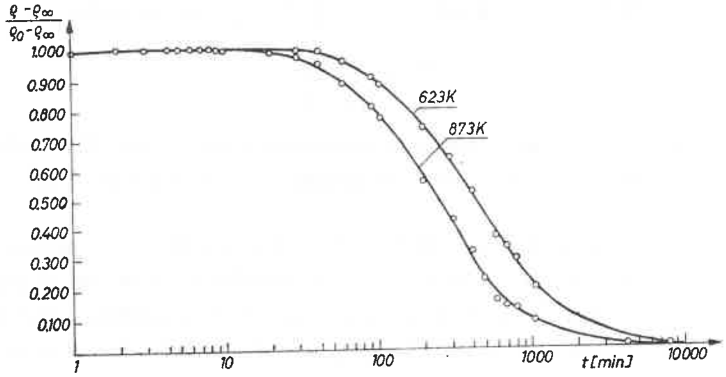

Fig. 1. Normalized ageing curves at 369 K after solutioning from 623 and 873 K for αFe-0.012 % N samples

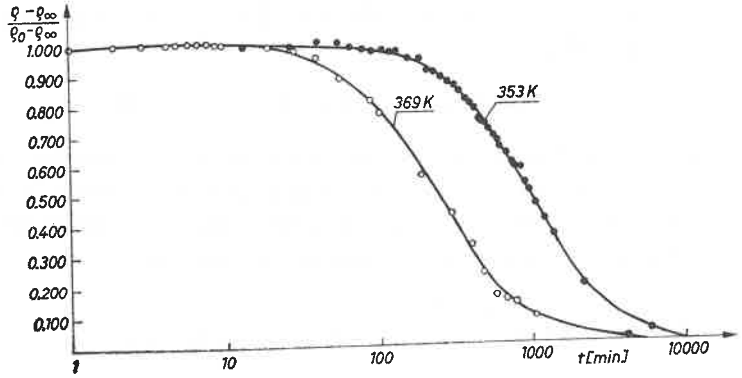

Fig. 2. Normalized ageing curves at 353 and 369 K after solutioning from 873 K for αFe-0.012 % N samples

and the effect of ageing temperature on the above phenomenon in conditions of constant solutioning temperature were studied. In Fig. 1 the isothermal ageing curves at 369 K, after solutioning from 623 or 873 K, are presented. In Fig. 2 the normalized isothermal ageing curves at 353 and 369 K, after solutioning from 873 K are presented. The results of parameter fitting calculations for each model compared with the experimental curves are compiled in Table I. In column 2 the designation and number of models are given according to the notation introduced in Section 1 of this paper. Column 3 contains the designations of fitted parameters, according to the Marquardt algorithm. Columns 4–6 give the optimum values obtained for these parameters and the values of χ^2 obtained, in this case, for individual models. In this specification the first-order model (2) was not taken into account, because all of the isothermal curves, except the on esmeasured at high temperatures, have a nucleation period (Fig. 3). For lower ageing temperatures this model is valid only for longer ageing periods. In order to determine, whether the Johnson–Mehl model (3) or the Damask–Danielson–Dienes models (5) and (6) best describe the kinetics of nitrogen precipitation from αFe, a series of isothermal curves were determined in a tem-

TABLE I

The results of calculation of precipitation models fitting to experimental curves

No	Model designation and number of formula	Fitted parameters	$T_s = 369$ K, $T_q = 623$ K				$T_s = 369$ K, $T_p = 873$ K				$T_s = 353$ K, $T_q = 873$ K			
			$\chi^2 \cdot 10^4$	b_1	b_2	b_3	$\chi^2 \cdot 10^4$	b_1	b_2	b_3	$\chi^2 \cdot 10^4$	b_1	b_2	b_3
1	2	3	4				5				6			
1	Johnson-Mehl (3)	$b_1 = \tau$, $b_2 = n$	2	605.4 min	1.12	—	3	346 min	1.07	—	4	1452 min	1.28	—
2	Fujita (4)	$b_1 = (\frac{1}{2}KK')^{1/2}$	55	$2.03 \cdot 10^{-3}$ min^{-1}	—	—	76	$3.14 \cdot 10^{-3}$ min^{-1}	—	—	24	$0.88 \cdot 10^{-3}$ min^{-1}	—	—
3	Damask, Danielson, Dienes (5)	$b_1 = \beta$, $b_2 = \frac{2}{p}$	2	$2.04 \cdot 10^{-2}$	$8.81 \cdot 10^{-2}$	—	3	$3.97 \cdot 10^{-2}$	$8.34 \cdot 10^{-2}$	—	1	$0.52 \cdot 10^{-2}$	$13.9 \cdot 10^{-2}$	—
4	Damask, Danielson, Dienes (6)	$b_1 = \frac{1}{2}\delta$, $b_2 = \varphi$ $b_3 = \frac{2}{p}$	1	−0.533	0.04	0.043	2	−0.664	0.094	0.03	1	−0.113	0.006	0.112
5	Koiwa (7) $K_n = K$, $K_n' = 0$	$b_1 = K \cdot c_0$	26	$1.14 \cdot 10^{-3}$ min^{-1}	—	—	30	$2.49 \cdot 10^{-3}$ min	—	—	27	$3.87 \cdot 10^{-3}$ min	—	—
6	Koiwa, $K_n = nK$, $K_n' = 0$ (8)	$b_1 = c_0 \cdot K$	11	$0.92 \cdot 10^{-3}$ min^{-1}	—	—	13	$1.70 \cdot 10^{-3}$ min^{-1}	—	—	15	$0.32 \cdot 10^{-3}$ min^{-1}	—	—
7	Koiwa, $K_1 = \alpha K$, $K_n = K$, $n \neq 1$ $K_n' = 0$ (9)	$b_1 = \alpha$, $b_2 = c_0 \cdot K$	8	0.35	$2.85 \cdot 10^{-3}$ min^{-1}	—	9	0.62	$3.21 \cdot 10^{-3}$ min^{-1}	—	8	0.21	$2.33 \cdot 10^{-3}$ min^{-1}	—
8	Koiwa, $K_1 = \alpha K$, $K_n = nK$, $K_n' = 0$, $n \neq 1$ (10)	$b_1 = \alpha$, $b_2 = c_0 \cdot K$	4	0.23	$2.64 \cdot 10^{-3}$ min^{-1}	—	5	0.52	$2.92 \cdot 10^{-3}$ min^{-1}	—	4	0.14	$2.41 \cdot 10^{-3}$ min^{-1}	—

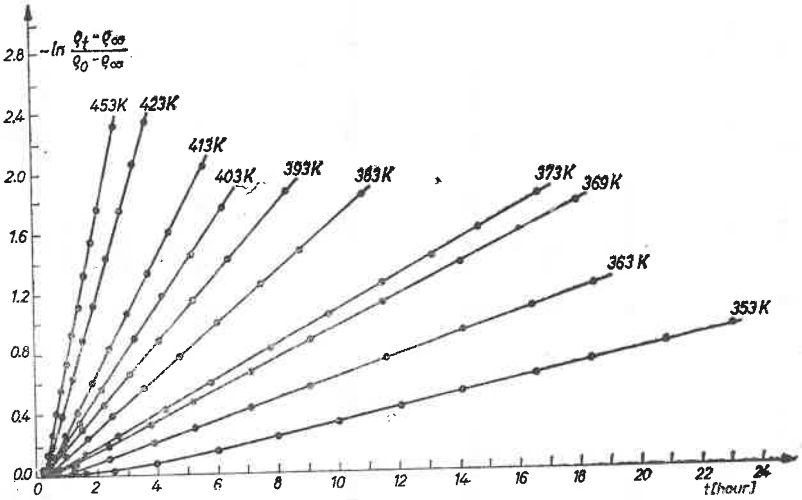

Fig. 3. Precipitation isotherms in αFe-N after solutioning from 873 K in the system of $\left(-\ln\frac{\varrho_t-\varrho_\infty}{\varrho_0-\varrho_\infty}, t\right)$ coordinates

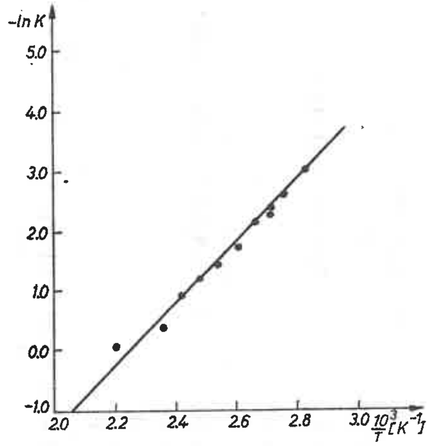

Fig. 4. Dependence of the growth rate constant of nitrogen precipitation from αFe on ageing temperature in αFe-N samples

perature range of 353 to 453 K. The results of measurements obtained for various ageing temperatures, after solutioning the samples from 873 K, are shown in Fig. 3, in a system of $\left(-\ln\frac{\varrho_t-\varrho_\infty}{\varrho_0-\varrho_\infty}, t\right)$ coordinates. It can be seen that all the isotherms, except for initial ageing periods, are arranged along straight lines. This supports the fact that the precipitation kinetics for longer ageing periods can be described by a first-order kinetic equation. The slopes of the rectilinear parts of the isotherms were determined and the results of calculations are presented in the form of $-\ln K = f\left(\frac{1}{T}\right)$ dependence (Fig. 4). As can be seen, the experimental points are arranged along a straight line. Using the Arrhenius equation, the diffusional parameters of the phenomenon of nitrogen precipitation from αFe were calculated for the growth period. Using the least square method, the value $Q_w = (046 \pm 0.03)$ eV obtained for the precipitation activation energy and for the pre-exponential factor the value $K_w = (45 \pm 2)\mathrm{s}^{-1}$.

6. Discussion of the results

Diffraction investigations using TEM for thin foils and carbon extraction replicas showed that nitrogen precipitates from solid solution in the form of $Fe_{16}N_2$ nitride.

A number of experimental papers recently appeared for these alloys in which the precipitation kinetics was described mainly by the Johnson–Mehl model, while other models [16, 17] were omitted. As yet no experimental paper appeared in which the precipitation kinetics was analysed by various models and we decided, which of these models best describes the kinetics of nitrogen precipitation from a supersaturated solid αFe-N solution.

As best, one may consider such a precipitation model which for the optimum fitting parameters, b_k, gives an Euclidean distance comparable to the experimental error as well as the correct time dependence for the whole precipitation period and correct distribution of precipitated particles. For models giving low values of χ^2, the choice of the model may be additionally affected by its behaviour at various ageing temperatures by a physical fitting parameters, b_k, and by the dependence of b_k on time and the ageing temperature. In this paper the estimation of models was confined to the values of χ^2, the behaviour of the time dependence of the model at various ageing temperatures and to the appreciation of the activation energy and the pre-exponential factor values of the precipitation phenomenon for the growth period.

From the specification in Table I it follows that the least χ^2 values give Damask, Danielson and Dienes models (5), (6) and then the Johnson–Mehl model (3). The chain reaction model gives more correct results when it becomes more complicated, i.e., after introduction of reaction rate constants dependent on clusters size, introduction of impeded creation of pairs and small clusters decomposition.

From Fig. 3 it appears that all the precipitation isotherms for longer ageing times arrange themselves along straight lines. The deviation from rectilinear parts, occurring for short ageing periods, is due to the existence of the nucleation period. The lower the ageing temperature, the longer the time required for the nucleation period to exist. At high ageing temperatures the nucleation period may be shorter than the time of the first measurement so that the nucleation period is practically not observed and all the precipitation processes will be best described by the first-order kinetic equation (2). Thus, it appears that such a model may be assumed to be the correct one for nitrogen precipitation from αFe, for which the time dependence for longer ageing periods is described by an exponential function. This postulate, with a low χ^2 value, is fulfilled only by the Damask, Danielson and Dienes models.

The Johnson–Mehl formula does not meet these requirements. If the model (3) gives a good agreement for the initial ageing periods with $n > 1$, then it does not agree for longer ageing periods. In addition for this model to be in agreement for longer ageing times with $n = 1$, the Johnson-Mehl formula turns to a solution having a first-order kinetic equation but without the nucleation period. So formula (3) may describe moderately well the phenomenon of nitrogen precipitation from αFe in the region of high temperatures or for medium periods of ageing. At low ageing temperatures this model may approximate the precipitation phenomenon only within a confined time interval.

The resultant time constant of the precipitation phenomenon for the growth period varies as a function of the ageing temperature (Fig. 4) according to an exponential law. The parameters of the Arrhenius law for constant K are the following:

$$Q_w = (0.46 \pm 0.03)\ \text{eV}, \qquad K_{0w} = (45 \pm 2)\ \text{s}^{-1}. \tag{15}$$

The activation energy value is close to the result obtained in [14] for the same alloys by Brinkman–Meechan method [18, 19] $Q = (0.55 \pm 0.05)$ eV.

The value of Q_w may be compared with the activation energy of nitrogen atoms diffusion in αFe. It is generally assumed that at low temperatures the activation energy of interstitial atoms diffusing in the matrix of B.C.C. metals is equal to the activation energy of directional ordering, Q_p, determined by the internal friction or migrational magnetic after effect method. Snoek relaxation, conditioned by interstitial atom jumps between neighbouring octahedral interstices was used in these investigations. For Q_p energy, the value of (0.769 ± 0.004) eV was reported [20]. Thus, the activation energy of the precipitation phenomenon found here is considerably lower than the activation energy of the directional ordering. The latter value corresponds to the activation energy of the bulk diffusion in a perfect lattice, because in the case of internal friction or migrational magnetic after effects measurements, the structural defects usually lead to the appearance of a new relaxation.

On the other hand for precipitation processes which take place through elementary jumps in long distances, the presence of the structural defects may lead to an increase in the diffusion coefficient [21–23]. Among other things, an increased diffusion coefficient in αFe-C and Fe-Ni-C alloys was observed [24–27] as a result of the existence of dislocations and vacancies.

Model (5) provides additionally a change in the value of the activation energy of the precipitation due to existence of the binding energy, $\bar{B}$, of atoms in precipitates. Using this model one gets for the Q_w energy the following expression:

$$Q_w = Q_p - \left(\frac{p-2}{2}\right) \cdot \bar{B}. \tag{16}$$

The Johnson–Mehl model, which is now commonly used to describe the precipitation process in αFe-N(C), does not predict the change in the precipitation activation energy.

The value of the resultant pre-exponential factor obtained in this paper also differs from the pre-exponential factor of bulk diffusion. This difference is explained by model (5) from which the resultant pre-exponential factor is expressed by the formula:

$$K_{0w} = \left(\frac{2}{p}\right)^{1/2} \cdot (c_0)^{p/2} \cdot K_0, \tag{17}$$

where the constant, K_0, depends on the vibrations of the lattice atoms and the entropy [11]. For the values of p (Table I) and c_0 in the alloys investigated, for K_0 one derives a value of the order of $10^{13} s^{-1}$, i.e., a value close to the Debye frequency of the crystal lattice.

The activation energy for the growth period, Q_w, of precipitation phenomenon, is smaller than the activation energy, Q_p, of the bulk diffusion in a perfect lattice for two reasons, namely the presence of structural defects and the existence of the binding energy between interstitial atoms precipitates.

The effect of structural defects on the activation energy of homogeneous precipitation in αFe-N samples was studied previously [28]. It was found that with an increased dislocation density over 30% cold-work, the activation energy of homogeneous precipitation was decreased additionally by about 0.12 eV.

It is noteworthy that the Damask–Danielson–Dienes formula was derived with the assumption that the precipitation period is much longer than the time of nitrogen atom pairs and triplets formation. Using the results obtained in [29], relative to the kinetics of C-C pair formations in αFe, the above assumption may be checked. The time for C-C pair formation in αFe at 254.2 K is about 3 hours. The period of N-N pair formation will be still shorter because the coefficient of the nitrogen diffusion is greater than that for carbon atoms in the lattice of alpha iron. Using the parameters of nitrogen atom precipitation from αFe, reported here, the precipitation time constant at a temperature of 254.2 K may be calculated which is in the order of magnitude of 2×10^5 hrs. Thus, the equilibrium approximation assumed by Damask, Danielson and Dienes is entirely reasonable.

Model (6), which gives low values of χ^2, takes into account the nuclei existing immediately after solutioning. However, it is difficult to estimate their number because structural defects also have a great effect on the precipitation. The quenched-in vacancies, originating from solutioning of the solid solution from high temperatures may, on the one hand, make convenient nucleation sites and, on the other hand, accelerate the diffusion process limiting the precipitation phenomenon. From Fig. 1 it appears that an increased solutioning temperature results in accelerated precipitation. This may be related to various concentrations of vacancies, quenched in from high temperatures. A similar result was obtained in [28], where, among other things, the effect of the solutioning temperature on the position of minimum on the isochronal curves was investigated.

In summary we believe that model (5) and (6) best describe the phenomenon of nitrogen precipitation from αFe in a wide time interval and for various ageing temperatures. The parameters of these models have their physical interpretation and the results obtained for the diffusional quantities may be explained by these models.

7. *Conclusions*

1. The kinetics of nitrogen precipitation from supersaturated solid αFe-0.012% N solution in the temperature range of 353 to 453 K is described best by the Damask–Danielson–Dienes models (5), (6).

2. The precipitation kinetics for longer ageing periods is described by a first-order kinetic equation (2).

3. The activation energy of precipitation for the growth period, $Q_w = 0.46$ eV, is lower than the activation energy for perfect lattice bulk diffusion $Q_p = 0.769$ eV.

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